\frac{A_02}{32}
Conference chair
A. Vedda
Department of Materials Science, University of Milano-Bicocca

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G. La Pietra, F. Moretti
A. Vedda
Acknowledgements

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Dipartimento di Scienze dei Materiali
ISU (Istituto per il Diritto allo Studio Universitario)
European Physical Society
Provincia di Milano
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SIOF (Società Italiana di Ottica e Fotonica)

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<td><strong>PLMo1 “Defects as Centers for Chemical Reactivity on Oxide Surfaces”</strong></td>
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<td>KMoA</td>
<td>“Time resolved luminescence of solids excited by femtosecond pulses in VUV”</td>
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<td>OMoA1</td>
<td>“Exciton and anti-site defect-related luminescence in Lu$_2$Al$<em>5$O$</em>{12}$ and Y$_2$Al$<em>5$O$</em>{12}$ garnets”</td>
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<td>“Time-Resolved Luminescent Spectroscopy of Strontium Fluoride Crystals doped with Rare Earth ions under Vacuum Ultraviolet Excitation”</td>
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<td>K. Ivanovskikh, V. Pustovarov, B. Shulgin</td>
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<td>OMoA3</td>
<td>“VUV 5d – 4f luminescence of Gd$^{3+}$ doped into CaF$_2$”</td>
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<td>V.N. Makhov, S.Kh. Batygov, L.N. Dmitruk, M. Kirm, G. Stryganyuk, G. Zimmerer</td>
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<td>OMoA4</td>
<td>“Own defects and impurities synchronize their influence on luminescent properties of tungstate crystals”</td>
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<td>S. Nedilko, O. Chukova, Yu. Hizhnyi</td>
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<td>OMoA5</td>
<td>“The dose dependence and the firing effects on the luminescence of quartz”</td>
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## MONDAY JULY 10 - AFTERNOON

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<td>Aula Magna</td>
<td><strong>PLENARY SESSION</strong> Chair M. Nikl</td>
<td><strong>PLMo 2 “Confinement Effects in Luminescent Nano-Insulators” C. Dujardin</strong></td>
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<td>14:40</td>
<td>Aula Magna</td>
<td><strong>SESSION Mo C - Nano-crystals, defects at surfaces and interfaces I</strong></td>
<td>Chair S. Feofilov</td>
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<td>14:40</td>
<td>Aula Magna</td>
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<td>C. Dujardin</td>
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<td>15:30</td>
<td>KMoD</td>
<td>“Recombination processes in rare-earth doped MAI₂O₄ (M = Ca, Sr) persistent phosphors investigated by optically-detected magnetic resonance” S. Schweizer, B. Henke, U. Rogulis, W. Yen</td>
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<td>16:00</td>
<td>OMoC1</td>
<td>“Effect of oxygen precursor on the interface between (100)Si and HfO₂ films grown by atomic layer deposition” S. Baldovino, S. Spiga, G. Scarel, and M. Fanciulli</td>
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<td>16:00</td>
<td>OMoD1</td>
<td>“Atomistic Simulation of Point Defects in ReAlO₃ Scintillators” C.R. Stanek, B.P. Uberuaga, K.J. McClellan, A. Chroneos, M.R. Levy and R.W. Grimes</td>
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<td>16:20</td>
<td>OMoC2</td>
<td>“Extended defects in organic molecular materials: the role of crystal growth mechanisms” M. Moret, M. Campione, L. Raimondo, A. Sassella, S. Tavazzi, D. Aquilano</td>
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<td>Colloids, nano-crystals, and aggregates (PMo01-PMo21)</td>
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<td>Electronic excitations, excited state dynamics, radiative and non-radiative relaxations (PMo40-PMo47)</td>
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<td>Excitons, impurities, and defects I (PMo48-PMo65)</td>
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<td>Radiation effects I (PMo66-PMo91)</td>
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**TUESDAY JULY 11 - MORNING**

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| 9:00  | **PLENARY SESSION** Chair O. Schirmer  
PLTu1 “Defects and Photorefraction: A Relation with Mutual Benefits”  
* M. Imlau |

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| 9:00  | **SESSION Tu A – Colour centers**  
Chair S. Schweizer  
Lecture Hall U6-4  
9:55  
**KTuA** “Defect creation in topaz: comparison between neutron and gamma irradiation”  
K. Krambrock, L.G.M. Ribeiro, M.V.B. Pinheiro, A.S. Leal, W. de Brito, M.A. de B.C. Menezes |
|       | **SESSION Tu B – Computational methods I**  
Chair J.M. Vail  
Lecture Hall U6-5  
9:55  
**KTuB** “O- bound hole polarons in oxide materials”  
O. F. Schirmer |
| 10:25 | **OTuA1** “Optically-detected magnetic resonance of molecular color centers CO2- and NO3 in gamma-irradiated beryl”  
|       | **OTuB1** “First-principles modeling of defects in advanced nuclear fuels”  
E.A. Kotomin, Yu. Mastrikov, Yu. Zhukovskii, P. Van Uffelen, V.V. Randinella |
| 10:45 | **OTuA2** “Optical absorption study of Fe2+ and Fe3+ spectra in beryls”  
A. Galli, M. Fasoli, I. Fontana, F. Moretti, G. Spinolo |
|       | **OTuB2** “Comparison between models of insulator and semiconductor thin films islanding”  
F. Lallet, A. Dauger and N. Olivi-Tran |
| 11:05 | **COFFEE BREAK** |
| 11:30 | **SESSION Tu C – Excitons, impurities, and defects II**  
Chair V. Nagimyi  
Lecture Hall U6-4  
11:30  
**KTuC** “Optical transitions in pairs of trivalent ion-interstitial fluorine in alkaline earth fluorides”  
E. Radzhabov, M. Kirm, A. Nepomnyashchikh |
|       | **KTuD** “Photosensitive defects in nominally pure and doped cubic boron nitride crystals”  
S. V. Nister, D. Ghica, M. Stefan, E. Goovaerts and T. Taniguchi |
| 12:00 | **OTuC1** “Ionic mechanisms in the optically stimulated luminescence of quartz”  
M. Martini, A. Galli |
|       | **OTuD1** “Optical and electron paramagnetic resonance studies on radiation defects in Mn-activated RbCdF3”  
B. Henke, S. Schweizer, U. Rogulis |
| 12:20 | **OTuC2** “TSL, PL and optical properties of X-ray and gamma irradiated RbMgF3:Mn2+”  
C.J. Dotzler, G.V.M. Williams, A. Edgar |
|       | **OTuD2** “Irradiation effects in Ba-halide crystals”  
N. Kristianpoller, W. Chen, D. Weiss, D. Kuzmin and R. Chen |
| 12:40 | **OTuC3** “Multisite structure of RE3+ optical centres in photorefractive Sr1-Ba1-Nb2O6 crystals”  
A.B. Kutsenko, S.E. Kapphan, R. Demirbilek, R. Pankrath, S. Podlozhenov |
|       | **OTuD3** “Trap spectroscopy of N- and B-doped 6H-SIC”  
P. Kulis, A. Sarakovskis, M. Springis, I. Tale |
| 13:00 | **OTuC4** “Transition dipoles interaction of SH - SH ions in KCl”  
A.D. Afanasiev, K.V. Kazakov and A. Kuznetsov |
|       | **OTuD4** “Soft X-ray excitation of luminescence in wide bandgap crystals”  
E. Meltchakov, B. Vidal, I. Kamenskikh, A.N. Vasil’ev, A. Belsky, S. Nannarone, M. Pedio, A. Giglia, N. Mahne, M. Coreno, M. de Simone, M. Danailov |
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<td>PLTu2 “Some aspects of ion implantation technique in nanostructured materials”</td>
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<td>OTuE1 “Photoluminescence of Ho³⁺:YVO₄ crystals”</td>
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<td>S. Polosan, M. Bettinelli, T. Tsuoi</td>
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<td>OTuF1 “Dependence of long-lived defect creation on excitation density in LiF, MgO and SiO₂”</td>
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<td>A. Lushchik, T. Kärner, Ch. Lushchik, E. Vasil’chenko</td>
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<td>OTuE2 “Electronic excitations and defects in laser crystals”</td>
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<td>V.A. Pustovarov, I.N. Ogorodnikov, N.S. Bastrikova, A.A. Smirnov, L.I. Isaenko, A.P. Yelisseyev</td>
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<td>KTuG “What do hydroxyl ions tell us about the structure and defects of oxide crystals”</td>
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<td>L. Kevács</td>
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<td>OTuG1 “Optical Properties of Vitreous TiO₂ - SiO₂ Over a Wide Spectral Range”</td>
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<td>D.Y. Smith, C.E. Black, C.C. Homes, and E. Shiles</td>
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<td>OTuH1 “Magnetism due to defects/oxygen vacancies in HfO₂ thin films”</td>
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<td>N. Hong Hong, N. Poirat, and J. Sakai</td>
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<td>OTuH2 “Charged oxygen vacancy centres in BaTiO₃ thin films”</td>
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<td>A.M. Slipenyuk, V.V. Laguta, M. Maglione, M.D. Glinchuk and I.P. Bykov</td>
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<td>OTuG3 “Identification of Defect Trap Related Europium Sites in Gallium Nitride”</td>
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<td>Z. Fleischman, V. Dierolf, C. Munasinghe, A.J. Steckl</td>
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<td>OTuH3 “The effect of gamma-irradiation on the optical properties of a-Ag7.5(Sb0.1Ge0.3Se0.6)92.5 thin films”</td>
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<td>A.M. Salem, S.H. Moustafa and S.Y. Marzouk</td>
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**CONFERENCE EXCURSION**
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<td><strong>PLENARY SESSION</strong> Chair C. Pedrini</td>
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<td><strong>PLTh1 “Defects in Diamond: Bright Light for the Quantum World” J. Wrachtrup</strong></td>
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<td>9:00</td>
<td><strong>SESSION Th A – Phonons, electron-phonon interactions II</strong> Chair O. Schirmer</td>
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<td>Lecture Hall U7-2</td>
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<td>9:25</td>
<td><strong>KThA “Electronic structure and spectroscopic properties of interstitial oxygen species in the nano-porous complex oxide 12CaO.7Al2O3” P.V. Sushko, D. Munoz Ramo and A.L. Shluger</strong></td>
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<td>10:00</td>
<td><strong>OThA1 “Raman studies of ferroelectric domain walls in lithium tantalite and niobate” P. Capek, G. Stone, C. Sandmann, V. Dierolf, C. Althouse, V. Gopolan</strong></td>
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<td>10:45</td>
<td><strong>OThA2 “Nanoclusters and their temperature evolution in crystals with real and incipient phase transitions” Yu.F. Markov, K. Knorr, E.M. Roginskii</strong></td>
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<td><strong>COFFEE BREAK</strong></td>
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<td>11:30</td>
<td><strong>SESSION Th C – Radiation Effects II</strong> Chair V. Dierolf</td>
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<td><strong>KThC “Displacement energy threshold of yttria stabilized zirconia” J.M. Costantini, F. Beuneu</strong></td>
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<td>12:00</td>
<td><strong>OThC1 “Comprehensive study of PLZT X/65/35 (X=0.04 and 0.10) ceramics irradiated by different pulsed electron beams” V. Efimov, E. Efimova, S. Khasanov, D.I. Kochubey, V.V. Kriventsov, A. Kuzmin, B.N. Mavrin, G. Remnev, V. Sikolenko, A. Sternberg, S.I. Titiuniukov</strong></td>
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<td>12:40</td>
<td><strong>OThC3 “Modelling irradiation induced metastability in ceramic thin films” P.M. Ossi</strong></td>
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<td>13:00</td>
<td><strong>OThC4 “Relaxation emission of electrons and photons from Rare GAs Solids: correlation and competition between TSL and TSEE” E.V. Savchenko, I.V. Khzyzhniy, G.B. Gumenchuk, A.N. Ponomaryov, V.E. Bondybye</strong></td>
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<td>13:00</td>
<td><strong>SESSION Th D – Scintillation, energy transfer and storage, carrier trapping II</strong> Chair M. Martini</td>
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<td>Lecture Hall U6-5</td>
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<td>13:00</td>
<td><strong>KThD “Energy transfer and charge carrier capture processes in wide band-gap scintillators” M. Nikl</strong></td>
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<td>13:00</td>
<td><strong>OThD1 “Europium-doped barium halide x-ray scintillators” J. Selling, M.D. Birowosuto, P. Dorenbos, S. Schweizer</strong></td>
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<td>13:00</td>
<td><strong>OThD2 “Thermoluminescence study of cerium-doped lanthanum halides” O. Selles, M. Fasoli, A. Vedda, M. Martini, D. Gourier</strong></td>
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<td>13:00</td>
<td><strong>OThD3 “Synthesis, structure and thermoluminescent properties of nanocrystalline ZrO2 powder and its possible neutron dosimetry applications” T. Rivera, H.R. Vega, J. Azorin, E. Manzanares, C. Furetta and J.A.I. Diaz</strong></td>
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<td>13:00</td>
<td><strong>OThD4 “Time behaviour of scintillating response and role of defects in Ce or Pr-doped crystals” J.A. Mares, A. Beillerova, M. Nikl, A. Vedda, C. D’Ambrosio, K. Blazek, K. Nejezchleb</strong></td>
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<td>PLENARY SESSION</td>
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<td>SESSION Th E – Electronic excitations, excited state dynamics, radiative and non-radiative relaxations II&lt;br&gt;Chair M.C. Mozzati&lt;br&gt;Lecture Hall U6-4</td>
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<td>COFFEE BREAK</td>
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<td>17:10</td>
<td>POSTER SESSION II</td>
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<td>Impurity-vacancy complexes, dielectric relaxations, ionic diffusion (PTh01-PTh09)</td>
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<td>Defects at surfaces and interfaces (PTh10-PTh20)</td>
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<td>Modeling and computational methods (PTh21-PTh35)</td>
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<td>Excitons, impurities, and defects II (PTh36-PTh51)</td>
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<td>Optical devices, photorefractive materials, lasers (PTh52-PTh60)</td>
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<td>Phonons, electron-phonon interactions (PTh61-PTh68)</td>
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<td>Radiation effects II (PTh69-PTh97)</td>
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<td>Scintillation, energy transfer and storage, carrier trapping (PTh98-PTh109)</td>
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| 9:00  | PLENARY SESSION Chair R. Jackson  
   PLFr1 “Transport in defective ionic materials; from bulk to nanocrystals’’ A.V. Chadwick |
| 9:00  | SESSION Fr A – Excitons, impurities, and defects III Chair I. Tale  
   Lecture Hall U6-4 |
| 9:00  | SESSION Fr B – Nano-crystals, defects at surfaces and interfaces II Chair C. Dujardin  
   Lecture Hall U6-5 |
| 9:55  | KFrA “Toward control of point defects in lithium fluoride thin layers’’ R.M. Montereali, F. Bonfigli, T. Marolo, V. Musi, E. Nichelatti |
| 10:25 | OFrA1 “EPR of Cu$^{2+}$ in lithium tetraborate single crystals’’ G. Corradi, A. Watterich, K. Polgár, V. Nagirnyi, A. Hofstaetter |
| 10:25 | OFrB1 “Extended positron-trapping defects in insulating MgAl$_2$O$_4$ spinel-type ceramics’’ H. Klym, A. Ingram, O. Shpotyuk, J. Filipiecki, I. Hadzaman |
| 11:00 | COFFEE BREAK |
| 11:00 | SESSION Fr C – Defect centers in fluoride crystals Chair M.Kirm  
   Lecture Hall U6-4 |
| 11:00 | SESSION Fr D – Computational methods III Chair E. Mihokova  
   Lecture Hall U6-5 |
| 11:00 | KFrD “Colour in gemstones: a solution to the puzzle of ruby, emerald and alexandrite’’ J.M. García-Lastra, M.T. Barriuso, J.A. Aramburu, and M. Moreno |
| 12:00 | OFrC2 “Theoretical modelling of the photoconversion and aggregation of oxygen centres in calcium fluoride’’ A.S. Mysovsky, E.A. Radzhavov, M. Reichling, J. Sils, P.V. Sushko and A.L Shluger |
| 12:00 | OFrD1 “Computer modelling of the optical properties of rare-earth doped metal fluorides’’ R.A. Jackson, M.E.G. Valerio, J.B. Amaral, M.A. Couto dos Santos |
| 12:20 | OFrC2 “Radiation damage in RE$^{3+}$ doped fluorides’’ A.V. Gektin, N.V. Shiran |
| 12:40 | CONFERENCE CLOSING |
ABSTRACTS
Oral Presentations
Thin MgO(100) films have been prepared on Ag(100) und Mo(100) substrates. Color centers are not present on these MgO surfaces but can be induced by electron bombardment. $F^+$ and $F^0$ centers may be identified with scanning tunneling spectroscopy and found to be located not on terrace but rather on edge sites primarily. This is corroborated by electron spin resonance experiments. Methods are described to engineer surfaces with particular defects and thus its interaction with both, molecules and metal atoms, can be studied. Additional techniques such as Fourier-Transform Infrared Spectroscopy allow us to get closer insight into the influence of defects on the properties of adsorbed atoms and molecules. Thin alumina films have been studied with respect to reactivity of NO before and after defects on the oxide surface have been decorated with Pd nanoparticles.
In addition to the conventional synchrotron radiation (SR), development of new generation VUV light sources with extremely high peak power and brilliance, based on the free electron laser (FEL) concept as well as on principles of higher order harmonic generation (HHG) in a gas, has initiated a new direction in the investigation of luminescence properties of solids [1, 2]. Due to the ultra-short pulses such sources are perfect tools for studies of relaxation dynamics of electronic excitations in solids and for investigation of interactions of matter with an intense light pulse itself [3]. Generated tuneable short wavelength laser radiation allows a convenient excitation of electrons both from the valence band and inner-shell levels to the conduction band in a number of solids. SR due to its inherent time resolution is indispensable tool in such studies as well.

We report on room temperature investigation of luminescence properties and emission decay kinetics of well-known scintillator crystals, CdWO₄ and BaF₂, excited by HHG laser radiation generated by PLFA facility of the SLIC centre in Saclay, France. The 800 nm fundamental pulsed beam of 30 fs duration was focused in a gas cell filled either with Ar or Kr to generate in non-linear process photons with energy higher than 15 eV. As-generated VUV beam or that further monochromatised by metal filters was focused down to ~20 µm spot on the sample by a parabolic mirror. The excitation density was varied by moving samples out of a focal plane.

Variation of excitation density resulted in changes of the emission spectra of BaF₂ accompanied with the shortening of decay kinetics and in changes of decay kinetics of CdWO₄. In the case of BaF₂ at higher excitation densities, the UV luminescence of self-trapped excitons was quenched while the intensity of cross-luminescence caused by radiative recombination of valence electrons with Ba 5p holes, was preserved. In the case of CdWO₄ only changes in the emission decay kinetics resulting in the appearance of short components in the emission decay of small-radius Frenkel excitons were observed without significant changes in emission spectra. Such components are not observed at the excitation by conventional UV light. Results obtained will be compared with those recorded using other excitation sources such as FEL, SR, ionising radiation as well as optical excitation. Also advantages of time-resolved spectroscopy will be discussed.

Financial support by the Access to Research Infrastructures activity in the FP6 of the EU (contract RII3-CT-2003-506350, Laserlab Europe) and by the Estonian Science Foundation (Grant 6538) for conducting the research are gratefully acknowledged.

References

OMoA1

EXCITON AND ANTI-SITE DEFECT RELATED LUMINESCENCE IN Lu₃Al₅O₁₂ AND Y₃Al₅O₁₂ GARNETS

Yu. Zorenko¹, A. Voloshinovskii¹, M. Nikl², K. Nejezchleb³, V. Mikhailin⁴, V. Kolobanov⁴, D. Spassky⁴

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⁴ Physical Faculty, Moscow State University, 119899 Moscow, Russia

Intrinsic emission of complex oxides with the garnet structure was analysed by means of the time-resolved luminescence spectra and decay kinetic under excitation by the pulse X-ray and synchrotron radiation (SR) at 10–300 K. Single crystals (SC) and single crystalline films (SCF) of Lu₃Al₅O₁₂ (LuAG) and Y₃Al₅O₁₂ (YAG) garnets were measured, which are characterised by the significant differences in the concentrations of anti-site defects (AD) of LuAl and YAl-types due to substantial difference in the conditions of their crystallization. For this reason, the LuAG and YAG SC and SCF are very useful model objects for study of the nature of the intrinsic emission of these complex oxides, consisting mainly of the exciton-based and AD luminescence [1].

The STE emission peaking at the 4.94 eV and 4.765 eV was observed in the YAG and LuAG SCF at 10 K, under the excitation by SR with an energy of 7.4 eV and 7.2 eV, respectively, i.e. in the exciton range of these garnets [1,2]. Important differences of the intrinsic luminescence in the YAG and LuAG SC with respect to the SCF are: (i) much larger (nearly one order of magnitude) intensity of the STE emission in SC; (ii) the low-energy shift of the STE luminescence bands with respect to that of SCF and peaking at 4.36 eV and 4.34 eV in the LuAG and YAG SC, respectively. Three component decay kinetics extending over the ns, hundreds ns and few µs ranges is typical for STE emission in the SCF and SC that evidences the existence of two types of triplet STE with different energies of their formation.

Intrinsic luminescence bands peaking at 3.68 eV and 3.70 eV in the LuAG and YAG SC, respectively, at 300 K and showing the different three-component complex emission decay, are caused by the radiative relaxation of the triplet excitons localized directly at then YAl and LuAl AD. This YAl and LuAl AD emission is completely missing in the luminescence spectra of YAG and LuAG SCF, what evidences the absence of AD in the SCF of these garnets [1,2]. Emission of the YAl and LuAl AD at 300 K is excited in the bands at 6.99 and 6.8 eV located at the low-energy side of the YAG and LuAG SC absorption edges. Furthermore, at 10 K the excitation maxima of STE emission at 7.05 and 6.9 eV in the LuAG and YAG SC, respectively, are close to the corresponding excitation peaks of the LuAl and YAl AD luminescence.

We conclude that the radiation decay of the STE-like state stabilized around the nearest AD predominantly takes place in YAG and LuAG SC as distinct to SCF where STE emissions is observed only at the unperturbed regular sites of garnet lattice. Relatively small Stokes shift and low intensity of the STE emission (due to low cross section for e/h recombination) in SCF reflect the nature of the STE emission in these garnets as a radiative recombination of electrons localized at the 4s+5d levels of Lu³⁺ or Y³⁺ ions with the self-trapped hole (STH) localized at 2p-unbound levels of singly charged O ions as opposed to AHC where two-halide STH localization takes place [3].

References
TIME-RESOLVED LUMINESCENT SPECTROSCOPY OF STRONTIUM FLUORIDE CRYSTALS DOPED WITH RARE EARTH IONS UNDER VACUUM ULTRAVIOLET EXCITATION

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Urals State Technical University-UPI, Mira str. 19, 620002 Ekaterinburg, Russia

Luminescent VUV spectroscopy of rare earth (RE) ions doped into wide band crystals is one of the upcoming field of research that arise from new technical applications for materials with optical activity in the VUV range (VUV excited phosphors, VUV emitters and fast VUV scintillators). In this connection we carried out a time-resolved VUV spectroscopic study for trivalent RE ions doped into SrF$_2$ crystals, which are among the promising materials. The experimental researches were performed at the SUPERLUMI station of HASYLAB (DESY, Hamburg) and consist of time-resolved emission spectra (in 130-750 nm range under selective UV/VUV excitation), excitation spectra (50-320 nm) and luminescence decay kinetics measurements at T= 8 and 300 K.

Time-resolved VUV emission spectra for Nd$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ doped crystals have been measured. An emission spectrum of SrF$_2$:1%Nd$^{3+}$ shows the relatively broad intensive bands connected with the parity-allowed 4f$^2$5d$^1$ → 4f$^3$ transitions. Er$^{3+}$ and Tm$^{3+}$ doped crystals demonstrate no emission from a low spin (LS) state of 4f$^{n-1}$5d configuration. It is caused by a small energy separation of the LS and high spin (HS) states that makes multi-phonon non-radiative relaxation highly probable. A slow emission (decay time from microsecond range) connected with 4f$^{n-1}$5d(HS)$→$4f$^n$ radiative transitions were observed in the spectra for both ions. A surprising discovering was in observing of very fast (decay time ~ 0.5 ns) emission bands at 146.5 nm for SrF$_2$:1%Er$^{3+}$ crystals. We assume the fast luminescence originates from the $^2$T$_2$(5I$_8$) excited state of Er$^{3+}$ ions situated at the low symmetry sites, in which energy difference between $^2$E and $^2$T$_2$ subconfigurations can be noticeably smaller.

In excitation spectra for Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ ions in SrF$_2$ the transitions to levels of $^2$E and $^2$T$_2$ subconfigurations was identified and analysed. The ligand-to-metal F$^-$ → Ln$^{3+}$ and O$^{2-}→$ Ln$^{3+}$ charge transfer transition in SrF$_2$:1%Eu$^{3+}$ was studied. For Tm$^{3+}$ and Er$^{3+}$ ions in SrF$_2$ the excitation spectra of the d-f and f-f emission demonstrate opposite behaviour that reflects partly the variation of absorption coefficient in the transparency range and the competition in the energy transfer processes to the emitting levels of 4f$^{n-1}$5d and 4f$^n$ configurations in this ions [1,2].

The work was supported by Russian Foundation for Basic Research (grant 05-02-16530).

References
OMoA3

VUV 5d → 4f LUMINESCENCE OF Gd3+ DOPED INTO CaF2

V.N. Makhov1, S.Kh. Batygov2, L.N. Dmitruk3, M. Kirm3, G. Stryganyuk4, G. Zimmerer4,5

1 P.N. Lebedev Physical Institute, Leninskii Prospect 53, Moscow 119991, Russia
2 General Physics Institute, Vavilov Str. 38, Moscow 119991, Russia
3 Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia
4 Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany
5 Institut für Experimentalphysik, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Recent studies [1-3] have revealed that some Gd3+ containing fluoride crystals emit VUV luminescence (hν ~ 10 eV) which is due to interconfigurational 4f65d → 4f7 transitions in the Gd3+ ion. In the present work the spectral and temporal characteristics of VUV, UV and visible luminescence from CaF2 doped with Gd3+(0.1%) and Ce3+(0.05%) have been studied under excitation by synchrotron radiation near and above the edge of interconfigurational 4f7 → 4f65d transitions in Gd3+ and 4f → 5d transitions in Ce3+. High-resolution (~1 Å) VUV emission and excitation spectra as well as decay kinetics of VUV luminescence have been measured using SUPERLUMI set-up operated at the DORIS storage ring of HASYLAB at DESY. The obtained Ce3+ 5d → 4f emission and 4f → 5d excitation spectra well correspond to well-known spectra of Ce3+ centre in CaF2 in a site of tetragonal (C4v) symmetry where charge compensation of Ce3+ is achieved by an nearest-neighbor interstitial fluorine ion [4,5]. The VUV emission spectrum from CaF2:Gd3+,Ce3+ shows a narrow zero-phonon line at 77660 cm⁻¹ followed by a broad side band centred near 77100 cm⁻¹. The decay time of the VUV luminescence is 8.5 ns. The excitation spectrum of VUV luminescence agrees well with the Gd3+ 4f7 → 4f65d absorption spectrum in CaF2:Gd3+ obtained in [6] and completely coincides with the excitation spectrum of orange luminescence (around 590 nm), which is due to 4f7 6G7/2 → 6P1 transitions in Gd3+. The zero-phonon line and other features in VUV emission spectrum clearly correlate with the structures observed at the onset of the excitation spectra. The obtained results confirm that the VUV luminescence observed in CaF2:Gd3+,Ce3+ originates from 4f65d → 4f7 transitions in Gd3+. Well resolved fine structure due to zero-phonon lines and vibronic lines along with broad side-bands observed in VUV emission and excitation spectra of CaF2:Gd3+,Ce3+ indicate intermediate electron-lattice coupling between the 4f65d electronic configuration of the Gd3+ ion and the lattice vibrations in CaF2:Gd3+,Ce3+ system.

References

OWN DEFECTS AND IMPURITIES SYNCHRONIZE THEIR INFLUENCE ON LUMINESCENT PROPERTIES OF TUNGSTATE CRYSTALS

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The peculiarities of the luminescence mechanisms in scintillation tungstate crystals AWO₄ (A = Pb, Cd, Zn) is still the subject of discussion. Especially the role of own and impure defects to determine luminescent and scintillation characteristics attract great attention despite on the large number of published works which are in touch with this problem.

We present results of complex experimental and theoretical studies of optical features of CdWO₄, PbWO₄ and ZnWO₄ both undoped and doped with RE ions: praseodymium, samarium, and dysprosium. Mentioned crystals possess different crystalline structures. It should be pointed the anionic sub lattice of the last ones formed by the WO₆ superscript 6− molecular anions when anionic sub lattice of PbWO₄ crystal is constructed by the WO₄ superscript 2− molecular group. The electronic structure of these crystals were calculated by full potential Linear Augmented Plane Wave (FLAPW) method implemented in WIEN2k program code [1] and using. The perfect crystals, the crystals with RE impurities and oxygen vacancies (WO₃ groups) were considered. The structures of the electronic bands, the energy of electronic levels, optical spectra were obtained. Results of the calculations of perfect and defect crystals are compared with experimental data on reflection and luminescence excitation in wide energy region (20 - 1200 nm) using synchrotron radiation at SUPERLUMI station (HASYLAB, Hamburg, Germany).

Analysis of all the obtained data allow us to discuss the similarity and peculiarities of own matrix defects and RE ions impact on the luminescence properties of mentioned self – activated phosphors. Structures and correlations between centres those originate intrinsic and impurity luminescence are discussed.

References

THE DOSE DEPENDENCE AND THE FIRING EFFECTS ON THE LUMINESCEENCE OF QUARTZ

A. Halperin

Racach Institute of Physics, The Hebrew university of Jerusalem, Jerusalem, 91904, Israel

Papers on the dose dependence of thermoluminescence of quartz have been published in recent years by research groups from various countries. These papers show that untreated quartz gives very strong superlinearity (up to slopes of 3), while firing the samples at high temperatures reduces the dose dependence to linearity and increases the thermoluminescence intensity by more than one order of magnitude. In addition, the thermoluminescence peak at 110°C was found to shift nearly 40°C after firing to 950°C. Two of the papers describing the above effects are given in references [1] and [2]. Almost all the investigators who describe the above effects refer to a theoretical paper by Kristianpoller et al [3] which shows that adding a competing energy level to the energy system of quartz, gives a set of equations which can be solved numerically for various sets of given parameters, when the results explain all the above effects.

Preliminary work in our laboratory did not show the above effects. Unlike other investigators who used quartz powders, we preferred to use single crystals of quartz. To obtain a better resolution of two or more neighbouring thermoluminescence peaks, we reduced the rate of heating in the luminescence measurements of 10°C per minute, compared to 400°C per minute or more in the other dose effects investigations. These and more sets of measurements in our work lead to a better understanding of the dose related effects in quartz.

References

The recent observation of room temperature ferromagnetism in transition metal (TM) doped oxides, denoted as diluted magnetic oxides (DMO), has stimulated a strong interest for future application of these materials in spin-electronics devices. In spite of the early promising results, some issues still have to be clarified, e.g. how to better control the dopant concentration and how to improve the ferromagnetism and explain its nature. For the most part, the studies have been addressed on thin films grown with pulsed laser deposition, reactive sputtering, molecular beam epitaxy and ion implantation. Their structural, magnetic and transport properties present different behaviours also for nominally identical stoichiometries and doping levels, showing that there is still an unsatisfactory knowledge about the best deposition method and post-deposition treatments, also causing conflicting claims concerning the existence and the origin of ferromagnetism. In this respect TiO$_2$ is rather important: early studies showed the presence of ferromagnetism in anatase and rutile phases of Co-doped TiO$_2$ and contrasting evidences have been, afterwards, reported. Indeed, the mechanisms responsible for ferromagnetism in DMOs are still under debate: double-exchange and bound magnetic polarons formation are all potentially playing a role depending on the doping level, oxygen stoichiometry and possibly related free charges.

In this frame the study of TM-doped single crystals has been virtually neglected, notwithstanding the growth in equilibrium conditions is expected to produce segregation-free and homogeneous samples, at least for low concentration of dopants, which can be profitably compared to samples produced in out-of-equilibrium conditions to clarify the relationship between growth kinetics and, for example, unwanted TM cluster formation. In addition, the effect of the host matrix alone on the magnetic properties of DMOs has not yet been thoroughly clarified.

In the present work we show the feasibility of an alternative technique of growth in equilibrium conditions from suitable melts (Na$_2$B$_4$O$_7$) and we report on magnetic investigations of TM (TM = Cr, Mn, Fe, Co, Ni and Cu) - doped TiO$_2$ rutile single crystals, checked in their homogeneity by micro-Raman spectroscopy. The observed coexistence of paramagnetic and ferromagnetic behaviour at room temperature is discussed also in connection with the magnetic properties arising from the TiO$_2$ host matrix.
INVESTIGATION OF FERROELECTRIC NANOPOWDERS BY ESR METHOD

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We present results of experimental and theoretical investigation of ferroelectric nanopowders by ESR method. The manifestation in radiospectroscopy spectra of size driven ferroelectric–paraelectric phase transition at some critical particle average size $\bar{R} = R_c$ was the main goal of consideration. Iron doped (0.01mol%) BaTiO$_3$ samples were prepared by rate-controlled method with different particle sizes, which depend on annealing temperature. ESR measurements of BaTiO$_3$ nanopowders were carried out in the temperature region 20$^0$C-120$^0$C. The transformation of the Fe$^{3+}$ ion ESR spectra symmetry from tetragonal to cubic one was observed under nanoparticle sizes decrease or temperature increase. The asymmetry and broadening of right hand side shoulder of the Fe$^{3+}$ cubic symmetry ESR line observed at room temperature for the sample with $\bar{R} \leq 40nm$ was shown to be related to the contribution of the paramagnetic centers from the region in the vicinity of the particles surface. Deconvolution of the cubic line and the core and shell model application allowed to estimate the width of this region, $\Delta R=3$nm. Essential influence of the nanoparticle size distribution and the temperature dependence of polarization on the observed spectra were demonstrated by the fitting of the theory with experiment. The method of $R_c$ value extraction from the ratio of the different symmetry ESR lines intensities is proposed. Obtained value of particles critical size is $R_c \approx 40$nm. Nanoparticles size distribution function characteristics and spontaneous polarization temperature dependence were extracted from the ESR data on the base of proposed theory.
OMoB2

EPR EVIDENCE OF STATIC DISORDER IN LANGASITE-TYPE SINGLE CRYSTALS

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²National Institute for Materials Physics, Magurele 77125, Romania
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⁴Ghent University, B-9000 Ghent, Belgium

The gallosilicate crystals form a large class of acentric crystals with trigonal symmetry presenting substitutional disorder due to statistical occupation of two cations in some crystallographic positions. Therefore the environment around a specific site is changed according to this distribution. The intrinsic disorder can be put in evidence by variation of spectroscopic data of some ions placed in specific crystallographic sites. Among the spectroscopic methods electron paramagnetic resonance (EPR), due to its high sensitivity to symmetry and crystal field strengths, gives valuable information about the local disorder around the paramagnetic impurity.

In the paper EPR data on Gd³⁺ and Cr³⁺ ions doped langasite (LGS, La₃Ga₅SiO₁₄) and langatate (LGT, La₃Ga₅.₅Ta₀.₅O₁₄) crystals are reported. These are analysed according to the following hypotheses:

(a) the single crystals have stoichiometric composition and a low concentration of defects [1];
(b) the Ga³⁺ and Si⁴⁺ cations are statistically distributed in the D-tetrahedral sites in LGS and Ga³⁺ and Ta⁵⁺ cations are distributed among trigonal-pyramidal octahedral sites in LGT [2];
(c) Gd³⁺ ions occupy the distorted Thomson cubes, and Cr³⁺ the octahedral sites. Both sites have a local symmetry.

EPR spectra have been recorded in X and Q bands. The main characteristics are: Gd³⁺ spectrum is complex, with broad asymmetric lines, like a glass spectrum. The transitions at g_{eff} = 6, 2.8, 2 are the most important. Such spectrum can not be explained without accepting a large distribution of spin Hamiltonian parameters [3]. Cr³⁺ ions are subjected to a strong low symmetry crystal field which splits the ground state in two doublets. Only transitions in the lowest doublet are observed even in Q band, with a large zero field splitting. Line width variation is used to estimate the distribution of spin Hamiltonian parameters. The EPR results are correlated with other spectroscopic data, optical absorption spectra, fluorescence spectra or Mössbauer spectroscopy data for ¹⁵¹Eu [4]. Theoretical calculations of electric field potential and gradient performed in a point charge approximation with fractional ionic charges [5] are presented and corroborated with the EPR data.

References

Recent studies in our group have shown that reduction processes may occur under irradiation on lanthanides ions in aluminoborosilicate glass. In particular, we observe by luminescence the reduction of Sm$^{3+}$ into Sm$^{2+}$ during $\gamma$- or $\beta$-irradiation [1,2]. We also showed that for Gd-doped glasses there are two sites of Gd$^{3+}$ ions attributed to network modifier and network former ones. Changes occurring under irradiation result in conclusion of reduction processes of Gd$^{3+}$ in Gd$^{2+}$ taking place inside the aluminoborosilicate glass which leads to the possible changes in Gd local environment [3]. These changes in the oxidation state under irradiation are important to study for other lanthanides ions (Ce and Nd) because these will give information on the behaviour of actinides ions under irradiation during waste confinement. The purpose of this work is therefore to determine the local environment changes around Nd and Ce under $\beta$-irradiation in aluminoborosilicate glasses as a function of rare earth oxide content and the dose. Glass structural changes under irradiation have been studied using EPR spectroscopy and luminescence.

It is well-known that for some rare-earth elements that EPR signal can be obtained only at low temperatures. Our EPR measurements carrying out at helium temperature (4 K) have shown that $\beta$-irradiation process affects valence state of cerium ions: new line appearing at the content of CeO$_4$ more than 3 wt.% can not be ascribed to defects produced during irradiation. According to concentration and dose dependences the line can be attributed to paramagnetic Ce$^{3+}$ ions resulting from Ce$^{4+}$ reduction under irradiation. The effect of CeO$_4$ content concerns the decreasing the total amount of defects and changing of relative proportion of electron and hole defects with increase of cerium doping level. Under $\beta$-irradiation, changes of the Nd environment are detected for all doses of irradiation. We saw also strong modification of defects nature and concentration under ionizing radiation as a function of the rare earth doping into these glass compositions.

References

LOCALIZATION AND MOVEMENT OF NATIVE INTERSTITIALS IN CHLORINATED SrCl$_2$:Fe CRYSTALS

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Short X-ray irradiation at low temperatures (80 K) of chlorinated SrCl$_2$:Fe$^{2+}$ crystals produces several primary Fe$^{+}$ and Fe$^{3+}$ paramagnetic centres with non-cubic symmetry, which have been previously studied by magnetic resonance (EPR, ENDOR) spectroscopy [1 – 4]. Because the resulting Fe$^+$/Fe$^{3+}$ centres were produced by short irradiation at temperatures where no significant ionic movement is present, it is expected that precursor Fe$^{2+}$ centres with similar structure/symmetry were present in the as-grown crystal.

Further annealing treatments, at temperatures higher than 200 K, of such irradiated crystals results in the annealing/conversion of some of the primary Fe$^+$ paramagnetic centres in new, secondary Fe$^+$-type paramagnetic centres. The EPR investigations show that the secondary Fe$^+$ centres formation is determined by the presence and thermally activated movement of the native interstitial anions and alkali impurities towards the Fe$^+$ ion. Both precursor Fe$^{2+}$ and resulting Fe$^+$ paramagnetic centres are perturbed by these native interstitials which were inserted in the crystal lattice during the crystal growth in a chlorine atmosphere.

References

Solar, cosmic, laser and nuclear reactor radiations lead to the appearance of defects in complex oxides and to inevitable performance degradation of devices based on these materials. The study of radiation defects is the only way of understanding degradation mechanisms, of an estimation of the lifetime of the crystals in different environments, and possible reducing a radiation damage of devices. Since most of radiation defects are paramagnetic (or can be recharged to a paramagnetic state), the magnetic resonance methods, EPR and ENDOR are the most suitable methods for their study.

The present work reports the EPR/ENDOR and simultaneous EPR/optical study of defects in single crystals irradiated by visible, UV and gamma photons, electrons, protons and neutrons. Among investigated oxide materials are LiNbO$_3$, Li$_2$B$_4$O$_7$, KTiOPO$_4$, Ba$_{0.77}$Ca$_{0.23}$O$_3$ and so on. Isochronal annealing in air and additional light illumination has been used for the determination of the stability of radiation defects. Computer simulation of observed spectra (see Figure) allowed us to determine spectroscopic characteristics and models for more than dozen paramagnetic defects.

Analyzing obtained data we came to the conclusion that all observed radiation defects can be divided into five basic groups:
1. F-like centres with $g \approx 2.00$ representing an electron trapped by an oxygen vacancy,
2. Centres in the form of the O$^0$ - O$^-$ (or O$_2^-$) complex consisting of one regular site oxygen and one interstitial oxygen or of two oxygen ions in regular sites near a metal vacancy (hole traps),
3. Recharged ions knocked out from their regular lattice sites,
4. Recharged impurity ions,
5. Recharged regular lattice ions near intrinsic or extrinsic lattice defects.

The dominated types of defects formed under visible, UV and gamma photon irradiation are centres created by lattice defects trapped electron or hole, recharged impurity ions and recharged regular lattice ions near intrinsic or extrinsic lattice defects. The neutron irradiation creates stable Frenkel pairs (interstitial ions and vacancies). The obtained characteristics of different interactions and derived models of radiation defects can be used as cornerstones for theoretical calculations.
First papers on luminescent nano-insulators appeared about ten years ago. In [1], unusual luminescence properties of ZnS:Mn$^{2+}$ were presented. From this time, the number of papers relating synthesis as well as luminescent properties of nano-insulators has always increased due to the interest for new phosphors. About hundred papers are obtained in 2005 with a bibliographic search with nano* and luminescence and insulators. Nevertheless, this number remains quite small as compared to semi-conductors such as CdS. In fact, the optical properties appear to be synthesis-depandant and contrary to [1] the luminescence yield often drops when the particle size is decreased (see [2] for illustration). In fact, the yield of very efficient systems as bulk cannot be improved and, due to surface effects, the fluorescence properties are degraded. Nevertheless, interesting and unusual properties can be observed in these systems.

In this contribution, a review of the confinement effects which affect the optical properties will be presented. This confinement appears in different ways: quantum, structural, surface effects. Since all these effects can be dependant on the preparation routes, most popular elaboration protocols with there advantages and drawbacks will be presented as well. Finally, some applications which would benefit of these doped nano-insulators will be discussed.

Chemical vapour deposition has turned out to be a promising synthesis technique that provides nanometre-sized MgO cubes with characteristic surface defects. On this model system, specific surface anions can be selectively addressed by monochromatic UV light and give rise either to photoluminescence emission or to persistent charge separation effects [1].

The optical surface properties of these nanocrystals can be altered via the admixture of a second metal component. Although CaMgO mixtures are thermodynamically forbidden on a macroscopic scale, Calcium ions can be distributed homogeneously in MgO nanocrystals with average sizes in the range between 5 and 40 nm. Subsequent thermal activation leads to calcium ion segregation into the nanocrystal surface which, in addition to the synthesis parameters, provides efficient means for manipulating the optical surface properties of insulating oxide nanocrystals [2]. A novel material with unexpected photonic behaviour, such as enhanced photoluminescence emission which is also red-shifted with respect to those of CaO and MgO, was found.

References

OMoC1

EFFECT OF THE OXYGEN PRECURSOR ON THE INTERFACE BETWEEN (100)Si AND HfO₂ FILMS GROWN BY ATOMIC LAYER DEPOSITION

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The interface quality is a crucial issue in the identification of a suitable oxide to replace SiO₂ in ultra-scaled MOS-based devices. Among the various candidates, HfO₂ grown by Atomic Layer Deposition (ALD) has shown promising functional properties.

The aim of this work is to investigate the effect of different oxygen precursors, in particular H₂O and ozone, on the interface characteristics. The interface states are investigated with capacitance and conductance measurements providing in particular the density of states (Dₖ). Electrically Detected Magnetic Resonance (EDMR) spectra and their angular dependence (Fig.1) allowed the identification of the microstructure of the dominant paramagnetic defect acting as recombination centre.

Figure 1: EDMR spectra observed at room temperature for (HF-last)Si/HfO₂ interface for different angles between the magnetic field H and the [100] direction. The solid lines show the measured data. The thin dotted lines are the constituent lines and the dashed lines represent the overall result of the deconvolution.

The combination of water and HfCl₄ produced a thin film showing an Si/SiO₂-like interface [1], where the predominant electrically active defect is the P₁₀, a trigonal centre pointing in the [111] direction [2]. On the other hand, ozone generated a highly defective interface, with defects still showing a trigonal symmetry, but pointing in a different direction. Post growth annealing in N₂ strongly affects the interface properties of the ozone grown sample: the density of defects decreases with the increase of the annealing temperature reaching a minimum at 600°C that remains unchanged for higher temperatures. In correspondence of this minimum, the interface microstructure transforms into a more Si/SiO₂-like interface.

References
OMoC2

EXTENDED DEFECTS IN ORGANIC MOLECULAR MATERIALS: THE ROLE OF CRYSTAL GROWTH MECHANISMS

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Relevant physical properties and potential technological applications of organic molecular materials rely on intrinsic molecular properties as well as on packing symmetry adopted in the crystalline state. Since organic molecular materials can be employed both as single crystals and thin films (e.g. grown by vacuum sublimation and molecular beam deposition, respectively), care must be taken in order to produce high quality crystals. Unfortunately, independently of the optimization of the specific growth techniques, growth mechanisms active under the selected experimental conditions can lead to formation of severe defects other than those usually recognized, i.e. screw and edge dislocations, stacking faults, twinning, and local molecular disorder. Indeed, recognition of specific crystal surface patterns, together with rationalization of symmetry requirements necessary for such phenomena to occur [1-3], led to the discovery of new cases of polymorphic-polytypic transitions in the realm of protein crystals [1]. The same phenomena are recognized here also for a series of well known organic semiconductors (oligothiophenes and polyacenes) whose crystals and thin films display characteristic spiral steps interlacing (Fig. 1). These patterns reveal different stacking sequences of a basic structural motif within the same crystal giving rise to periodic polysynthetic twins and complex polytypes. Therefore, the crystalline material exhibits different physical properties depending on the selected region of the crystal growth volume, such as, for example, a different directional dispersion in the optical response [4].

Figure 1.  a) Spiral growth outcrops (black arrows) on a tetracene crystalline thin film (scale bar 2 µm). b) Growth hillock with interlacing of steps on a quaterthiophene single crystal surface (scale bar 50 µm).

References
Eu- and Nd-doped calcium aluminate and Eu- and Dy-doped strontium aluminate phosphors show long persistent green and purple phosphorescence, respectively [1]. The phosphorescent dynamics are very complicated and different models for the mechanism of phosphorescence have been proposed. However, a clear identification of the centres involved is not yet accomplished.

The phosphorescence which was induced by prior UV-excitation at 4.2 K quenches in high magnetic fields, but it can be increased significantly by applying microwave radiation (93.7 GHz) yielding resonance lines for appropriate magnetic fields. This method is henceforth called recombination luminescence detected electron paramagnetic resonance (RL-EPR).

We attribute the phosphorescence to a recombination of distant donors and acceptors which were generated by the UV-excitation. The RL-EPR spectra show a structureless resonance line at about 3390 mT (SAO) and 3365 mT (CAO) as well as a group of lines centred at about 3310 mT. The resonance at 3390 mT / 3365 mT shows no angular dependence, whereas the line group at 3310 mT shows significant changes in structure. Since the g values of the RL-EPR line at 1.97 (SAO) and 1.99 (CAO), respectively, are smaller than two, we attribute them to donors. The line groups centred at 2.02 are assigned to acceptors. The spectral dependence of the RL-EPR spectra, detected for different emission wavelengths (the recombination luminescence was detected either integrally or with the use of different edge filters), shows that the isotropic line (donor) has no spectral dependence, but the low field group (acceptor) shows significant changes for SAO as well as for CAO crystals.

The angular dependence of the RL-EPR line of the donor in CAO and SAO shows that we have an isotropic centre, whereas the line group of the acceptor is clearly angular dependent. Since the g values of the donors do not change upon doping these traps are intrinsic. The angular dependence of the line group at 2.02 is caused by different centre orientations and by a superposition of resonance lines of at least two acceptors. The fact that we deal with at least two acceptors can be deduced from the spectral dependence of the RL-EPR spectra.

References

OMoD1

ATOMISTIC SIMULATION OF POINT DEFECTS IN REALO$_3$
SCINTILLATORS

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Current state of the art devices entrusted with the detection of special nuclear material require significant improvement for modern threat reduction (TR) applications. Historically, new radiation detector materials have been developed through Edisonian trial and error (i.e. “if it's dense, try it”). However, empirical development alone is unlikely to achieve the improvement in detector materials necessary for vital TR applications. Rather, as astutely posited by M.J. Weber, scintillator detector materials are more likely to be improved by the fundamental understanding and subsequent control of point defects responsible for non-radiative transitions [1].

In this paper, we respond to Weber’s “call to arms” by employing atomistic simulations to describe the defect behaviour for a range of REAlO$_3$ compounds (where RE corresponds to a rare earth atom or yttrium). Specifically, we predict the intrinsic disorder mechanisms, the defects associated with Me$^{3+}$ activation as well as oxidation mechanism of Me$^{3+}$ to Me$^{4+}$. Furthermore, we interpret the experimental results [2] of co-doping schemes aimed at reducing the concentration of electron trap sites. Our interpretation via atomistic simulation [3] reveals valuable detail regarding the evolution of defect structure. This evolution is probed at longer time scales via temperature accelerated dynamics (TAD), revealing even more defect structure subtlety.

Ultimately, we intend to use to defect structure information gathered to optimize actual candidate scintillator compounds. Therefore, it is imperative that the simulation results described here are “integratable” into a complete development program consisting of theory, synthesis and characterization elements. We finally discuss the potential structure of this feedback loop.

References

Bismuth Germanate (Bi$_4$Ge$_3$O$_{12}$ - BGO) have been the focus of several studies due to the interest in scintillator materials. It has a wide variety of applications in medicine and high energy physics [1,2], and is often used in the single crystalline form. Due to the difficulty to produce good quality, large samples, there is a general search for the substitution of single crystals by ceramic in many areas where scintillators are applied, and scintillator ceramics have already some applications as radiation detectors [3,4]. The growth of BGO single crystals is widely reported in the literature [5,6] but there are only some few references concerning the synthesis of BGO ceramics.

The advantages of using ceramics instead of single crystals are the homogeneous distribution of dopants, high output in mass production and the facility to conform ceramics in a large variety of shapes and sizes so improving the scintillator production process and usability.

The present work reports the production and characterization of BGO scintillators doped with Cr$^{3+}$. Single phase Bi$_4$Ge$_3$O$_{12}$ in pure state and containing up to 1 % of the Cr$^{3+}$ were produced via a solid state route and their luminescent properties were investigated (absorption and emission spectra and radioluminescence). When excited at 200-230 nm, pure BGO ceramics presented a wide photoluminescent band emission centred at 500 nm, assigned to the Bi$^{3+}$ internal transitions. For the doped samples under the same excitation, this wide band was superposed by the emission peaks of the dopant.

Computer modelling was also employed to understand the Cr$^{3+}$ - doping process in the BGO matrix. The modelling strategy follows the methodology presented in previous works [BGO ICDIM, BGO REI] where the material is modelled via a set of par wise potential acting between the ions. Such inter-ionic potential where obtained empirically, by fitting the parameters to the BGO structure, elastic constants and the refraction index [BGO ICDIM]. The incorporation of the Cr$^{3+}$ dopant was modelled considering the possibility of substitution at both Bi$^{3+}$ or Ge$^{4+}$ sites. In the latter a range of possible charge compensation schemes were devised and the corresponding solution reactions were used to calculate the most probable defect. The final positions of the neighbouring atoms to the Cr$^{3+}$ dopant were thus used to estimate the site symmetry and this leads to the interpretation of the optical properties of the Cr$^{3+}$ in the BGO matrix. (The authors are grateful to MCT/PADCTIIICNPq, FINERP and CAPES for the financial support. ACSM and GCS wish to acknowledge the grants from PIBIC/CNPq)

References:

DEFECTS AND PHOTOREFRACTION: A RELATION WITH MUTUAL BENEFITS  

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Intrinsic and extrinsic defects are at the origin of photorefraction in several photorefractive materials, i. e., materials, where the refractive index is changed upon light irradiation. In electrooptic photorefractive crystals, for instance, exposure to an inhomogeneous light pattern redistributes charge carriers from deep defects (donors) into traps (acceptors) and a spatial distribution of the electric field results which modulates the refractive index via the Pockels effect. In this basic process the photon cross section of the donor defect and the effective trapping cross section of the acceptor define the properties of the photorefractive response such as its dispersive behavior. In the usual case various types of extrinsic and intrinsic defects may simultaneously contribute to photorefraction. For instance, photo-excitation of charge carriers from deep Fe^{2+}-donors to shallow Nb_{14}^{4+/5+}-antisite defects, resp., has been adopted for nonvolatile hologram recording in LiNbO$_3$, the most widely studied representative of photorefractive electrooptic crystals. This allows to expand the field of important photorefractive applications, such as high-density holographic data storage [1].

![Figure 1: Holographic data storage in the electrooptic photorefractive crystal LiNbO$_3$:Fe. A multitude of holograms is recorded by spatial and angular multiplexing via a photo-induced spatial redistributions of charges from extrinsic Fe-defects. Particular holograms with 100 kBit-content each become visible at 16 spatial positions via spectral diffraction of white-light.](image)

Vice versa, a benefit of defect physics from photorefraction emerges with increasing importance in recent years; i. e., photorefraction was successfully applied as a useful and comprehensive tool for purposes of defect center analysis. For instance, the relation of photorefractive light scattering to extrinsic Ce$^{3+/4+}$-defects was investigated in the oxide Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_5$:Ce [2]. This far-field scattering results from optical noise within the crystal bulk, which is amplified via the nonlocal photorefractive response. The magnitude and dispersive behavior of light-amplification are directly related to the photoelectric charge redistribution between Ce$^{3+}$ and Ce$^{4+}$-defects; this reflects the basic principle by which scattering allows to analyze the defect structure. As an outstanding advantage, this contact-free optical method can be applied for in-situ investigations of the defect structure, e.g., during thermal treatments, or for spatially resolved investigations by applying focused laser beams.

The talk highlights the far-reaching mutual benefit of defects and photorefraction which is demonstrated with oxidic photorefractive media as examples. Modern optical methods based on space-charge wave excitation, photo-induced light scattering and ultra-fast holography are presented.


Neutron and gamma irradiations are commercially applied on topaz to enhance its colour leading to different shades of blue. In general, neutron irradiation turns colourless topaz immediately blue, whereas gamma irradiation leads to brown colours. The latter can be bleached by thermal treatments at about 200°C resulting in weak to medium blue colours.

Topaz with general formula Al$_2$SiO$_4$(F,OH)$_2$ has orthorhombic crystal structure with space group $Pbnm$ and $Z=4$. The colour centres that are responsible for the blue and brown colours are still not identified. Recently, we have identified by electron paramagnetic resonance (EPR) an O$^-$ hole centre interacting with two Al ions on a (OH)$^-$ lattice site which is stable until 500°C, the same temperature at which the blue colour is lost [1].

In this work defect creation by neutron and gamma irradiation in topaz from four different regions in Brazil is studied by EPR and optical absorption. In addition, all samples were characterized for impurities by neutron activation and X-ray fluorescence spectroscopy. We show that the brown colour of topaz is correlated with a defect which shows an isotropic EPR line at room temperature with $g = 2.015(1)$ and line width of 5.8(3) mT in all types of samples. The related defect is produced by gamma irradiation and is thermally stable up to 200°C, the same temperature at which the brown colour fades out. In contrast, neutron irradiation leads to the formation of the peroxy radical (O$_2^-$) [2,3] which is stable until 800°C.

Dose dependencies of defect creations for both irradiation techniques and thermal annealing experiments are discussed in terms of possible defect models, some of them in contrast to existing literature [4]. It is shown that the type of defects created by the different irradiations are independent on the mining region, i.e. independent on the different extrinsic impurities.

References

Several paramagnetic centres have been identified in γ-irradiated beryl with conventional EPR: Fe$^{3+}$, Mn$^{2+}$, the methyl radical (CH$_3$) and the atomic H$^0$ centre, among others [1]. These type of centres are observed in morganite and goshenite, the slightly pink or colourless varieties of beryl after γ-irradiation. Most samples turn blue after irradiation, some slightly yellow. Based on the analysis of the optical absorption spectrum and on the magnetic circular dichroism of the absorption (MCDA) it was argued that the colour centre responsible for the absorption bands resulting in the blue colour is a molecular paramagnetic CO$_3^-$ centre located at the centre of the structural channels of beryl [2]. The NO$_3$ radical, due to its similar electronic configuration, has also been suggested as a potential candidate for the blue colour centre but no definitive proof has been given up to now.

The main patterns of the optical absorption bands in this type of beryl have been explained by the $^2A'_2 \rightarrow ^2E'$ transition of a trigonal ($D_{6h}$) CO$_3^-$ at 14490 cm$^{-1}$ coupled to a totally symmetrical ($A_1$) breathing mode of about 1020 cm$^{-1}$ [2]. Although most lines could be ascribed to vibrational replicas of the 14490 cm$^{-1}$ absorption band, many features of the spectra remained unexplained. Two of them were: the band at 16020 cm$^{-1}$ whose MCDA signal is opposite in sign to the band at 14490 cm$^{-1}$ and the splitting of the latter, which was much larger than expected from the spin-orbit interaction of the CO$_3^-$ radical [2].

In this work we identify, with optically-detected magnetic resonance (ODMR) via the magnetic circular dichroism of the absorption (MCDA), the NO$_3$ and CO$_3^-$ molecular centres trapped in the structural channels of gamma-irradiated beryl. We confirm that, along with the CO$_3^-$ identified by Edgar and Vance (1977) [2], the NO$_3$ is also responsible for the blue colour by introducing several absorption peaks between 14500 cm$^{-1}$ and 18000 cm$^{-1}$ (720 nm down to 540 nm). Their individual contributions to the overall many-peak optical spectra have been established and all optical transitions could be explained in terms of a combination of crystal-field and spin-orbit split $^2A'_2 \rightarrow ^2E'$ transition plus vibronic replicas.

References


A variety of beryls, inclusive of blue aquamarine, heliodore and goshenite, spanning an iron concentration range of two orders of magnitude has been studied by absorption spectroscopy down to 16 K and in the energy range 10000-50000 cm⁻¹. By the aid of d⁶(Fe²⁺) and d⁵(Fe³⁺) Tanabe-Sugano diagrams for octahedral symmetry, a detailed interpretation of the crystal field spectra has been given. The comparison with reference spectra of aqueous solutions and hydrated crystals containing Fe²⁺ and Fe³⁺ turned out to be quite useful: the spin-forbidden transitions of Fe²⁺ have been observed for the first time in these diluted systems and attributed. The colour centre absorption, its thermal instability and contribution to the colour of these crystals has been considered. The allowed charge transfer transitions, ligand-to-metal, for both Fe²⁺ and Fe³⁺ have been observed in the low iron containing goshenites above 32000 cm⁻¹ and up to 50000 cm⁻¹.

Figure 1: Absorption spectra of beryls of different colour. Spectra are taken at low temperatures (16K).

References
O-BOUND HOLE POLARONS IN OXIDE MATERIALS

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Holes in oxide materials can be created by optical or chemical doping. Such holes tend to be captured at O\textsuperscript{2-} ions next to (negatively charged) acceptor defects. Usually several oxygen sites of this type are equivalent with respect to the acceptor position, facilitating tunnelling of the hole between them. The energy lowering by spontaneous lattice polarization, however, in most cases is larger than the tunnelling stabilization, causing self-localization at one of the equivalent sites. This represents the formation of a small polaron. Optical charge transfer of the polaron to a neighboring equivalent site under Franck-Condon conditions leads to wide intense absorption bands, typically extending into the visible. This makes such bound polarons potent color centres.

The mechanism of polaron formation and of their optical excitation is outlined. Next the observation is treated that the energy of the band peaks depends strongly on the topology of the clusters, i.e. whether a polaron can choose between 2, 4, 6 or 12 equivalent sites, causing absorption bands typically peaked near 4, 2.8, 2.3 or 1.3 eV, resp. After consideration of these highly symmetric paradigms of bound polarons their occurrence in various materials is discussed specifically.

![Figure 1: Optical absorption of an O\textsuperscript{-} polaron bound to Ge\textsubscript{Si} in α-quartz. On the basis of a polaron stabilization energy of 0.85 eV and the presented theory the band given as full line is predicted](image)

Examples are given for bound polarons and their optical absorptions in the following classes of materials (always listing one representative compound and one acceptor defect): MgO (Mg vacancy), Al\textsubscript{2}O\textsubscript{3} (Mg\textsubscript{Al}), LiNbO\textsubscript{3} (Li vacancy), BaTiO\textsubscript{3} (Na\textsubscript{Ba}), sillenite Bi\textsubscript{12}TiO\textsubscript{20} (Bi\textsubscript{Ti} antisite defect), Quartz (Ge\textsubscript{Si}), NiO (Li\textsubscript{Ni}), smoky quartz (Al\textsubscript{Si}) and other gemstones. The role of hole polarons for various applications of oxide materials is pointed out.
Most of atomistic modelling of nuclear fuels in the literature have concentrated so far on oxides, while very little is done on advanced fuel like nitrides. Therefore, we present results of the first-principles atomistic modelling of UN and defects therein, necessary for interpretation of existing experimental data and planning of new experiments.

Using the DFT plane wave computer code VASP, combined with the supercell model, we have calculated the lattice constant, bulk modulus and the electronic density distribution in perfect fcc UN crystals that are in good agreement with experimental data. The Bader (topological) effective charges are estimated to be ±1.6 e, indicating the chemical bonding between U and N atoms.

Point defects were simulated using large supercells, up to 128 atoms, with a complete structure optimization. The calculated formation energy for N vacancy is 9.4 eV, whereas its migration energies along the (001) axis is predicted to be 3.5 eV. The N vacancies hardly affect the lattice constant (0.17% compression for 3% vacancy concentration), whereas the local lattice deformation is characterized by 0.7% inward displacement of six nearest U atoms. This is accompanied with the localization of the electron density of missing N atoms mostly on these six U atoms. In the case of a U vacancy, characterized by the formation energy of 9.1 eV and the lattice energy gain of 1 eV, the electronic density redistribution is spread over a larger region.

The modelling of the Frenkel and Schottky pairs gives their formation energies of 4.6 eV and 3.8 eV, respectively. The lattice relaxation energy in the former case is quite substantial (2.3 eV). Analysis of the interstitial N atom formation process shows a quite non-trivial behaviour: the N ion leaves most of its charge on six U ions surrounding the N vacancy. On the other hand, the interstitial N atom in its equilibrium position attracts an additional electron density from the nearest neighbours which makes its effective charge nonzero (-1.07 e) but essentially smaller than it has in a host crystal site (-1.6 e). This effective charge is close to that experimentally estimated. The calculated activation energy of the N interstitial migration along the (001) axis is 2.7 eV, smaller than that of N vacancy and in perfect agreement with the experiment. This confirms the suggestion that the interstitial migration is the main mechanism of N diffusion in UN fuel.

Additionally, we studied O impurity substituting for an N atom as well as local lattice deformations and charge redistributions induced by point defects and defect pairs.

In the end, we discuss the thermodynamic approach aimed at predicting temperatures and defect concentrations at which O impurities are effectively aggregated in an UN matrix.
OTuB2

COMPARISON BETWEEN MODELS OF INSULATOR AND SEMICONDUCTOR THIN FILMS ISLANDING

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The aim of the study is to compare theoretically two thin layer synthesis methods, sol-gel route and Chemical Vapour Deposition (CVD) processing. We are going to detail a theoretical model which allows one to simulate the islanding of polycrystalline thin films, synthesize via sol-gel processing, in the light of some models reported for CVD processing in the literature.

The synthesis of self-organized quantum dots (QD's) can be achieved through dewetting of a thin film during vaporized atoms condensation on a substrate. Size distribution, morphology and crystalline orientation of the resulting nanometre scale islands are controlled by the relaxation of the strained film. Such a phenomenon is well known for semiconductor devices and has already been modeled for CVD processes involving Stranski-Krastanov (SK) growth mode [1]; experimental studies have been carried out on systems as \{PbSe/PbTe\} [2], \{Ge/Si\} [3], \{CeO₂/Al₂O₃\} [4]. The main results show that during SK growth, the formation of QD's starts after the deposition of the so called “wetting layer” on the substrate [5]. Above a critical thickness, the QD's can initiate by nucleation or surface roughening from the layer previously deposited. Whatever the case, QD's formation kinetics are function of the growth rate and the working temperature [1]. Eventually, the equilibrium shape of each QD's depends on the minimization of its internal energy [2-4].

However, a thin film may be also deposited on a substrate via sol-gel route which involves a spontaneous evolution without deposition; the QD's are formed after annealing of the film at high temperature (>1000°C). This method has been successfully employed to synthesize oxide QD's as \{ZrO₂/Al₂O₃\} [6]. Furthermore, few theoretical approaches have been developed to understand the fundamental mechanisms associated to it [7-8]. Thus, we have developed a Monte Carlo approach, derived from the Solid on Solid model, to simulate the islanding of polycrystalline thin films without deposition [9]. The thin film is divided in 10000 domains, each of them containing about 1000 atoms. At the first stage of computation, the height is the same for all domains while each of them gets a random crystallographic orientation (with regard to the substrate and the neighbours). Then the algorithm works through the Metropolis scheme. During the whole computation time, the height and the crystallographic orientation of each domain are likely to evolve.

References:

OPTICAL TRANSITIONS IN PAIRS OF TRIVALENT ION - INTERSTITIAL FLUORINE IN ALKALINE EARTH FLUORIDES

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Trivalent ions incorporated into lattice of alkaline-earth fluorides are accompanied with charge-compensating interstitial fluorines. Nearest position of interstitial fluorine is favourable in CaF2, giving tetragonal symmetry to centre. The next nearest position of interstitial fluorine is favourable in BaF2 lattice, giving trigonal symmetry to centre. If trivalent ion has no own optical bands a new type of transitions can be observed – the transitions between impurity metal and interstitial fluorine. Such absorption in vacuum ultraviolet region and luminescence in ultraviolet region were identified in CaF2 and BaF2 crystals doped with LaF3 or YF3 impurity.

Shift of fundamental absorption edge to low energies was observed in vacuum ultraviolet region of CaF2 and BaF2 crystals doped with YF3 or LaF3 impurity. The more impurity concentration the larger shift was observed. The concentration of impurity varied from 0.01 weight. % to few percents. Evidently the impurity absorption bands are very closed to exciton absorption bands so one could not observe the impurity band maximums. The shift becomes near 0.5 eV for 1% of LaF3 and near 0.4 eV for 1 % of YF3 impurity. New luminescence bands are observed under excitation into impurity region. The bands have maximums near 4 eV in BaF2 and near 5 eV in CaF2. The emissions have decay times near 4-7 microseconds at 10 K. No fast components were observed.

Unempirical calculations of absorption and triplet-singlet luminescence of crystal cluster, containing the impurity ion-interstitial fluorine pair were performed using PCGamess code [1]. Crystal cluster was surrounded by few tens of effective core potentials of Ca or Ba and then up to 10 thousands of point charges [2]. Geometry optimisation shows the significant distortion in ground state, but much less distortion in triplet excited state, when hole localized on interstitial fluorine and excited electrons occupied the Y or La atomic levels. Calculations of absorption show that the transitions from interstitial fluorine to impurity metal have the energies near 1.5 eV less than transition in pure crystal cluster and have the oscillator strengths near 0.1-0.3. Triplet – singlet luminescence energies were calculated as near 4 eV in BaF2 and near 5 eV in CaF2.

The experimental and calculation results lead us to conclusion that the observed Y or La – impurity absorption and luminescence belong to transitions between charge compensating fluorine - trivalent metal pairs.

References
IONIC MECHANISMS IN THE OPTICALLY STIMULATED LUMINESCEENCE OF QUARTZ

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Among the many centres found in crystalline quartz it is well known that Al, substitutional for Si, is always present, in different concentrations, giving rise, at Room Temperature, to ionic migration of the associated alkali ions.

Many authors evidenced that these alkali ions are involved in trapping and in OSL respectively.

We have focused our attention on the OSL in quartz that is now widely used in sediment dating, although the trapping-detrapping mechanisms have not yet been clarified. Bulk synthetic crystalline quartz, with known concentrations of Al and alkali ions has been used.

Looking at the light emitted under optical stimulation (wavelength 470 nm), the intensity of the emission as a function of the power of the stimulating light has been measured at different temperatures.

There is evidence that an ionic migration is at the basis of the OSL phenomenon, linking OSL emission with the TSL peaks known as “110°C” and “325°C”.

This result is supported by different OSL efficiency in quartz samples differently oriented, perpendicular or parallel to the optical “c” axis.
Irradiation of pure and impurity doped RbMgF$_3$ with high energy electrons leads to a variety of defect centres [1]. In the case of Mn$^{2+}$ doping, it has been reported that ($F$-centre)-Mn$^{2+}$ complexes occur statistically, which show high oscillator strengths when compared with isolated Mn$^{2+}$ ions. The large increase (up to $10^5$) in the oscillator strength is believed to arise from the appearance of spin-allowed 3d transitions in the ($F$-centre)-Mn$^{2+}$ complexes that are forbidden in isolated Mn$^{2+}$ ions [1]. Thermal processing at temperatures of up to 700 K leads to additional centres attributable to $F$-centre diffusion and clustering to $F_2$- and $F_3$-centers and the above mentioned complexes, but there has been no evidence for substantial thermal annealing of the defects [1, 2]. While models have been proposed to explain the radiation-induced defects in RbMgF$_3$:Mn$^{2+}$, it is clear that the understanding of the defect centres can be improved by systematic thermally stimulated luminescence (TSL) measurements as well as studying the effect of moderate and low energy and low intensity irradiation.

In this report we present the results from TSL, photo-luminescence (PL) and optical absorption measurements on RbMgF$_3$:Mn$^{2+}$ after X-ray and $\gamma$-ray irradiation at room temperature. Several glow peaks can be observed even after exposure to low doses. The corresponding emission arises from isolated Mn$^{2+}$ ions in the crystal. We discuss the results from measurements on samples with a wide range of Mn$^{2+}$ concentrations, which has enabled us to obtain a better understanding of the low dose radiation-induced defects in RbMgF$_3$:Mn$^{2+}$. We also report the observation of optically stimulated luminescence (OSL) and present a possible model.

References

MULTISITE STRUCTURE OF RE$^{3+}$ OPTICAL CENTRES IN PHOTOREFRACTIVE Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ CRYSTALS

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We did perform a comprehensive study of the properties and the possible origin of multiple optical centres formed by RE$^{3+}$ ions in the lattice of congruent Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBN) crystals.

SBN crystals allow modification of its photorefractive properties due to a variation of the Sr/Ba ratio and possibilities to accommodate a wide range of dopants of high concentration. The best known dopant is Ce$^{3+}$, which increases photosensitivity, spectral response and response time of doped SBN samples [1]. Local symmetry, energy structure, crystal lattice sites occupation and its dependence on doping concentration of RE impurity ions are of interest for optimization regarding photorefractive applications of this material. Recent ESR studies of Ce$^{3+}$:SBN [2] did not achieve the conclusive results, which also are not in agreement with the data of Ce$^{3+}$:SBN IR-spectroscopy [3]. We continued the research using Eu$^{3+}$ and Er$^{3+}$ ions as more sensitive optical probes for analysis by selective spectroscopy. Optical studies of Eu$^{3+}$ and Er$^{3+}$ doped SBN (doping levels 50–24000 ppm) were performed using the high-selective method of combined excitation emission spectroscopy, which did demonstrate earlier it’s rewarding potential for spectral distinction of different centre configurations, which are simultaneously present in the host lattice [4]. As a result we could distinguish and determine the detailed energy diagrams (“fingerprints”), polarization properties and concentration dynamics of the main Eu$^{3+}$ (three) and Er$^{3+}$ (five) types of optical centres formed in SBN host lattice with a degree of structural disorder. The observed strictly exponential decay of the luminescence of these centres indicates their predominantly fixed position in the crystal lattice. Further we used the data obtained to determine the origin of the individual RE$^{3+}$ centres. As a qualitative tool to characterise the local environment of RE$^{3+}$ centres we used measurements of the linear Stark effect on the multiplet splittings of the RE$^{3+}$ terms under application of an external electric field in different orientations relative to the C-axis of the sample [5]. In order to distinguish crystal lattice sites of RE$^{3+}$ impurity with the same local symmetry we studied the effect of high hydrostatic pressure (diamond anvil cell technique) on the electronic structure, which radically differs for the RE$^{3+}$ centres in different crystallographic positions. The results are discussed in accordance with shell-model analysis of Ce$^{3+}$ incorporation into SBN [6].

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References

TRANSITION DIPOLES INTERACTION OF SH–SH IONS IN KCL

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The resonance phenomenon is an instance in vibrational molecular spectroscopy of an interaction between transition dipoles (TD-interaction). A classical example is Fermi resonance in CO$_2$, in which two adjacent energy levels are shifted from each other. TD-interaction plays an important role in the formation of contours of IR bands of SF$_6$, CF$_4$, NF$_3$ and OCS dissolved in liquid Ar, Kr and Xe. Another example of such an interaction is found in solid-state physics – the diatomic molecular impurity defects in alkali halides. The pair lines were observed at temperatures near 4 K for SeH$^-$ – SeH$^-$ and SH$^-$ – SH$^-$ molecular pairs in KCl [1]; their intensities exhibited a dependence on the squared concentration and their half widths were less than 0.05 cm$^{-1}$. We undertook a quantum-mechanical calculation of frequencies and intensities of the pair lines of SH$^-$ – SH$^-$ [2, 3], but only for fundamental transitions; it was made in an approximation of a dipole-dipole interaction, but yielded satisfactory agreement between theory and experimental data.

In this work we propose a theoretical analysis of these experimental results and a new technique to calculate the frequencies and intensities for TD-interaction of molecular defects XH$^-$ in ionic crystals. In a dipole approximation, the frequencies and intensities of vibrational transitions of diatomic dimers $^n$XH$^- - ^n$XH$^-$ are found for exact ($m=n$) and quasi-exact ($m\neq n$) resonances. Elements of the interaction matrix are obtained with regard to the mechanical anharmonicity in second order of perturbation theory for the case of a linear dependence of the dipolar moment of a diatomic molecule on the vibrational coordinate. The expressions obtained are applied to the calculation of overtones in the absorption spectrum of dimers $^n$SH$^- - ^n$SH$^-$ in a KCl crystal.

References

PHOTOSENSITIVE DEFECTS IN NOMINALLY PURE AND DOPED CUBIC BORON NITRIDE CRYSTALS

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Electron Spin Resonance (ESR) remains the best method for the identification and characterization of paramagnetic point defects in insulators and semiconductors. Our research interests have been focused in the last years towards using ESR as the main tool in determining the presence and local/atomic properties of point defects in cubic boron nitride (c-BN), a synthetic, diamond-like superhard material with enormous potential as a multifunctional material for devices operating in extreme conditions.

Because c-BN is usually available in submillimeter sized crystalline powders, the best approach in such studies is to combine low (X-band) frequency ESR measurements on such powder samples with high (W-band) frequency measurements on selected single crystallites. Such correlated multifrequency studies, in a broad temperature range, which combine the high absolute sensitivity and broad microwave powers range of the X-band ESR measurements with the possibility to do anisotropy studies with very high spectral resolution on oriented single crystals, in the W-band, has resulted in the unambiguous identification of the so-called D- and A-type paramagnetic point defects in nominally pure, grey-dark and amber colored c-BN crystalline powders, respectively [1-3]. New paramagnetic point defects have been latter identified by W-band ESR in Be-doped, blue c-BN single crystals [4].

We shall present here the results of further W-band ESR investigations on nominally pure, amber colored and Be-doped c-BN single crystals, which have been illuminated at low temperatures in the UV-VIS range. Strong variations in the concentration of the previously observed (native) paramagnetic centers, as well as the production of new, photoinduced centers have been observed in both nominally pure, amber colored and Be-doped c-BN single crystals as a function of the energy of the incident light. The analysis of these results reveals the simultaneous presence in amber colored c-BN, besides the paramagnetic A1, A2 and A3 centers, of other EPR silent centers. The possible structural models and position in the gap of the associated local states shall be discussed.

References

Mn-activated RbCdF$_3$ shows an increased Mn$^{2+}$ luminescence after x-ray or ultra-violet (UV) irradiation. This effect is caused by an increase of the oscillator strength of the originally forbidden Mn transition that becomes partially allowed due to interactions between Mn and spatially-correlated radiation defects like F centres. We report the results of a study using optical and electron paramagnetic resonance spectroscopy of radiation defects in RbCdF$_3$ doped with 0.0003% to 1% Mn$^{2+}$.

The photoluminescence (PL), and the x-ray excited luminescence (XL), of Mn-activated RbCdF$_3$ show an intense emission at 560 nm that can be attributed to Mn$^{2+}$; the corresponding PL excitation shows several bands between 300 and 520 nm that are typical for Mn$^{2+}$ in $O_h$ crystal field symmetry. After x-ray or UV (< 270 nm) irradiation, an additional broad PL excitation band centred at about 310 nm occurs. The intensity of the Mn$^{2+}$ PL and XL increases with increasing x-ray or UV dose. High-intensity bleaching in the wavelength range from 280 to 420 nm reduces the Mn$^{2+}$ emission to the original pre-irradiated level.

The observed effect is probably caused by radiation-induced F-centres (electron trapped at a fluorine vacancy) in the vicinity of the Mn$^{2+}$ ions. For high irradiation doses the PL intensity cannot be increased any further; it saturates, as does the XL intensity. The saturation can possibly be attributed to a fixed concentration of fluorine vacancies, determined by the Mn$^{2+}$ concentration. Recent work on Mn-activated RbCdF$_3$ [3] indicates that x-ray or UV irradiation leads to a hole trapped at the Mn site (Mn$^{3+}$) with the electron trapped on the fluorine vacancy, forming an F-centre. We performed electron paramagnetic resonance (EPR) measurements before and after x-irradiation and measured the relative number of Mn$^{2+}$ ions.

References

Effects of X, β and VUV radiation on some composed Ba-Halide crystals such as BaFBr, BaFCl, BaF2:CuCl2, BaFBr:CuCl2, as well as on samples doped with various rare-earth ions have been studied. Methods of optical absorption and of luminescence were applied: X-luminescence (XL), Photoluminescence (PL), thermoluminescence (TL), phototransferred TL (PTTL) and optically stimulated luminescence (OSL) as well as emission and excitation spectra were measured. Absorption measurements and TL excitations were performed at room temperature (RT) and at liquid nitrogen temperature (LNT). Optical stimulation for PTTL and OSL investigations were carried out at LNT in samples that had previously been X or β irradiated at RT. Results were compared to those induced in nominally pure BaF2 crystals. The possible application of Eu2+ doped BaFCl as efficient X-ray storage phosphor was previously investigated [e.g.:1, 2].

The TL excitation spectra showed maxima at the long-wavelength tail of the fundamental absorption and in the doped samples also at longer wavelengths. The TL induced by monochromatic VUV radiation showed essentially the same peaks and the same thermal activation energies as the TL induced by X or β irradiations in the same sample, indicating that the same defects were induced by the different types of radiation. Thermal stability of the radiation induced defects has also been investigated. The XL and PL efficiencies of some of the tested samples was relatively high and the emission bands were located in a spectral region were the common photomultiplier tubes are most sensitive. The TL efficiency of some of the samples was of the same order of magnitude as that of the known TL dosimetric material LiF: Mg, Ti (TLD 100).

References


Despite the evident progress in SiC crystal growth, uncontrollable point defects and impurities persist in the material at the level $10^{15} – 10^{16}$ cm$^{-3}$. They act as carrier trap centres in SiC-based electronic devices. Thermostimulated luminescence (TSL) represents an extremely sensitive tool for detecting of defects acting as electron and hole traps in luminescent materials. Further investigation of trap photostimulation spectra allows obtaining the optical characteristics of defects involved in radiation energy storage-recombination.

It is stated that UV-irradiation results in accumulation of several TSL peaks. For B-doped samples results the main TSL peak is observed at 100 K [1] or 240 K [2]. Additional TSL peaks at about 175 K and 280 K are reported by W. Hartung et al. as well [3]. It is found that for N-doped crystals peak temperature of the main TSL, depending on doping-compensation conditions vary from 75 K to 115 K [1]. Using shape analysis of the whole TSL peak [4] the trap parameters are reported by several authors. When compared with parameters typical for recombination by release of free electron or hole activation, the obtained values of energy and frequency factor for above mentioned TSL peaks are rather low: ie. $0,080\text{eV/9,03 } 10^4 \text{s}^{-1}$; $0,135 \text{eV/1,4 } 10^5 \text{s}^{-1}$ respectively [1].

In this study, we report the on the trap spectroscopy of intrinsic and N- or B-doped SiC single crystal using fractional glow technique [5]. The FGT allows obtain during the whole TSL process both the effective activation energy and frequency factor as stimulation temperature function. TSL and FGT investigations are provided from 10 to 350 K after irradiation either by the X-rays or by the monochromatic nanosecond light pulses (YAG-Nd pumped optical parametric resonator).

After irradiation in the direct band transition region (5,0-5,8eV) and indirect band transition and impurity absorption region below at 3,1 eV the luminescence decay is represented by temperature-independent afterglow following hyperbolic decay up to about 40 K. TSL of undoped and N- or B-doped samples show 6 broad peaks at 108 K; 122 K; 132 K; 200 K and 320 K (heating rate 10 Ks$^{-1}$). Three emission bands are present at 2,68 eV (108 K; 122 K; 132 K peaks), 2,24 eV (all peaks) and 1,9 eV (200 K peak).

Analysis of the FGT data show that TSL peaks are broadened due to decay of traps distributed in activation energies. Temperature independent low temperature afterglow in all samples arises due to tunnelling recombination in the spatially correlated donor – acceptor pairs. Analysis of the activation energy and frequency factor values allows to suggest that the main low temperature TSL peaks arise due both the over barrier recombination in donor–acceptor pairs as well as the recombination of released electrons or holes with deep recombination centres responsible for 2,24 eV and 1,9 eV luminescence.

The evaluation of TSL accumulation spectra by pulsed laser excitation of N- and B-doped SiC in spectral range from 0,8 to 3,0 eV are discussed.

References
SOFT X-RAY EXCITATION OF LUMINESCENCE IN WIDE BANDGAP CRYSTALS

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During last decades, the experiments with VUV synchrotron radiation in the energy range up to 30 eV has significantly advanced the understanding of fundamental phenomena and mechanisms of the energy relaxation and transfer in solids (the first threshold of the inelastic e-e scattering [1], the crossluminescence [2], the energy transfer from host to doping ions [3], etc…). Recently, an availability of new light sources expanded experimental opportunities in the soft X-ray energy region (100 – 1000 eV).

Soft X-ray photon creates in solid one electron and one core hole with the energy of several hundreds of eV. Such primary electronic excitations (EEs) relax with creation of a number of low energy EEs. The spatial distribution of these secondary excitations depends strongly on the energy and the nature of primary one. The non-uniform distribution of EEs affects all relaxation phenomena such as defect creation and photon emission.

We will present and discuss luminescence characteristics of a set of wide bandgap crystals (BaF2, CsCl, LuAP:Ce, YAG:Yb, YLF:Yb, GGG:Yb [4]) excited in the range from 90 to 850 eV. The data were collected at the banding magnet beamline (BEAR) of the electron storage ring of third generation ELETTRA in Trieste. An excellent brightness of this source allowed us to measure the luminescence excitation spectra in the soft X-ray energy range with a high resolution. We used a spectrometer with CCD to collect entire luminescence spectrum of crystal for each value of excitation energy.

We will give a special attention to changes of the light yield in the vicinity of absorption edges of the elements coming in the soft x-ray range. The analysis of the spectra reveals interaction effects between closed secondary EEs, which influence the energy conversion process in crystals.

References

SOME ASPECTS OF ION IMPLANTATION TECHNIQUE IN NANOSTRUCTURED MATERIALS

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In the last decade, metal nanoclusters (NCs) embedded in insulating matrices have received increasing interest due to their peculiar optical, magnetic, and catalytic properties when the size is comparable to or less than the electronic mean free path. Glass based composites are, in general, expected to play an important role as materials for various nanotechnology applications, due to the low cost, ease of processing, high durability, resistance and high transparency, as well the possibility of tailoring the behaviour of the glass-based structures. Metallic NCs embedded in glass can increase the optical third-order susceptibility of the matrix by several order of magnitude, making such systems interesting candidates to be used as optical switches. Interesting for optical amplifiers, the possibility of energy transfer between nano-metal structures to Er ions, out of resonance wavelength. The presentation deals with metal nanoclusters composites synthesized by ion implantation and formed by clusters of binary transition metals alloy embedded in silicate glasses, in which the cluster concentration is below the percolation limit (dispersed clusters).

Some case studies will be presented in which ion-beam-based techniques are exploited either for the synthesis or for the structural or compositional modification of composites. As far as the technological properties of the studied systems are concerned, some results will be presented about the nonlinear optical properties of metal-based NCs composites and energy transfer mechanisms in glasses containing Erbium ions and molecular-like metal structures.
Rare-earth-activated insulating materials play an important role in today’s optical technology for applications such as solid-state lasers, scintillators, fibre amplifiers, and phosphors. The parity-forbidden intraconfigurational f-f transitions in rare earth ions, which are exploited in many of these applications, are characterized by very narrow absorption and emission lines. Temperature dependent high-resolution absorption measurements can provide a deep insight into the ion’s local crystal field and its interaction with the host lattice [1].

This contribution is aimed to provide examples for high resolution Fourier transform spectroscopy performed on different host materials (namely fluoride and borate single crystals) doped with trivalent Ce, Dy, Ho, Er, and Tm ions. The optical investigation will be discussed also emphasizing the key role of the unified picture for the various dopants in the same material provided by theoretical calculations in the framework of a single-ion model [2]. The role of the rare earth concentration on the absorption spectra will be shown. Hyperfine splittings will be presented for Ho doped yttrium aluminium borate single crystal [3].

Finally the Er$^{3+}$ narrow lines detection will be exploited as a sensitive probe for the nature and origin of different surroundings in SnO$_2$ nanoclusters embedded in a glassy silica matrix.
OTuE1
PHOTOLUMINESCENCE OF Ho$^{3+}$:YVO$_4$ CRYSTALS

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Rare-earth doped crystals present several interesting features, for example intense infrared emissions and long metastable-state lifetimes which make them good candidates for lasers. Laser action at 1.6-2.1 µm is required for eye-safe devices. For example, Ho$^{3+}$-doped YAG crystals exhibit the laser emission at 2.1 µm [1]. Few studies have been made on the optical properties of Ho$^{3+}$:YVO$_4$ crystals [2], especially in the case of the infrared emission of around 2.0 µm as a possible laser transition. We observed intense and broad infrared emission bands. Besides the infrared emission bands, we observed at 15 K a broad emission in the visible range at 610 nm as shown in Fig.1. The excitation band for this broad emission is located at 380 nm which is near the edge of the band gap of the crystal. This emission band could be attributed to vanadium centres different from VO$_4^{3-}$, as no Ho$^{3+}$ transition can be seen in the spectra. Previously a broad emission band was observed at 475 nm with an excitation at 337 nm (N$_2$ laser) and was attributed to the oxygen vacancies in the crystals, which in certain preparation conditions become more yellow than others [3]. The 610 nm broad emission band was observed at low temperature in highly doped crystals with a Ho$^{3+}$ concentrations of more than 0.5 %. Discussion is given on the origin of the broad emission band.

References

The rare earth doped (potassium, rubidium)-lead double (chloride, bromide) APb$_2$X$_5$:RE (A≡K, Rb; X≡Cl, Br) crystals are promising new materials emitting in wide spectral region from UV up to mid IR. Laser action of KPC:RE crystals was obtained with Nd (1.06 µm), Dy (2.4 µm) and Er (4.6 µm) [1]. In Refs. [2-4] we have started a study of the luminescent and optical properties for both the pure and doped KPC crystals at 10K. The main goal of the present work is a luminescent and optical spectroscopy study of the other crystals of the APb$_2$X$_5$ family. The study was carried out by means of the low-temperature luminescence VUV spectroscopy with the time-resolution. Time-resolved and steady-state photoluminescence (PL) spectra in the energy range from 1.2 eV to 4.1 eV, PL excitation spectra and reflectivity in the broad energy range from 3.7 eV to 20.6 eV, and the decay kinetics of PL were measured for APb$_2$X$_5$ and APb$_2$X$_5$:RE (RE≡Ho, Tb, Nd, Er, Pr) single crystals at the SUPERLUMI experimental station of HASYLAB using synchrotron radiation (SR). All the examined APb$_2$X$_5$ crystals were grown in the Institute of Mineralogy & Petrography [5].

The low-temperature (T=8 K) luminescence spectra of the undoped APb$_2$X$_5$ crystals comprise of the broad emission bands at 2.05-2.4 eV. The PL decay kinetics obeys an exponential law with a microsecond time-constant, the PL excitation spectra fall in the energy ranges of both the excitonic absorption and 'band-to-band' (hν>E$_g$) transitions. We conclude that the 2.4 eV (KPC) and 2.05 eV (RPB) intrinsic luminescence bands in these crystals are due to the radiative annihilation of the triplet excitons. The 1.9 eV emission band is due to defects. The rare earth (Pr, Er, Nd, Ho, Tb) doped crystals exhibit the characteristic luminescence of the appropriate activators. Their PL can be excited not only in the energy range of hν<E$_g$ and in the energy range of the excitonic absorption, but also in the energy range of the band-to-band transitions at hν>E$_g$. This fact points to the efficient energy transport in these crystals arisen from migration of either excitons, or charge carriers with their recombination on the rare earth activators at the latter stages.

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References

The E’δ centre is one of the most important paramagnetic point defects in amorphous silicon dioxide (a-SiO₂) primarily for the applications of this material in the field of electronics [1]. This defect was observed in X-ray and γ-ray irradiated bulk a-SiO₂, in thermally grown thin SiO₂ films upon annealing, and in buried oxide layers obtained by oxygen implantation (SIMOX) [1]. The principal characteristics of the electron paramagnetic resonance (EPR) spectrum of the E’δ centre are a main resonance line showing nearly isotropic g tensor (g≈2.002) and a pair of lines with magnetic field separation of ~10 mT, supposed to arise from hyperfine interaction of the unpaired electron with a 29Si nucleus (I=1/2) [1,2].

In spite of its relevance, the microscopic structure of the E’δ centre has not been definitively established. Until now four distinct models have been proposed for this point defect and their main features are here summarized. The model proposed by Griscom and Friebele consists in an electron delocalized over an [SiO₄]⁴⁻ vacancy decorated by three Cl⁻ ions [2]. Tohmon et al. [4] have proposed a model consisting in a ionized single oxygen vacancy with the unpaired electron nearly equally shared by the two Si atoms. Finally, Vanheusden and Stesmans [5] and Zhang and Leisure [6], have suggested that the unpaired electron involved in the E’δ could be delocalized over a five Si cluster or over the four Si atoms of a pair of nearby oxygen vacancies, respectively.

In order to support one or another model, a key role is played by the intensity ratio, ζ, between the 10 mT doublet EPR signal and that of the main resonance line of the E’δ centre, that assumes distinct values depending on the number of Si atoms explored by the unpaired electron. The present work reviews the experimental investigation by electron paramagnetic resonance (EPR) on the E’δ centre induced in γ-ray irradiated oxygen deficient a-SiO₂ materials. This study has driven to the determination of the intensity ratio between the hyperfine doublet and the main resonance line of this point defect. On the basis of this estimation we have pointed out that the unpaired electron wave function of the E’δ centre is actually delocalized over four nearly equivalent silicon atoms, shedding new light on the microscopic structure of this technologically relevant point defect also as a probe for embedded silicon clusters.

References

OTuF1

DEPENDENCE OF LONG-LIVED DEFECT CREATION ON EXCITATION DENSITY IN LiF, MgO AND SiO2

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The irradiation of wide-gap dielectrics causes the creation of both short-lived and long-lived (LL) Frenkel pairs (FPs). A comparative experimental study of the processes of LL defect creation by photons (6-70 eV), X-rays (30-50 keV), electrons (2-30 keV, ~300 keV), α-particles (~5 MeV) or swift heavy ions (SHIs, $^{84}$Kr, $^{197}$Au, $^{238}$U with energies between 0.8 and 2.5 GeV) has been carried out in the LiF, MgO and SiO2 crystals, pure and doped with luminescent impurity ions. The irradiation by VUV photons and electrons was performed at 8 or 300 K and by SHIs, at 300 K. The radiation-induced defects were investigated by UV and VUV spectroscopy methods at 8 and 300 K and using the thermoactivation spectroscopy methods at 8-800 K.

In wide-gap LiF crystals ($E_g \approx 14.2$ eV) with self-trapping excitons and holes, the creation energy of LL (stable) FPs is $E_{FP} < E_g$. The efficiency of F-H pair creation by photons or electrons at 8 K under conditions of low density of electronic excitations (EEs) is low because the crowdion-type mechanism of defect separation along closely-packed anion rows is impossible (H interstitials are oriented along $<111>$). High local density of EEs at the decay of a cation exciton ($E \approx 62$ eV) [1] or in the tracks of SHIs (see also [2]) stimulates the interdefect separation in F-H pairs even at 8 K. In LiF, the radiation-induced processes are rather different in the tracks of SHIs and in peripheral regions, where bremsstrahlung radiation is responsible for defect creation. The number ratio of F2 and F centers as well as a relative intensity of thermally stimulated luminescence at 600-700 K with respect to that at 420-560 K is drastically higher in SHI tracks. These effects are caused by thermal spikes in the ion tracks. In MgO crystals $E_{FP} > E_g$ and free excitons do not undergo self-trapping. The energy released at the recombination of relaxed (cold) electrons (e) and holes (h) is insufficient for FP creation under conditions of low density of EEs formed at the irradiation. However, the recombination of hot carriers provides the energy release higher than $E_{FP}$ and the probability of such hot recombination with the creation of FPs is high enough under SHI-irradiation of MgO. The creation and annealing processes of F, F+ centers and neutral oxygen interstitials have been compared under irradiation of MgO by SHIs or fast neutrons. In SiO2 with self-trapping excitons and $E_{FP} > E_g$, the radiation resistance in the bulk is lower than in MgO. The measuring of the spectra of subnanosecond hole intraband luminescence has shown that, in contrast to MgO, there is the energy gap of ~1.5 eV inside a wide valence band of SiO2. This gap facilitates the FP creation in SiO2 due to hot e-h recombination. The prospects of “luminescent defence” against FP creation at hot recombination of carriers in the materials doped with luminescent impurities are discussed (see also [3]).

References

Crystals of LiF are widely used in radiation dosimetry and their thermoluminescence, TL, properties have been extensively investigated. For instance, at least eight glow peaks have been observed between 100 and 500 °C in pure LiF following irradiation with γ rays and special physical treatments in order to generate well defined colour centres, CC. Moreover, a link was established recently between F$_3^+$ centres and the temperature region of the glow curves below 180 °C [1,2], and between F$_3$ centres and the temperature region of the glow curves from 180 to 250 °C [3]. The same method has been applied now to the samples of Fig. 1, and annealing experiments were also performed to gather more information on the thermal evolution of the involved CCs.

Figure 1: TL glow curves of a LiF crystal irradiated with γ rays at RT, sample A, and irradiated with γ rays at RT and annealed at 200 °C, sample B.

The latter measurements have shown that F$_2$ centres anneal at slight higher temperatures than F$_3$ centres, and sample B still shows an intense glow peak at 263 °C. The implications of these observations for TL will be discussed in details.

References


Oxide crystals are produced for practical applications where the presence of hydroxyl ions in the material may be either desirable or undesirable [1]. It is widely accepted that OH\(^-\) ions enter the lattice from the ambient atmosphere during the preparation process, when the crystals are grown in air at high temperatures (~ 600 – 1600 °C) from melt or solution. The relatively low concentration of OH\(^-\) ions in as-grown crystals makes it possible to study them as isolated diatomic molecules in the lattice. Due to the light hydrogen atom the frequency of the localized vibrational mode is higher than the vibrational frequencies of the host matrix. The stretch mode frequency of the hydroxyl ion in various oxides lies between 3200 – 3700 cm\(^{-1}\) where the crystals are usually transparent and the OH\(^-\) band can easily be detected by the high resolution FTIR absorption spectroscopic technique. The information obtained from the vibrational frequency of the OH\(^-\) ions, and from the pleochroism of the absorption bands can be used to determine the structural site of the hydroxyl defect in the crystal lattice. The anharmonicity of the stretching mode obtained for O-H vibrations and the weak coupling to phonon bands derived from the temperature dependence of the OH\(^-\) band parameters will also be surveyed in some complex oxides such as tungstates, molybdates etc. The effect of a structural phase transition on the O-H vibrational frequency in LaGaO\(_3\) crystal will be presented as an example for the relation between the crystal structure and the OH\(^-\) vibration.

Hydroxyl ions are assumed to occupy oxygen sites compensating some other kinds of intrinsic or extrinsic defects by their surplus positive charge. This behaviour of OH\(^-\) ions allows probing the defect structure of the crystals by studying the spectroscopic properties of hydroxyl ions influenced by their surroundings. In the present lecture we show how the composition of some non-stoichiometric niobates and tantalates (e.g. LiNbO\(_3\), LiTaO\(_3\), K\(_2\)Li\(_2\)Nb\(_5\)O\(_{15}\), and Sr\(_3\)Ba\(_{1-x}\)Nb\(_2\)O\(_6\)) can be characterized by the shape of the OH\(^-\) bands. The relation between the OH\(^-\) band parameters and the crystal properties will also be discussed in doped materials. As an example for practical applications the role of hydroxyl ions in the thermal fixing of holographic gratings via their kinetic behaviour will be presented in photorefractive LiNbO\(_3\) crystals.

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References

We studied the optical properties of Ti-doped vitreous silica from the far IR to the VUV and identified IR and UV absorptions associated with the titanium dopant. This system is of interest because, below ~10% TiO$_2$, Ti$^{4+}$ ions substitute for Si$^{4+}$ ions to form a covalently bonded, continuous random network of SiO$_4$ and TiO$_4$ tetrahedra. In contrast, common glasses consist of random networks of SiO$_4$ tetrahedra intercalated by modifier ions (e.g., Na$^+$, Ca$^{2+}$) that introduce ionic bonds. The principal IR absorption associated with titanium occurs at 940 cm$^{-1}$ (117 meV). It lies in a deep minimum of the silica-matrix absorption, and appears to arise from an asymmetric vibration involving oxygen atoms bridging SiO$_4$ and TiO$_4$ tetrahedra. That is, it is a perturbed form of the strong silica absorption at 1076 cm$^{-1}$ that involves the oxygen atoms bridging SiO$_4$ tetrahedra. There are indications of similar perturbations of silica's weaker IR-active modes that lie at longer wavelengths. A strong UV absorption of Ti$^{4+}$ lies between 5 and 7 eV, just below the exciton peak of undoped vitreous silica. It is attributed to a charge-transfer transition involving excitation of the isolated TiO$_4$ tetrahedra, and can be viewed as a bound exciton consisting of a Ti$^{3+}$ ion and a hole shared by the four oxygen neighbours. The electronic absorption of the silica matrix, especially the silica exciton, is broadened significantly. The separate IR and UV contributions of the titanium dopant to the refractive index in the visible have been found by moments analysis. Comparison of TiO$_2$–SiO$_2$ glass with other glasses shows that the IR spectra are similar, but that their UV spectra differ considerably. Thus, the broad range of refractive indices displayed by optical glasses arises almost exclusively from differences in electronic, not ionic, polarization.

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EFFECT OF INTRINSIC LOCALIZED MODES ON PHONONS: APPEARANCE OF LINEAR LOCAL VIBRATIONS

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A number of studies have shown that strongly localized excitations can exist in perfect nonlinear lattices [1,2]. The frequency of such a vibration depends on its amplitude and lies outside the phonon spectrum. A recent investigation has predicted rather long lifetimes [3]. Such vibrations are called intrinsic localized modes (ILMs) or discrete breathers or discrete solitons. The discovery of this intrinsic dynamical inhomogeneity should lead to other new features. For example, the appearance of an ILM should change the local phonon dynamics. This back reaction on the phonons should have physical consequences since the ILM could induce linear local modes (LLMs) outside the phonon spectrum.

Our goal is to examine the effect of an ILM upon the small amplitude vibrations of a 1-D chain with hard nonlinear intersite coupling. First we derive equations for small vibrations of the lattice in the presence of an ILM using the rotating wave approximation. To solve these equations, we apply the Lifshitz method. The results show that an ILM stabilizes the appearance of LLMs above the phonon spectrum. Next molecular dynamics simulations are used to verify these findings. In the simulations (see Fig.1), first an ILM is formed and the power spectrum calculated, next small shifts associated with a LLM are added and the power spectrum calculated again. Good agreement is obtained between the positions of the additional peaks and the theoretically found frequencies of the LLMs.

Fig. 1. Power spectra of ILMs for two different nonlinear parameter values with and without LLMs. The maximum frequency of phonons is at 1. Left: the main spectral feature is an even ILM. Right: same even ILM but with larger anharmonicity. Bottom panels: the even ILM; middle panels: an ILM perturbed by an odd LLM; top panels: an ILM perturbed by an even LLM. Although the dotted and solid lines differ by $10^2$ in the LLM amplitude its frequency remains unchanged. The amplitude patterns are shown for some of the different modes.

References

GaIn is one of the most promising semiconductor hosts for rare earth (RE) based emitters and lasers. Its direct wide bandgap allows for visible wavelength emission, and the ability to tailor the bandgap through III-N alloying enables matching this material system to many RE ions. LEDs have been realized for a number of different RE dopants in GaN and most recently optically excited laser emission has been demonstrated for Eu:GaN grown on Si substrate in a process that is compatible with regular Si electronic processing [1]. In the pursuit of an electrically-pumped laser, it becomes important that all the RE ions within the laser cavity are effectively excited. To this end, the presence of different RE incorporation sites complicates this goal and requires the detailed characterization of these sites in terms of energy states and their ability to be excited electrically.

We performed site-selective combined excitation-emission spectroscopy (CEES) studies on Eu$^{3+}$-doped GaN layers. The samples were grown using Interrupted Growth Epitaxy (IGE) with varying interruption sequences. We identified numerous Eu$^{3+}$ incorporation sites, which exhibit different relative emission intensities as the growth conditions are varied. We show that the Eu ions exhibit pronounced electron-phonon coupled sidebands in their excitation spectra whose source has previously been unclear.

Most notably, we found defect-trap related Eu-sites exist that can be excited over a wide spectral range and that dominate the photoluminescence spectra for above bandgap excitation. Spectra obtained through cathodoluminescence, which simulates EL operation, are nearly identical to the emission spectra of these defect-trap related sites, indicating that these particular Eu ions would be the major contributors to EL emission in these samples. On the other hand, in experiments under resonant excitation the emission from these sites is rather weak indicating that they are minority sites in these samples.

References


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HIGH DIELECTRIC CONSTANT OXIDE FILMS, INFLUENCE OF PROCESS ON STRUCTURAL FEATURES AND PROPERTIES: THE CASE OF HfO₂ SOL-GEL FILMS

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The nanostructure of high dielectric constant “high k” films, including porosity, grain structure and extended lattice defects in crystallized films, is a key factor for their application in microelectronics. Our paper is focused on elaboration and characterisation of HfO₂ sol-gel films. Mono- and multilayer HfO₂ films of have been deposited by sol-gel route starting from hafnium ethoxide precursor, on Si [100] wafer substrates.

The structural features of the films were determined by TEM and AFM measurements. The structural changes induced by the densification / crystallization process during classical annealing between 400 and 600°C, were followed through systematic TEM observations. The film density was calculated by correlating RBS spectrometry and XTEM thickness measurements. The dielectric constant was determined by capacitive measurements.

Crystallization in the quasi amorphous deposits starts around 450°C. Nanopores of 2 to 5 nm in size are already formed in the amorphous oxide matrix during densification. Further crystallization of the films does not modify much the pore size and density. The final density of monolayer films annealed at 600°C was calculated as about 60% of the bulk value, but this density reaches 80% of the bulk value in the case of four layer films. The dielectric constant was measured as 10 for two layer films and as 25 for four layer films, i.e. very close to the value of the bulk material.

The crystallization process observed in the sol-gel HfO₂ films starts from several nucleation centres and extends rapidly in the film plane (see Fig.1). In the case of multilayer films, the crystallization of a subsequently deposited layer is strongly influenced by the crystalline orientation on the surface of the previously deposited layer. The thickness of the SiO₂ layer formed at the interface with the Si substrate is strongly dependent on the annealing temperature and on the film porosity. The role of these different features has been regarded with respect to the dielectric properties.

![Figure 1. Plan view and cross section TEM images from a HfO₂ monolayer film annealed at 600°C for 30 minutes.](image-url)
OTuH1

MAGNETISM DUE TO DEFECTS/OXYGEN VACANCIES IN HfO₂ THIN FILMS

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HfO₂ is known as an insulating oxide that can be used as a dielectric layer for nanometer-scale electronic devices. Its high dielectric constant makes it a potential candidate to reduce the leakage current, so that it can be substituted for SiO₂ to be a gate dielectric material. On the other hand, HfO₂ is an attractive oxide due to its superior electrical performance. Basically HfO₂ is known to be non-magnetic.

In general, ferromagnetic insulators (FI) are rare since in insulating compounds, most probably, spins tend to couple with each other antiferromagnetically. With the shed light from the resulting research on introducing room temperature ferromagnetism by doping transition-metals into semiconducting oxides, we undertook an investigation of doping transition-metals in HfO₂ in the thin film form to verify if such a doping can result in some kind of insulating ferromagnets. It was expected that doping of magnetic elements might help the isolated spins in HfO₂ to interact one to the other ferromagnetically through the RKKY interaction.

Ni and Fe: HfO₂ thin films are all room temperature ferromagnetic with a rather large magnetic moment. However it is clear that oxygen treatments could define to make the sample to be ferromagnetic or reversibly switched to become diamagnetic and vice versa. So that it comes to the point that most probably, the dopant is not the main reason for the found magnetism in this type of insulating oxide thin films, but more likely in these families, FM seems to be due to defects and oxygen vacancies.

Surprisingly, room temperature FM was observed in un-doped HfO₂ films on Yttrium Stabilized Zirconia. It is known that neither Hf⁴⁺ nor O⁻² is magnetic. On the other hand, HfO₂ bulk is clearly diamagnetic. Moreover, there is no contamination in any substrate, and there is also no way to attribute such a large magnetic moment to impurities. Certainly thin film form, which might create necessary defects or oxygen vacancies, must be the main reason for this un-doped insulating oxide to become ferromagnetic at room temperature. Oxygen annealing that to fill up oxygen vacancies could reduce the magnetic moment enormously, and in the case if those are filled up completely, the ferromagnetic ordering could be well destroyed, so that the samples might well return to be diamagnetic as that of the bulk. This confirms the assumption that magnetism in this system originates from defects/oxygen vacancies.

Consequently, a big question is addressed if the doping of transition metals indeed plays any key role in producing FM in non-magnetic oxides, or it is just add some contribution to the magnetic ordering that already exists in the host? Thus, several issues must be clarified: the role of anisotropy, the connection between defects and magnetism, oxygen vacancy, d⁰ magnetism, etc in order to elucidate the nature of interactions that produces such high-temperature FM in such insulating oxide thin films.
Radio frequency sputtering is a useful way to process ferroelectric thin films. Textured polycrystalline BaTiO3 thin films are spontaneously grown on amorphous substrates and their mean orientation can be monitored using a bias during the growth. We look for a link between the films texture and the point charge defects in the films.

Electron Spin Resonance (ESR) is an efficient tool to probe such point defects. In a previous report [1], we have shown that, even in polycrystalline samples, rotation spectra can be recorded taking as a reference the substrate surface. We could ascribe the ESR lines to Ti$^{3+}$ centres associated with Oxygen vacancy. The centre shows tetragonal symmetry along cubic <100> axes with g-factors: $g_// = 1.997$, $g_\perp = 1.904$ The density of such centres was depending on the films texture showing that there is a connection between point defects and the crystalline mean orientation. Moreover, annealing the films at $300\,^\circ C$ under Oxygen flow was able to remove most of the ESR intensity. We thus unambiguously demonstrated that BaTiO$_3$ films contain a high density of Ti$^{3+}$-VO centres. Such defects were never found in bulk BaTiO$_3$. This means that they could result in thin films from the strongly un-equilibrium conditions of the sputtering deposition process which takes place at low temperatures.

In this report, we will further evidence the electron localisation on the Ti$^{3+}$-VO centres performing in situ illumination experiments. To this aim, the films were irradiated by an optical beam at low temperatures (4K) and with several wavelengths. The intensity of the ESR line and thus the density of the Ti$^{3+}$-VO centres could be tuned for wavelengths between 365 nm and 850 nm. This shows that electrons are trapped on low energy levels in the band gap. This is consistent with the electronic defect structure models of BaTiO$_3$.

We thus found that the ESR investigation of ferroelectric thin films is very useful in two ways:
- even if the films are polycrystalline, conclusive insight in the electronic structure and local symmetry of defects can be drawn
- defects stabilization in films can confirm the electronic structure models of highly polarisable matrices which is sometimes not possible in bulk materials.

References
THE EFFECT OF $\gamma$-IRRADIATION ON THE OPTICAL PROPERTIES
OF $a$-$Ag_{7.5}(Sb_{0.1}Ge_{0.3}Se_{0.6})_{92.5}$ THIN FILM

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The amorphous behaviour of $Ag_{7.5}(Sb_{0.1}Ge_{0.3}Se_{0.6})_{92.5}$ chalcogenide thin films deposited at room temperature onto glass substrates by thermal evaporation technique was investigated by means of X-ray diffraction technique. The surface morphology as well as the elemental chemical composition of the as-deposited films were investigated via scanning electron microscopy. The optical transmission and reflection spectra of as-deposited films and that exposed for different $\gamma$-dose were recorded at room temperature in the wavelength range 500-2500nm. Systematic studies of the refractive index, extinction coefficient, and optical band gap have been presented as a function of the $\gamma$-dose. The dispersion of the refractive index for such films are discussed in terms of the single-oscillator Wemple-DiDomenico model, beside a graphical representation for the surface and energy loss function were also presented.
It was the wide-gap insulating oxide that made silicon the semiconductor of choice, to such a degree that silicon technology has transformed our lives. Its roles of surface passivation and a lithographic material are essential, but its role as the gate dielectric is especially sophisticated. Even though challenged by newer materials, like HfO₂, the silicon dioxide dielectric will be around for some time. I want to discuss some of the key defect processes in the way this oxide is created, in the way it performs, and how it fails. I shall also discuss its materials context. What materials must work alongside it? Are there similar defect processes in quartz? To what extent do silica glasses share properties with the gate dielectric oxide? And are there new phenomena to exploit?
KWeA

A NARROW BAND, GREEN-RED COLOUR CENTRE LASER IN LIF FABRICATED BY FEMTOSECOND LASER PULSES

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Typically, materials used for optical applications have wide-band-gaps such as SiO2 glass, sapphire and diamond. Due to the wide-band-gaps, it is difficult to process these materials with conventional light. A femtosecond (fs) laser defies this limitation since the fs pulse can generate light pulses with extremely high peak power densities up to about several hundreds TW/cm². Therefore, it is expected to process any materials including optically transparent dielectrics with this high power fs-laser.

It has been also considered so far that colour centres in lithium fluoride (LiF), in the form of bulk or film, are only produced with low-ionizing irradiation due to its wide-band-gap of up to ~14 eV. Recently we reported, for the first time, simultaneous fabrication [1] of the laser-active F2 and F3⁺ colour centres and fine-pitched micrograting structures in bulk LiF with a holographic technique [2] using a pair of interfering fs-laser pulses. Moreover, the present technique was also applied [3, 4] to the first production of a pulsed distributed-feedback (DFB) laser in the red spectral region based on the F2 colour centres in LiF at room temperature (RT). In general, the F2 and F3⁺ colour centres in LiF, whose absorption bands are almost overlapping at 450 nm and emission quantum efficiencies are close to unity, are excellent candidates for producing visible laser action from the green-to-red spectral range.

In this contribution we will report the DFB colour centre laser in the green spectral region based on the F3⁺ colour centres at RT. Moreover, to obtain a stable, narrow band laser action, the two end surfaces of the bulk LiF were polished, almost parallel to each other and were deposited the Bragg mirrors. In addition, the second harmonic of fs-laser pulses (402 nm, 130 fs, 10 Hz) was used as an irradiation source for encoding a fine-pitched grating with fringe spacings as fine as around 350 nm inside the crystal. An intensity threshold for the F colour centre creation in LiF is around 9.6 TW/cm² and 3.2 TW/cm² for the 805 nm and 402 nm fs-laser pulses, respectively.

In our presentation, some recent work of a narrow band, green-red colour centre laser fabricated by fs-laser pulses with a view to developing novel optoelectronic devices will be discussed.

References

WHITE LIGHT SIMULATION BY UP-CONVERSION IN Yb\(^{3+}\)-Er\(^{3+}\)-Tm\(^{3+}\) DOPED TRANSPARENT OXYFLUORIDE GLASSES AND NANO-GLASS-CERAMICS

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The class of materials known as oxyfluoride nano-glass-ceramics results from heat treatment of the parent glass above the glass transformation temperature (T\(_g\)) to induce homogeneous nucleation and growth of a rare-earth doped nano-crystalline fluoride phase suspended in the residual, robust silicate based glass matrix.

We have already reported very promising results in this Er\(^{3+}\)-doped nano-glass-ceramics with respect to broad and flat optical amplification covering the C and S-band of WDM \([1]\). In the present work, transparent oxyfluoride glass and daughter nano-glass-ceramics doped with three rare-earth ions (32 SiO\(_2\), 9 AlO\(_1.5\), 31.5 CdF\(_2\), 18.5 PbF\(_2\), 5.5 ZnF\(_2\), 2.5YbF\(_3\), 0.5 ErF\(_3\) and 0.5 TmF\(_3\) mol\%) were successfully developed, where each dopant partitions efficiently to the fluoride PbF\(_2\)-based nano-crystals. Using infrared excitation at 980 nm and by additive synthesis of red, green and blue (RGB) up-conversion emissions, white light simulation has been achieved. The up-conversion processes involving these dopants were analysed by da Silva et al. in fluoride glasses \([2]\). Observed changes in the relative intensity between different up-conversion emissions are analysed in terms of the ambient temperature and the crystalline field of F\(^-\) ligands, when passing from an oxide environment in the glass to a fluoride environment in the nano-glass-ceramics \([3]\).

References:


Figure 1: Up-conversion emission spectra obtained by exciting at 980 nm the 2.5Yb\(^{3+}\)-0.5Er\(^{3+}\)-0.5Tm\(^{3+}\) doped oxyfluoride glass and nano-glass-ceramics samples at room temperature.

References:
SPECTROSCOPIC CHARACTERISATION OF THE PROMISING THIN-DISK LASER MATERIAL Yb:NaGd(WO4)2

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In recent years Ytterbium doped laser materials have become increasingly more important. Due to the simple two-manifold structure of the Yb-ion, processes like excited-state absorption, cross relaxation, and up-conversion do not take place. This and the small quantum defect leads to reduced thermal loading of the system, which makes Yb-doped materials of particular interest for high power applications. One established high power system is the diode pumped thin-disk laser [1]. To exploit the specific advantages of thin-disk lasers, high Yb-concentrations are necessary to reduce the disk thickness and achieve optimal heat transfer.

However, in many crystals such as YAG, a strong decrease in quantum efficiency is observed towards higher Yb-concentrations. This is due to energy migration and transfer to impurities, which leads to high thermal loading and limits the usability of highly doped Yb:YAG as active media so far [2,3].

The potential thin-disk laser medium Yb3+:NaGd(WO4)2 (Yb:NGW) is presented as a possible solution to this problem. Yb:NGW shows only a small decrease in quantum efficiency even at high concentrations. This effect is also observed in tungstates like KYW and KGW, however, unlike NGW these media cannot be grown by the more favourable Czochralski-method [4]. Therefore spectroscopic investigations at room- and low-temperatures, lifetime measurements, and structural investigations of the disordered NGW crystal will be presented for different Yb-concentrations. These will be compared to the properties of Yb-doped YAG, KYW, and LSB crystals. The key parameter, energy migration between the active ions, will be discussed in detail.

Furthermore, first thin-disk laser experiments with Yb:NGW as active medium are in progress and will be presented at the conference.

References

The origin of the change in photoactivity of anatase and rutile TiO₂ induced by substitutional N- and C-doping is under intense debate because of the importance in determining the photocatalytic properties of this material.

DFT calculations [1] have shown unambiguously, at variance with previous claims [2], that N-doping induces the presence of N 2p localized states just above the top of the O 2p valence band. In anatase this causes a red-shift of the absorption edge band towards the visible light region while in rutile the optical transition energy increases slightly (blue-shift towards UV region), in agreement with recent experimental observations.

These results have been further corroborated by combining Electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS) and DFT calculations in an effort to characterize the paramagnetic species present in N-doped anatase TiO₂ powders obtained by sol-gel synthesis [2]. The experimental hyperfine coupling constants are well reproduced by two structurally different N impurities, substitutional and interstitial. Calculations also show that N-doping leads to a substantial reduction of the energy cost to form oxygen vacancies in bulk TiO₂, suggesting that N-doping is likely to be accompanied by oxygen vacancy formation.

Also C-doping dramatically improves the photocatalytic activity of TiO₂ in the visible-light region. At low C concentrations, we find that under oxygen-poor conditions substitutional (to oxygen) carbon and oxygen vacancies are favoured, while in oxygen-rich conditions interstitial and substitutional (to titanium) carbon atoms are preferred. As for N-impurities, also C give rise to localized occupied states in the band gap, which may account for the experimentally observed red-shift of the absorption edge towards the visible. Furthermore, in analogy with the N-doping case also C-doping may favour the formation of oxygen vacancies in bulk TiO₂.

References

AB INITIO STUDY OF THE ELECTRONIC STRUCTURE AND PROPERTIES OF CHARGED DEFECTS IN ZrO₂ AND HfO₂

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The oxides ZrO₂ and HfO₂ are currently being the subject of an intensive research effort in relation to their role in heterogeneous catalysis and fuel cells, in the case of ZrO₂, and as a substitution of SiO₂ in gate dielectrics of MOSFETs, in the case of HfO₂. In both these materials oxygen vacancies are the dominant intrinsic defects, which also affect their chemical, mechanical, electric and optical properties. Despite a significant effort, very moderate degree of control of vacancy concentration was achieved, mainly due to ambiguities in their experimental identification. The theoretical characterisation of oxygen vacancies had also limited success, since most previous calculations were performed either within the local approximation to the density functional theory [1] known to significantly underestimate single particle band gaps and to overdelocalize shallow defect states. Some progress was recently achieved with the screened exchange approach [2], but reliability of these result is also uncertain, due to small system size.

Towards the full characterisation of oxygen vacancies in ZrO₂ and HfO₂ we present large scale periodic and embedded cluster calculations within hybrid B3LYP density functional. The periodic calculations were carried out using the CRYSTAL03 code and allowed effective atomic relaxation and accurate positioning of defect levels with respect to the band edges. The embedded cluster approach allows for detailed calculations of the defect properties in the quantum region with the effects of lattice polarization taken into account using classical force field model.

We confirm earlier suggestions that oxygen vacancies are amphoteric and may occur at five charge states (+2 to -2), and report their electrical properties as well as optical absorption spectra and paramagnetic parameters compared with experimental data [3]. Embedded cluster and periodic calculations predict the single particle band gaps of 6.8 and 6.1 eV in the monoclinic HfO₂ and 6.5 and 5.9 eV in the cubic ZrO₂ (experimental optical gap 5.9 and 5.6 eV for HfO₂ and ZrO₂). In both systems the V⁺ and V⁻ vacancy states are deep levels located approximately in the middle of the gap, while V²⁺, V⁻ and V²⁻ are shallow levels with the energies between 0.8 and 1.5 eV below the bottom of the conduction band. Based on our calculations we discuss various mechanisms of charging and discharging of vacancies under the electrostatic stress. In particular, effects of strong lattice relaxation on charge kinetics and negative U effects on vacancy charges are considered. We further discuss the effects of lattice relaxation, thermal disorder and possible vacancy migration and aggregation.

References

AB INITIO STUDY OF Cu\textsuperscript{2+} AND Ag\textsuperscript{2+}-DOPED CUBIC OXIDES: FROM STATIC TO DYNAMIC JAHN-TELLER EFFECT

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Despite the dynamic Jahn-Teller (JT) effect plays an important role in the mechanisms of transition metal oxides exhibiting colossal magnetoresistance \cite{Millis} or high-T\textsubscript{C} superconductivity \cite{Kabanov} there is however a crucial question which has not been solved yet: why a coherent tunnelling among equivalent adiabatic minima occurs for MO:Cu\textsuperscript{2+} (M: Mg,Ca) while for Cu\textsuperscript{2+} or Ag\textsuperscript{2+} in SrO a static JT situation is found \cite{Bersuker}. Furthermore there are still doubts about the actual values of the JT energy, E\textsubscript{JT}, the associated distortion (described by R\textsubscript{ax} and R\textsubscript{eq} impurity-ligand distances) and specially the energy barrier, E\textsubscript{B}, between equivalent minima of the E(Q\textsubscript{θ}≈3z^2-r^2; Q\textsubscript{ε}≈x^2-y^2) surface for d\textsuperscript{9} ions doped cubic oxides.

Searching to clarify all these relevant issues ab initio calculations on Cu\textsuperscript{2+} and Ag\textsuperscript{2+} doped cubic oxides have been carried out. For comparison purposes results obtained for NaCl:Rh\textsuperscript{2+} are discussed as well \cite{Garcia}.

As salient feature huge differences are found between |E\textsubscript{B}| = 511 cm\textsuperscript{-1} for NaCl:Rh\textsuperscript{2+} and the values for MgO:Cu\textsuperscript{2+} (|E\textsubscript{B}| = 4 cm\textsuperscript{-1}) and CaO: Cu\textsuperscript{2+} (|E\textsubscript{B}| = 20 cm\textsuperscript{-1}) \cite{Garcia}. This result supports the observation of a static JT effect in the first case while a coherent tunnelling for Cu\textsuperscript{2+}-doped MgO and CaO in agreement with experimental findings \cite{Bersuker, Vercammen}. Furthermore, |E\textsubscript{B}| for SrO:Cu\textsuperscript{2+} is found to be ~20 times bigger than that for MgO:Cu\textsuperscript{2+}, thus favouring a transition to a static JT when MgO is replaced by SrO for both Cu\textsuperscript{2+} and Ag\textsuperscript{2+} impurities. This conclusion \cite{Garcia} is again in accord with experimental results \cite{Bersuker}.

The present calculations also reproduce the elongated equilibrium geometry (R\textsubscript{ax} > R\textsubscript{eq}) observed for NaCl:Rh\textsuperscript{2+} and the compressed one (R\textsubscript{ax} < R\textsubscript{eq}) found for Cu\textsuperscript{2+} doped cubic oxides. This puzzling fact has been related to a big elastic coupling of MO\textsubscript{10} (M = Cu\textsuperscript{2+}, Ag\textsuperscript{2+}) complexes to the rest of the lattice. This coupling is shown to be able to modify the sign of anharmonic coupling constant and thus the nature of both the ground state and the equilibrium geometry \cite{Garcia} . The present study confirms the existence of a weak JT distortion (R\textsubscript{ax} - R\textsubscript{eq} = -7.5 pm) and E\textsubscript{JT} = 490 cm\textsuperscript{-1} for MgO:Cu\textsuperscript{2+} which can be compared with R\textsubscript{ax}-R\textsubscript{eq} = 24 pm and E\textsubscript{JT} = 1800 cm\textsuperscript{-1} for NaCl:Rh\textsuperscript{2+} where a strong JT effect is taking place.

Another relevant result concerns the variation of the average impurity-ligand distance along the series of cubic oxides. While for transition-metal impurities in fluorides or chlorides with sixfold coordination the impurity-ligand distance is usually close to the sum of ionic radii, for present cases it follows the host lattice parameter \cite{Garcia}. This different behaviour can be related to the bigger deformability of the O\textsuperscript{2−} ion in comparison to more rigid ions like F\textsuperscript{−}.

References

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Ferroelectric materials such as LiNbO$_3$ and LiTaO$_3$ play an important role in integrated and nonlinear optics. For the latter application, domain patterns are structured to obtain quasi-phase matching. This requires precise control of the domain growth with sub-micron spatial resolution. We have developed two novel methods for real-time imaging of ferroelectric domain walls in which (instead of destructive chemical etching and subsequent optical or electron microscopy) domain walls are imaged using the luminescence changes [1] of intentionally doped, dilute rare earth ions (e.g. Er$^{3+}$, Eu$^{3+}$):

1. In a laser confocal or a near field optical microscope, we monitored the luminescence spectrum of our probe ions during the ferroelectric domain nucleation and growth, both caused by an applied electric field. Spectral selection and the multi-site nature of our probes [2], allows us to perform these studies as a function of the probe defect’s local environment.

2. In an electron microscope, we can trigger the domain inversion by electron bombardment and the resulting build-up of charges near the sample surface. The inversion process (charging, nucleation, and growth) is monitored in this scheme with high spatial resolution (200nm) by detection of the simultaneously produced cathodoluminescence.

These new imaging methods open up new possibilities for advancing physical understanding of domain wall structure and other properties, as well as domain wall/defect interactions. For instance we find that domain wall widths and structures are dependent on the velocity of the domain wall motion. Moreover our methods are capable of providing active, real time feedback needed for precise laser writing of ferroelectric domain patterns [3].

References


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In this work we report on photo-transport properties and charge trapping phenomena have been studied in paraelectric KTaO$_3$ single crystals doped with $\sim$3%mol of Cu and V. Vanadium ions allow to obtain a better crystal homogeneity without changing the properties of the matrix, being isovalent with Ta. On the contrary copper ions, entering the Ta$^{+5}$ sites in two different charge states Cu$^{2+}$ and Cu$^{+}$, produce a charge deficit compensated by oxygen vacancies. A variety of phenomena associated to the Cu$^{2+}$/Cu$^{+}$ ratio have been observed. The comprehension of these phenomena are relevant in connection with prospective properties of KTa$_{1-x}$Nb$_x$O$_3$:Cu,V for electro-holography based devices.

The kinetics, the temperature dependence and the excitation spectra of photoconductivity (PC) have been measured between 15-300 K and at irradiation energy between 2-4.2 eV in KTaO$_3$:Cu,V single crystals, before and after reduction treatments at various temperatures.

Different transport and trapping mechanisms depending on the excitation energy have been observed. In all samples, under band-gap excitation the PC kinetics are characterized by very slow saturation times, while a faster time response was observed under excitation below band-gap. The more oxidized crystals exhibit higher PC intensities when $E_{\text{light}} > 3$ eV. At lower energies comparable PC intensities were observed in all samples. Finally, in more oxidized specimens, i.e. with a higher Cu$^{2+}$/Cu$^{+}$ ratio, a linear PC dependence on light intensity was measured suggesting a one center recombination process. Optical absorption, EPR and photo-EPR measurements were also performed in order to obtain complementary information that helped to formulate a model to explain the observed phenomena.
Swift heavy ions induced effect in LiF thin films were studied by glancing angle X-ray diffraction (GAXRD), optical absorption, photoluminescence (PL) and elastic recoil detection analysis techniques (ERDA). 200 nm thin LiF polycrystalline films [1] were deposited by electron beam evaporation method on glass at room temperature (RT) and 150 nm on Si substrates at different substrate temperature i.e. 77 (liquid nitrogen temperature, LNT), 300 (RT), 400 and 500 K. GAXRD results of pristine films showed reflections along (111), (220) at 2θ angle of 38.5 and 44.7. The reduction in the grain size (from 58 nm to 22 nm), estimated from (111) peak, was observed with decrease in the substrate temperature. 200 nm films were irradiated with 80 MeV Ni ions at fluences of 7 × 10^11, 1 × 10^12 and 3 × 10^12 ions/cm^2 at RT and LNT, whereas 150 nm films with different grain size were irradiated with 120 MeV Ag ions at a fluence of 3×10^{11} ions/cm^2 at RT. The reduction in the grain size of films with fluence was observed, which is attributed to strain induced fragmentation of grains. The optical absorption studies showed dominant absorption bands of F3 (390 nm) and F2 (445 nm) color centers [2,3] for the samples irradiated at RT. The LNT irradiated samples show a new band at 520 nm, corresponding to F4 colour centres, along with the bands of F3 and F2 colour centres. It is observed that the concentration of the colour centres increases with ion fluence. PL spectra of irradiated films showed two broad bands of F3+ and F2 colour centres at 535 and 665 nm, respectively [1,4]. The intensity of both bands (F2 and F3+) increases with fluence for both RT and LNT irradiation. The relative intensity of F3+ to F2 colour centres increases with fluence and is higher for LNT irradiated samples [5]. The reduction in the luminescence intensity of both the colour centres with grain size was observed. The behaviour of luminescence intensity with grain size is attributed to enhanced radiative lifetime of STE due to smaller grain size. ERDA measurements showed that Li and F are nearly equally present in the film, but reduction in the areal concentration of Li and F was observed indicating stoichiometric electronic sputtering in LiF [6]. The order of sputtering yield was 10^4 atoms/ion and it was found to increase with reduction in the grain size of the pristine film. The increase in the sputter yield can be understood in terms of grain size effect. The reduction in the grain size enhanced the grain boundaries scattering of electrons resulting in high electron-phonon coupling and hence the sputtering yield. On the other hand, first time lamellae formation in LiF thin films after a high fluence irradiation of 5 × 10^{13} ions/cm^2 at LNT with 120 MeV Ag ions under grazing incidence (~10°) was observed.

References

LiF and NaCl single crystals were irradiated with swift heavy ions ($^{12}$C, $^{50}$Ti, $^{58}$Ni, $^{74}$Kr, $^{152}$Sm, $^{197}$Au, $^{208}$Pb, and $^{238}$U) at the UNILAC linear accelerator of GSI. The kinetic energies were between 50 and 2600 MeV covering an electronic energy loss of 0.7 to 19 keV/nm. The irradiations were performed at 8 K and at room temperature (RT) using a cryostat that allows in situ absorption spectroscopy and thermo-stimulated luminescence (TSL) measurements without dismounting the irradiated samples. We studied the evolution of various colour centres as a function of ion fluence and irradiation temperature, and performed complementary measurements using thermal annealing and optical bleaching [1, 2].

For all crystals irradiated at 8 K we observed primary hole centres (I and H centres) of Frenkel pairs ($\alpha$– I and F – H centres). Due to their low migration energies (0.01 – 0.1 eV), these centres thermally annihilate between 10 and 200 K [3]. Therefore, the appearance of I and H colour centres indicates that transient heating of the track zones where these defects are created is rather low.

The efficiency of F-centre creation depends strongly on the energy loss of the ions [1, 2]. For both crystals, the F-centre production at low fluences and high ion energy loss (Au, Pb, U) is larger for irradiations at 8 K than at 300 K. The opposite effect is observed for lighter ions of lower energy loss (C, Ti, Ni).

Optical bleaching of F centres in NaCl and LiF crystals irradiated at 8 K leads to a decrease of F-centre concentration due to recombination with hole centres (H, H$_A$). Similar recombination processes between F and hole centres take place when annealing samples irradiated at 8 K. In contrast, optical bleaching of F centres in crystals irradiated at RT results in (1) recombination of F centres with V$_3$ hole centres (thermally stable at RT) and (2) aggregation forming more complex colour centres such as F$_n$ and F-centre aggregates [1].

The results are ascribed to thermo-stimulated separation processes of primary colour centres. To estimate transient track temperatures, thermal spike calculations are performed that take into account the finite velocity of heat propagation [2].

References


FIRST RESULTS ON SIMULTANEOUS SURFACE NANOSTRUCTURING AND OPTICAL ACTIVATION OF LITHIUM FLUORIDE CRYSTALS BY ION BEAM IRRADIATION

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First results on simultaneous surface nanostructuring and optical activation of lithium fluoride crystals by ion beam irradiation will be presented. An 800 eV off-normal Ar ions beam at different ion doses was used to produce periodic nanostructures at the surface of the crystal while generating optically active electronic defects. The samples were studied by atomic force microscopy and optical spectroscopy. After ion sputtering, smoothening of the initial quite large random roughness is achieved and well defined self-organized ripple structures appear, with a mean periodicity of 30 nm and a mean height of 3 nm. The simultaneous optical activation of the samples is due to the stable formation of $F_2$ and $F_3^+$ centres with intense photoluminescence in the visible spectral range.
WHAT MAY BE EXPECTED FROM THE MICROWAVE RESONANT CAVITY TECHNIQUE APPLIED TO RARE-EARTH-DOPED INSULATING CRYSTALS?


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Photoionization thresholds of rare-earth (RE) ions embedded in insulating crystalline hosts were measured for the first time in our laboratory using the so-called “Microwave Resonant Cavity Technique” (MRCT) [1]. This technique was inspired by measurements of semi-conducting material photoconductivity using microwave devices. MRCT measurements consist in detecting the changes of the Q-factor of a microwave cavity containing the sample under investigation after its irradiation by a pulsed laser. The determination of the RE photoionization thresholds was of course the primary purpose, with the aim of locating the 4f<sup>n</sup> levels of RE ions with respect to the host conduction band. As a matter of fact, the energy level diagrams of RE ions usually reported do not take this positioning into account and, consequently, lack the required information to help in understanding the complex processes associated with the absorption of high energy photons by RE-doped materials used as scintillators, ultraviolet lasing media or phosphors for fluorescent tubes and plasma display panels.

The experimental setup was built on the basis of a homodyne microwave bridge as used in electronic paramagnetic resonance spectrometers. Due to the expected weakness of the signals, a highly sensitive hardware had to be progressively developed. As a result, absorption and dispersion signals may be detected, corresponding to changes of the microwave cavity Q-factor and resonance frequency, respectively. Moreover, the experimental setup was modified in order to study the temperature dependence of the measured signals between room and liquid helium temperature [2]. As a result, detailed information concerning the photoionization dynamics may be nowadays obtained from our MRCT measurements.

This presentation aims to describe the various MRCT potentialities. Experimental results concerning either scintillating or laser materials will be presented and discussed as examples.

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The processes involved in the excited-state relaxation of non-bridging oxygen hole centres (NBOHCs) were studied in glassy SiO\textsubscript{2} using luminescence, optical absorption and photoelectron emission spectroscopy. It is shown that the photoexcited NBOHCs have generally a three channels of relaxation. Along with the radiative transitions giving luminescence band 1.9 eV there are a two non-radiative channels caused by transitions \( 2p_y \rightarrow 2p_x \) between sublevels of photoexcited \( 2p \)-state. The first non-radiative channel is connected with transformation of electronic excitation energy in thermal lattice vibrations and represents intracentre process of NBOHC luminescence quenching (activation barrier is 0.05 eV). The second non-radiative relaxation channel, in addition to the intracentre quenching, was established to become operative at temperatures above 370 K. This effect manifests itself in experiments as a negative deviation of the temperature-dependent luminescence intensity from the well-known Mott law.

This additional channel of non-radiative relaxation for excited NBOHCs is identified as thermally activated external luminescence quenching with an energy barrier of 0.46 eV. It is established that within the external quenching temperature interval a non-radiative transitions initiate migration of excitation energy, followed by the creation of free electrons. In the final stages, this relaxation process becomes manifest in the form of spectral sensitization of electron photoemission, which is excited in NBOHC optical absorption band.

As a result of realization of the specified process the transfer of excitation energy from NBOHC to the centres acting in a role of electron emitters takes place. It is supposed that as such electron emitting defects act a diamagnetic oxygen-deficient centres (ODCs) representing, in our case, the neutral oxygen vacancies. The similar effects of spectral-sensitized photoelectron emission excited in NBOHC optical absorption band are found out also in disordered surface layers of quartz single crystals after irradiation by fast electrons.

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Yttrium orthovanadate ($\text{YVO}_4$) is an insulating crystal (zircon tetragonal crystal structure) used in several important optical technologies, for example, as a solid-state laser host material. Neodymium doped $\text{YVO}_4$ crystals is widely used in diode pumped lasers and $\text{YVO}_4$ doped with ytterbium has been studied for potential laser applications, including high power short pulse uses. As is the case with many optical materials, $\text{YVO}_4$ suffers from growth-related defects and radiation induced damage. Radiation induced electronic excitations may participate in the energy transfer processes from host material to luminescence centres and, in turn, may play an important role in device performance of doped $\text{YVO}_4$ lasers.

In this work we present results of investigation of pure and $\text{Nd}^{3+}$ doped $\text{YVO}_4$ crystals by means of time-resolved luminescence spectroscopy. The second and fourth harmonic of YAG:Nd laser (532 nm and 266 nm respectively; 1 ns pulse duration) as well as electron beam accelerator (280 keV, 10 ns pulse) were applied for crystals excitations.

Broad luminescence spectra peaking near 2.8 eV were detected at room temperature for all investigated crystals (pure and Nd doped) under laser (266nm) and electron beam excitations. General accepted hypothesis is that a self-trapped exciton in the form of ($\text{VO}_4$)$^{3-}$ complex is responsible for this intrinsic luminescence band. However, intensity and decay time of this band are strongly depended on the dopant concentration. Increasing concentration of neodymium leads to decreasing of the intensity and decay time of intrinsic luminescence (~30 µs and ~500 ns at room temperature for nominally pure and for 0.7% $\text{Nd}^{3+}$ doped crystals respectively). In addition to main intrinsic luminescence band a fast luminescence (decay time shorter than 10 ns) was detected near 3.3-3.5 eV under electron beam excitations. Origin and nature of this band will be discussed.

Characteristic sharp luminescence lines of $\text{Nd}^{3+}$ (transitions $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$) were detected under direct excitation of neodymium ions (532 nm, transition $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{7/2} + ^2\text{G}_{5/2}$) as well as under band-to-band excitation (266 nm laser or electron beam). However, time evolution of neodymium related luminescence bands depends on excitation wavelength. After a high-energy excitation pulse a significant rise front of $\text{Nd}^{3+}$ luminescence (several microseconds) was observed. Such rise front is absent under a direct excitation of neodymium ions. The rise front is strongly dependent on $\text{Nd}^{3+}$ concentration and temperature. Remarkably, that the rise time of neodymium luminescence ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ lines) is very close to decay time of intrinsic luminescence (2.8 eV) for each $\text{Nd}^{3+}$ doped $\text{YVO}_4$ crystals. All this above mentioned experimental facts allow us to conclude that the migration of intrinsic exciton leads to energy transfer from host lattice to neodymium ions and rising time of $\text{Nd}^{3+}$ luminescence kinetic may characterize an energy-transfer rate.
THE ROLE OF Pb$^{2+}$ IONS IN THE LUMINESCENCE OF LuAG:Ce SINGLE CRYSTALLINE FILMS

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Single crystals of lutetium-aluminium garnet Lu$_3$Al$_5$O$_{12}$ (LuAG) doped with trivalent rare-earth ions (e.g., Ce$^{3+}$, Pr$^{3+}$) have high density, an intense and fast emission and high mechanical and chemical stability. Owing to these characteristics, these crystals have been considered as promising scintillator materials for imaging screens with high spatial resolution. Under excitation in the LuAG host absorption region, an intense slow intrinsic luminescence is observed arising from the Lu$_{AI}^{3+}$ antisite defects [1, 2]. The spectrum of this luminescence can be overlapped with the impurity-induced emission or absorption bands which influences considerably on the scintillation characteristics of the doped LuAG single crystals. In [2, 3] it was found that the concentration of the antisite defects is strongly suppressed in single crystalline films (SCF) grown by the Liquid Phase Epitaxy method. It was expected that the preparation of SCF instead of single crystal can significantly improve the characteristics of the scintillation materials. However, at the SCF preparation, a quantity of lead ions is introduced into the SCF due to the use of the PbO-containing flux for the SCF growth. The aim of this work was to study the characteristics of lead-induced centres in LuAG SCF and their influence on luminescence characteristics of LuAG:Ce SCF.

Steady-state and time-resolved emission and excitation spectra and luminescence decay kinetics were studied at 4.2-350 K under excitation in the 2.5-15 eV energy range for undoped and Ce$^{3+}$-doped LuAG SCF with different Pb$^{2+}$ and Ce$^{3+}$ concentrations. The spectral bands arising from Pb$^{2+}$ centres are identified. The processes of energy transfer from the host lattice to Pb$^{2+}$ and Ce$^{3+}$ ions and from Pb$^{2+}$ ions to Ce$^{3+}$ ions are investigated. The competition between Pb$^{2+}$ and Ce$^{3+}$ ions in the processes of energy transfer from the exciton state is found to be considerable, while in the band-to-band transitions region, the emission of Ce$^{3+}$ centres is mainly excited. At 11 K, the slow 4.3 eV emission of localized excitons is observed in LuAG SCF, which also compete with Ce$^{3+}$ ions in the energy transfer processes. Due to the overlap of the ~3.6 eV emission band of Pb$^{2+}$ centres with the 3.6 eV absorption band of Ce$^{3+}$ centres, the effective energy transfer from Pb$^{2+}$ ions to Ce$^{3+}$ ions takes place, resulting in the appearance of slow component in the luminescence decay kinetics of Ce$^{3+}$ centres. Thus, the results obtained indicate negative influence of Pb$^{2+}$-related centres, existing in LuAG SCF, on the Ce$^{3+}$ luminescence intensity and decay kinetics.

References

FEEDING THE $^4I_{13/2}$ Er$^{3+}$ LASING LEVEL BY INCREASING THE $^4I_{11/2}$ DECAY RATE THROUGH Eu$^{3+}$ AND Ce$^{3+}$ ENERGY TRANSFER

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Optical amplifiers based on low phonon energy glasses, such as tellurite glasses, exhibit some drawback exploiting the common pumping scheme for erbium doped fibre amplifiers that considers to excite at 980 nm the level $^4I_{11/2}$, from which there is a fast multiphononic transfer to the $^4I_{13/2}$ [1]. A strategy to increase the feeding rate of level $^4I_{13/2}$ upon 980 nm pumping is through the non radiative energy transfer to a suitable rare earth ion, such as Tb$^{3+}$, Eu$^{3+}$ or Ce$^{3+}$, to match the $^4I_{11/2}$ - $^4I_{13/2}$ energy gap [2, 3].

In this work we report on the spectroscopic properties of Er$^{3+}$-doped and Er$^{3+}$/Ce$^{3+}$-codoped tungsten-tellurite glasses, obtained by melt-quenching, and of Er$^{3+}$-doped and Er$^{3+}$/Ce$^{3+}$-codoped silica-hafnia waveguides obtained by sol-gel technique.

The study of de-excitation dynamics of the $^4I_{11/2}$ and $^4I_{13/2}$ Er$^{3+}$ states upon pulsed excitation at 532 nm and of the photoluminescence intensity for various pumping wavelengths show that Ce$^{3+}$ and Eu$^{3+}$ codoping are effective in favouring the population feeding of the $^4I_{13/2}$ Er$^{3+}$ level (see Figure). However, on the contrary of cerium, europium codoping also affects the $^4I_{13/2}$ Er$^{3+}$ radiative efficiency.

![Figure](image)

**Figure**: Decay traces of the $^4S_{3/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels upon pulsed excitation at 532 nm for the tellurite samples. The continuous curves are referred to the Er$^{3+}$-doped sample, while the symbol curves to the Er$^{3+}$/Ce$^{3+}$-codoped one.

References

Optically accessible defects in semiconductors with large band gap show a number of properties which make them interesting candidates for a controlled engineering of quantum states in solids [1]. The talk will concentrate on color centers in diamond. One of the particularly interesting defects, the nitrogen vacancy defect center, has an electron spin paramagnetic ground state. The fluorescence of this defect strongly depends on the spin state of the electron. Single defect centers can be isolated by optical microscopy. It was shown that the spin state of a single defect center can be determined by optical spectroscopy. Microwave and radiofrequency irradiation allows to manipulate single electron and nuclear spins (for example nitrogen and $^{13}$C) [2,3]. One can create arbitrary spin quantum states, for example Bell states, and probe its dephasing behavior which is a first step toward quantum information processing with defect centers. In order to generate large arrays of interacting defects single defect centers have been implanted in diamond [4]. The talk will describe experiments on these coupled defect center systems. In addition the use of color centers in diamond as single photon sources for quantum communication will be highlighted [5].

ELECTRONIC STRUCTURE AND SPECTROSCOPIC PROPERTIES OF INTERSTITIAL OXYGEN SPECIES IN THE NANO-POROUS COMPLEX OXIDE $12\text{CaO}\cdot7\text{Al}_2\text{O}_3$

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A nano-porous structure of the complex oxide $12\text{CaO}\cdot7\text{Al}_2\text{O}_3$ (C12A7) offers a possibility to form large concentrations of negatively charged interstitial species. The chemical composition of stoichiometric C12A7 can be represented using formula $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 2\text{O}^{2-}$, where $[\ldots]^{4+}$ forms a positively charged framework arranged in 12 cages. The positive charge of the framework is compensated by $\sim1.2\times10^{21}\text{ cm}^{-3}$ extra-framework (interstitial) O$^{2-}$ ions randomly distributed over the lattice. Such structure is responsible for its unusual electronic properties and high oxide ion conductivity [1]. Depending on the preparation conditions and post-treatment, the interstitial O$^{2-}$ ions can be replaced by other species such as oxygen radicals O$^-$ and O$_2^-$, molecular ions OH$^-$ and O$_2$$^2-$ and electrons. At large concentrations these species significantly alter the optical absorption spectra of C12A7. However, understanding the role of each extra-framework species requires detailed theoretical analysis.

In this communication we present a comprehensive characterisation of the optical, vibrational and magnetic properties of several oxygen-containing extra-framework species as well as calculate the relative energies of different extra-framework configurations. We employ an embedded cluster approach, which combines a quantum-mechanical treatment of a region of interest with a consistent classical description of the remaining part of the system. The method is implemented in a computer code GUESS; it allows one to account for the ionic and electronic contributions to the defect-induced lattice deformation as well as for the effect of the lattice deformation on the defect itself.

We found that the monovalent ions such as O$^-$, O$_2$$^-$ and OH$^-$ are significantly more stable in C12A7 framework (~3 eV per unit cell) than O$^{2-}$ ions, which is consistent with experimentally observed intake of O$_2$ and H$_2$O at corresponding atmospheres. This is due to both smaller lattice distortion induced by the monovalent species and a more homogeneous distribution of the negative charge density. The onset of the optical absorption in C12A7 containing doubly charged O$^{2-}$ and O$_2$$^2-$ species is about 3.0 eV. It shifts to lower energies (2.0 eV) when interstitial O$^-$, O$_2$$^-$ radicals are incorporated and to higher energies (5.8 eV) when predominantly OH$^-$ interstitials are present. The calculated stretching frequencies calculated for O$_2^-$ and O$_2$$^2-$, 1041 cm$^{-1}$ and 784 cm$^{-1}$ respectively, are in good agreement with the experimental data. Several configurations of OH$^-$ species and corresponding shifts of the stretching frequencies were also identified. Finally we show that the principal values of g-tensors can also be calculated with accuracy larger than 99%. These results allow one to fully characterise the chemical composition of C12A7 samples and to identify the approaches to modification of its optical absorption spectra.

References

AB INITIO STUDY OF THE VIBRATIONAL PROPERTIES OF TeO$_2$-BASED GLASSES

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TeO$_2$-based glasses are promising active materials for optical fibre amplifiers due to their large cross section for stimulated Raman scattering [1]. These properties are influenced by doping agents such as Na$_2$O or WO$_3$ added to improve the stability of the glass towards recrystallization. Despite the technological interest of these materials, a detailed description of their structure and of the dependence on doping of the structural properties and Raman response is still lacking. To address this issue we have performed ab-initio calculations on the structural and vibrational properties of the known crystalline phases of TeO$_2$ (alpha, beta, gamma) and of models of the tellurite glasses pure and W-doped generated by quenching from the melt within ab-initio molecular dynamics. The calculated structures of the glass compare well with X-ray and neutron diffraction data [2]. Moreover, calculated Raman and IR spectra are in good agreement with available experimental data [3] and allow us to identify the vibrational signature of the different structural units in the crystals and in the glasses. This work leads to a better understanding of the influence of the stabilizer on the structural properties and Raman response.

References

The univalent-mercury halide crystals Hg$_2$Hal$_2$ (Hal=Cl,Br,I) were used as model objects in these investigations. These family is isomorphic at room temperature and has especial crystalline structure, which consist of the parallel chains of the linear Hal-Hg-Hg-Hal molecules weakly bound with each other. The molecules form the body-centred tetragonal lattice $D_{4h}^{17}$ with two molecules in the unit cell. These crystals own unique physical properties (record-low velocity of TA-sound, record-high birefringence and very large acousto-optical interaction) and are used successfully in applications as basic units of polarizers, of acousto-optical filters, modulators, deflectors, acoustical delay lines etc.

The improper ferroelastic phase transitions (PT) $D_{4h}^{17} \to D_{2h}^{17}$ were observed at $T_c=186K$ (Hg$_2$Cl$_2$) and $T_c=144K$ (Hg$_2$Br$_2$). These PT were induced by the soft-TA mode at the X-point of the Brillouin zone (BZ) boundary of the tetragonal paraphase, accompanied by doubling of the unit cell and the X$\to$Γ folding in BZ. But in the isomorphic Hg$_2$I$_2$ PT does not occur even by cooling down to very low temperature (~1.5K) (incipient PT, $T_c \approx -20K$).

In present work in a wide interval of temperatures and wave vectors a phenomena of appearance of clusters, preceding to structural phase transitions in the Hg$_2$Hal$_2$ crystals was studied by the X-ray structure analysis and by various optical techniques.

At the X-points of the paraphase BZ the diffuse X-ray scattering was discovered and studied on cooling. The appearance of the scattering at the X-points, forbidden in paraphase, was induced by static and dynamic fluctuations of order parameter and bound with nucleation of low-temperature orthorhombic clusters in a high-temperature tetragonal matrix. At the cooling and approach to $T_c$, the clusters grow and by an elastic interacting, form the two-dimensional long-periodic superstructure, which at $T=T_c$ through chaotic state is transformed to low-temperature domains.

In result of these investigations the original information about the temperature behaviour of the ferrophase clusters in the tetragonal paraphase matrix was got. The temperature dependencies of susceptibility, correlation radius, shape and sizes of clusters and theirs anisotropy, the critical exponents were obtained. The nature and parameters of these clusters were discussed.

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MULTIFREQUENCY SPECTROSCOPY OF LASER ACTIVE CENTERS \(\text{Nd}^{3+}\) AND \(\text{Yb}^{3+}\) IN NEARLY STOICHIOMETRIC \(\text{LiNbO}_3\)

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Lithium Niobate (LN) has been of great interest for many years for both fundamental science and applications because of the unusual richness of its ferro-, pyro- and piezoelectric properties. Conventional LN crystals, grown from a congruent melt with lithium deficiency (\(X_{\text{melt}} = X_{\text{Crystal}} \approx 48.4\%\), where \(X = [\text{Li}]/([\text{Li}]+[\text{Nb}])\)), contain some percent of intrinsic (non-stoichiometric) defects and, consequently, have strong structural disorder. Crystals grown under special conditions from melts, to which potassium has been added, have extremely low intrinsic defect concentrations. These samples, called stoichiometric, have significantly decreased widths of spectral lines. This leads to the increased resolution of the optical and EPR/ENDOR spectra.

The X- and Q-band EPR investigations of the paramagnetic \(\text{Nd}^{3+}\) and \(\text{Yb}^{3+}\) ions in the temperature range between 4 and 50 K exhibited the existence of several different centres. Some of them have no angular dependence of the EPR lines for the magnetic field rotation in the XY crystallographic plane. This corresponds to axial C\(_3\) symmetry of the centre. All other centres have low symmetry C\(_1\). Since the EPR line width in the stoichiometric crystal is about 15 G, i.e. 10 times smaller than in the congruent sample, we were able to obtain new information:

- To discover 3 new \(\text{Nd}^{3+}\) and 4 new \(\text{Yb}^{3+}\) centres. The presence of nonequivalent centres manifests itself also in the multiband structure of observed optical spectra
- To resolve the line splitting of the low-symmetry spectra and to follow their angular dependencies
- To observe the hyperfine structure from the \(^{143}\text{Nd}\) and \(^{145}\text{Nd}\) isotopes (both with nuclear spin \(I=7/2\), natural abundance about 12% and 8%), and from the \(^{171}\text{Yb}\) and \(^{173}\text{Yb}\) isotopes (\(I=1/2, 14.4\%\) and \(I=5/2, 16.2\%\))
- To follow the angular dependencies of hyperfine components for the most intense centres
- To determine precisely all components of g-tensors and the orientations of main axes for four \(\text{Nd}^{3+}\) and five \(\text{Yb}^{3+}\) centres.

Narrow EPR lines allowed also investigating ENDOR on one selected line only (instead of the mixture of overlapping lines). Using Q-band ENDOR has lead to separation of the Li and Nb ENDOR lines due to higher magnetic fields in comparison with X-band. This separation facilitates deciphering and interpretation of observed spectra. The lattice positions of the \(\text{Nd}^{3+}\) and \(\text{Yb}^{3+}\) ions derived from the EPR and ENDOR data and effects produced by micro- and macro-imperfections of LN crystals will be discussed.

Carried our study of the laser active impurity defects on the atomic level is useful for both fundamental and applied science. Stoichiometric LN;\(\text{Nd}^{3+}\) and LN;\(\text{Yb}^{3+}\) are considered as a promising materials for the construction of high efficiency lasers with frequency doubling.
Lithium niobate crystals enable holographic recording and nonlinear optical frequency conversion. Important material properties are crucially determined by doping, e.g., with iron. Iron occurs in LiNbO₃ in two valence states, 2⁺ and 3⁺. Exposure with visible light excites electrons from Fe²⁺ to the conduction band. Inhomogeneous illumination yields a charge transport in the conduction band because of the bulk photovoltaic effect, diffusion, and drift. The electrons are finally trapped by Fe³⁺ sites, preferentially in the darker areas. Space charge fields build up and modulate the refractive index through the electro-optic effect. In nonlinear-optical experiments these refractive index changes, that are present also in nominally undoped crystals, are unwanted (“optical damage”) because they disturb the phase matching conditions and the beam profile.

We introduce a method that reduces the optical damage by nearly perfect oxidization of iron in LiNbO₃, i.e., almost all Fe²⁺ ions are oxidized to Fe³⁺. The crystals are congruently melting lithium niobate samples doped with 2 wt% iron oxide (Fe₂O₃) and nominally pure LiNbO₃ crystals. The samples are heated to 700 °C for 6 hours in air. During the entire process a voltage of 1000 V is applied with a current limitation of 0.1 mA. Absorption spectra of an untreated and a thermo-electrically oxidized iron-doped crystal are shown in Fig. 1. The absorption, that origins from Fe²⁺, is strongly suppressed apart from the Fe³⁺ absorption peak at 483 nm. The resulting concentration ratio of Fe²⁺ and Fe³⁺ is smaller than $2 \times 10^{-3}$. The optical damage is determined by the beam fanning of a focused laser beam of the wavelength $\lambda = 532$ nm and a power of 0.5 W. Photos of the beam fanning of an untreated and a thermo-electrically oxidized undoped crystal are shown in Fig. 2. The treated crystal shows obviously a strong reduction of the optical damage. Due to the oxidization no photo-excitatable electrons are left and consequently the photorefractive process is eliminated.

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Figure 1: Absorption spectra of an highly iron-doped crystal

Figure 2: Beam fanning of undoped crystals. Before and after the thermo-electrical oxidization. Left: oxidized, right: untreated
The local structure of ferroelectric domain walls and its dependence on intrinsic defects and dopants is of great interest both from a basic science and an application point of view. For instance, in the ferroelectrics LiNbO$_3$ and LiTaO$_3$ that are widely used in nonlinear and electro-optical devices, the stability, shape, switching fields and smallest achievable domain size are determined by the defect concentration. Using confocal Raman spectroscopy, we investigated the perturbation of the phonon modes across a domain wall as a function of sample stoichiometry (i.e.: the number of intrinsic defects). For all samples, we find that in the spectral vicinity of the E(TO8) and E(TO9) the Raman intensity below 600 cm$^{-1}$ is enhanced in the domain wall region. For LiNbO$_3$, the Raman spectrum of LiNbO$_3$ recorded with a 488 nm Argon laser is depicted in Fig. 1(a) (dotted line). The Raman intensity enhancement in the domain wall is clearly seen in the Fig. 1(a) (solid line) as a difference spectrum of domain as grown and domain wall Raman spectra. The integrated Raman intensity of the enhancement can be used for 2D domain wall imaging, see Fig. 1(b). In order to elucidate the origin of this enhancement and the nature of the responsible vibrational mode, we investigated the directional dispersion of the observed change and perform measurements under variation of pump and probe light polarization and sample orientation. On the basis of these results, we will discuss structural models of the domain wall.

![Figure 1](image)

**Figure 1:** (a) Raman spectrum of stoichiometric LiNbO$_3$ and the spectrum of the differences occurring within the domain wall region in regards to the as grown regions. (b) Image of a hexagonal domain recorded with the confocal Raman microscope. Contrast is only achieved within the domain wall.

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We have studied the colour centre production in yttria-stabilized zirconia single crystals with the (100) orientation, i.e. ZrO$_2$:Y with 9.5 mol% Y$_2$O$_3$, by electron irradiations at energies ranging between 1.0 and 2.5 MeV. On the basis of electron paramagnetic resonance (EPR) and UV-visible optical absorption measurements, we have previously shown that electron or heavy ion beams produce two paramagnetic centres stable at room-temperature: i) the first one is identified as an F$^+$-type centre (singly ionized oxygen vacancy) with an axial <100> symmetry, and small g-factor anisotropy ($g_{\perp}=1.972$ and $g_{\parallel}=1.996$), ii) the second one is similar to the well-known T-centre (Zr$^{3+}$ in a trigonal oxygen environment) with an axial <111> symmetry, and large g-factor anisotropy ($g_{\perp}=1.855$ and $g_{\parallel}=1.986$), which is also produced by UV and X-ray photon irradiations. We have plotted the concentration of the F$^+$-type centres measured by EPR versus fluence at variable electron energy. All low fluences, these growth curves, which are linear, cannot be rescaled versus the absorbed dose (in Gy). The slopes of the curves increase by a factor around 50 from 1.0 to 2.5 MeV. Such a large variation cannot be accounted for by the small increase of the O-atom elastic collision cross-section versus electron energy. Rather it can be fitted to the Y or Zr-atom cross sections by taking a large displacement energy threshold of about 75 eV much larger than the commonly used value of 40 eV. These data unambiguously confirm our previous results that F$^+$-type centres are produced by elastic collision processes. This is discussed on the basis of intrinsic and extrinsic defect calculations in pure and substituted zirconia. In contrast, the low-fluence growth curves of T-centres obtained at variable electron energies are reasonably well rescaled versus the absorbed dose, thereby confirming that these colour centres are produced by electronic excitation processes. A comparison is made with the available data on other oxide systems and in particular those in the fluorite structure.
Recently we have found [1, 2] effect of the influence of high-current pulsed electron beam with energy \( E = 800 \text{ keV} \) on the structure and lattice dynamics of ferroelectric \((\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3\) (PLZT 8/65/35) ceramics. The obtained results reveal transformation of the cubic perovskite \( \text{Pm-3m} \) (\( Z = 1 \)) into orthorhombic \( \text{Pmmm} \) (\( Z = 1 \)) structure for the sample irradiated by one pulse (dose \( 6\times10^{14} \text{ electrons/cm}^2 \)) and, as a consequence, the considerable growth in intensity, change position and number of Raman-active phonon modes. It should be noted that the annealing at 200 \( ^\circ \text{C} \) of the single irradiated sample leads to the partly restoration of the orthorhombic distortion. We believe that this effect is obviously related with complex action pulsed electron irradiation on sample. Electron beam irradiation includes the accumulation of powerful spatial charge (electric field \( \sim 10^7 \text{ V/cm} \)), shock wave and an appearance of power pulsed annealing.

In this work we present extended X-ray absorption fine structure (EXAFS) of the Zr K-edge studies in relaxor PLZT 10/65/35 and “hard” PLZT 4/65/35 ceramics irradiated by high-current pulsed electron beams of two types accelerators with next parameters: 1) energy \( E = 800 \text{ keV}, \text{beam current} 200 \text{ A}, \text{pulse duration} 2\times10^{-7} \text{ s}, \text{repetition rate} 0.5 \text{ Hz} \); 2) \( E = 500 \text{ keV}, \text{beam current} 5 \text{ kA, pulse duration} 6\times10^{-8} \text{ s}, \text{repetition rate} 0.5 \text{ Hz} \). The number of pulses is the same for the both cases. The annealing effect of irradiated samples at various temperatures was also considered. Lattice parameters, interatomic distances and angles before and after irradiation of PLZT 4 and 10/65/35 ceramics were precisely determined by high-resolution X-ray and Neutron Rietveld analysis. The correlation of the crystalographic parameters with phonon modes behavior in Raman scattering spectra was studied. The details of long range and local atomic structure distortions in irradiated samples are presented and discussed.

Possible mechanisms of pulsed electron irradiation effects in PLZT 4/65/35 and 10/65/35 ceramics are discussed.

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CHARACTERIZATION OF ULTRA-HEAVILY DAMAGED NaCl


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In this paper we present the progress made to (i) characterize the defect state of ultra-heavy damaged rock salt samples with up to more than 20 at% Na colloids, which had been irradiated at moderate temperatures (e.g. 100 ºC) up to $10^4$ MGy (1000 GRad), and (ii) understand their physical properties. The explanation of the observations by means of a variety of experimental techniques is not trivial and often the results obtained with different experimental techniques lead to conflicting interpretations. In heavily damaged samples both the intensity and width of the ESR line of Na particles behave anomalously. At first sight room temperature ESR measurements seem to indicate that with increasing damage (i.e. metallic Na) the size of the precipitates increases gradually. Low temperature ESR provides clear evidence that the Na particles in very heavily damaged NaCl are definitely not isolated conducting objects embedded in an insulating matrix. Below some critical temperature $T_c$, which depends on the damage level, the intensity of the ESR line decreases, while the line width increases. Above $T_c$ the behaviour of the ESR signal is similar to that of bulk metal, although the line width was always larger than for bulk Na. The observations can be explained by assuming that the colloids are arranged in quasi-1D clustered structures of metallic Na nano-particles.

Also melting in heavily damaged NaCl behaves anomalously. Three or even more Na melting peaks are observed, while at least one of them is affected by heat treatment at moderate temperatures. The melting and freezing properties of radiation-induced chlorine are complex. Only one Cl melting peak is found, but often more than one freezing peaks are present and a clear-cut explanation for this is not available yet. The pressure in the chlorine precipitates is ~1 kBar and the presence of more than one freezing peak suggests that the pressure in the two types of bubbles is different. Another option is that the extra freezing peaks are due to differences in super-cooling.

Raman scattering of Na colloids show (i) interesting power-law behaviour at low energies and (ii) unusual scattering peaks beyond the Brillouin zone of the NaCl matrix, which are, although they are not located at the characteristic frequencies of Na, assumed to be due to excitations of quasi-1D type conglomerates of Na nano-precipitates.

Recently, heavily damaged NaCl samples have been investigated by means of wide angle X-ray scattering (WAXS) and again intriguing, new results were obtained for the Na and Cl precipitates as well as for the NaCl matrix. High-resolution WAXS data indicate that (i) the ultra-heavy irradiated NaCl crystal lattice is quite perfect and (ii) that in contrast with the interpretation of results obtained with the above-mentioned techniques large Na and Cl-precipitates with diameters from 200 - 1000 Å are formed. At least the Cl-precipitate shape is substantially different from spherical. For both types of precipitates very strict orientation relationships with respect to the NaCl matrix are found. In addition to the earlier established Kurdjumov-Sachs OR for Na precipitates, the OR between solid chlorine and the host NaCl crystal is: $\{001\}_{\text{Cl}} // \{001\}_{\text{NaCl}}$, $<110>_{\text{Cl}} // <110>_{\text{NaCl}}$. 

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When a massive projectile with energy in the range of hundreds of keV is stopped in a target film nuclear collision cascades are likely to develop. These are associated to severe structural damage, up to the disruption of the crystalline structure. Looking at an isolated cascade, localised amorphisation can occur during the relaxation towards equilibrium of such a small volume of highly excited matter. Yet, dramatic amorphisability differences are observed in chemically similar compounds, irradiated under identical conditions. This long-standing, largely unsolved, basic problem has also important applicative implications. Given the strong dependence on structure of the mechanical, chemical and transport properties of a film, the structural stability of irradiated crystalline films is crucial to design coatings with predetermined properties. As a general model for the amorphous phase is lacking, empirical criteria were proposed to explain data on radiation-induced amorphisation in increasingly larger sets of materials. The degree of interpretative success of such criteria is not satisfactory.

We present the interface migration-charge transfer (IMCT) atomistic model for the nucleation of crystalline, or amorphous phases in non-metallic compounds, irradiated under conditions suitable to the formation of dense collision cascades. The space and time evolution of a prototypical cascade lead to non-equilibrium compositional and electronic density profiles at the interface between the cascade and the surrounding crystalline matrix. This occurs because one of film constituents preferentially migrates to the interface, which becomes enriched in it. Local charge transfer reactions (CTR), each involving a pair of dissimilar atoms of the initial compound, mimic system relaxation via formation of dimers of an effective compound.

The energy cost to produce one such dimer, the difference of formation enthalpy between each effective compound and the corresponding initial compound and the local strain associated to a CTR are calculated.

We analyse a meaningful set of compounds, including oxides, nitrides and carbides, whose structural stability under ion bombardment is known. Threshold values with a clear physical meaning are found in the above structure stability parameters. This allows for separating amorphised compounds from those retaining a crystalline structure upon irradiation. Thus IMCT model constitutes a single conceptual framework to interpret and to predict structure evolution in particle-bombarded ceramic materials.
Exposure of insulating materials to ionizing radiation initiates a sequence of relaxation processes involving a variety of radiation induced defects – defects of structure, holes and electrons self-trapped/trapped in the lattice, molecule fragments. A deep insight into relaxation processes is of considerable importance for an understanding the radiation effects and investigations on this subject have been spread to different classes of materials [1]. Recent studies of relaxation in pre-irradiated model wide-gap insulators – Rare Gas Solids (RGS) revealed new radiative mechanism of energy transfer from atomic to electronic subsystem [2]. This opens fresh opportunities to control relaxation cascades.

To study in more detail relaxation processes we developed technique for correlated in real time measurements of thermally stimulated exoelectron emission (TSEE) first detected from solid Ar [3], thermally stimulated luminescence (TSL) and emission of atoms. This presentation focuses on the results of studies of the relaxation channels – emission of exoelectrons and photons from RGS pre-irradiated by an electron beam. Films of pure and doped RGS (Ne, Ar, Kr and Xe) were condensed on a cooled substrate with a concurrent irradiation by slow electrons. Total and partial yields of TSL in VUV and visible ranges were measured along with the spectra of TSL. Yield of exoelectrons and photons were measured at different heating regimes – heating with a constant variable rate and step-wise heating.

Correlation between TSEE and TSL peaks was found in all RGS. This finding indicates common origin of the phenomena: thermostimulation expels electrons trapped in some kind of traps into the conduction band and then some part of electrons recombines with positively charged centres giving rise to the TSL while a part of electrons released from the same kind of traps escapes the sample. Depths of the TSEE active layers were determined. It was found that at low temperatures TSEE predominates. As the temperature is increased, the probability of recombination reactions increases as evidenced by rise of the intensities of intrinsic and extrinsic recombination emission peaks in comparison with the TSEE yield. Possible effect of a space charge in the condensed films is discussed.

References

ENERGY TRANSFER AND CHARGE CARRIER CAPTURE PROCESSES IN WIDE BAND-GAP SCINTILLATORS

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Research of scintillator and phosphor materials is one of rather active areas pursued in many academic and industrial laboratories due to increasing number of applications, in which the high energy photons, accelerated particles or neutrons are to be detected [1-3]. In scintillator materials the fast and efficient energy transfer from the host to emission centres is of paramount importance to achieve the most demanded materials with high efficiency and fast scintillation response of the order of tens of nanoseconds. While the choice of the emission centres for this purpose is rather restricted and based on the 5d-4f radiative transitions in Ce$^{3+}$, Pr$^{3+}$ or eventually Nd$^{3+}$ rare earth ions, variety of host matrices based on binary or complex fluorides, oxides, silicates, aluminates, etc. are under investigation. Mentioned efficiency and speed of energy transfer through the host lattice is often degraded by the presence of trapping levels in the material forbidden gap, which can temporarily capture migrating charge carriers and thus delay their delivery to the emission centres. Variety of point defects and material imperfections can be responsible for such undesired effects. It is often technological and intellectual challenge to understand the nature of such trapping levels, their relation to the manufacturing technology and to find out the most efficient recipes and ways to suppress these undesired phenomena to bring the material performance close to its intrinsic limits. Another difficulty appears in the cases when an backward energy transfer from the emission centres to the host lattice is enabled, which can also seriously degrade the material timing performance.

In this presentation several examples of such phenomena will be shown and a strategy of their study will be demonstrated using correlated experiments performed by the time-resolved emission spectroscopy, thermoluminescence and electron paramagnetic resonance methods. Namely, (i) removal of electron traps from the lead tungstate scintillator by trivalent ion doping and possible ways to increase its efficiency will be overviewed; (ii) codoping strategy in the Ce-doped aluminum perovskite and garnet structures leading to the suppression of the antisite defects in the bulk materials will be presented and (iii) creation and usage of the Ce-perturbed sites in GdF$_3$-YF$_3$ based solid solutions to achieve an efficient energy transfer from the Gd-sublattice to such centres in the fluoride host will be introduced. Ionization or thermal disintegration of the emitting species will be discussed for the Pr$^{3+}$-doped materials and the PbWO$_4$ exciton-based emission. Intrinsic tendency to create trapping states in the material forbidden gap and their relation to the production technology will be discussed and compared for the Ce- or Pr-doped scintillators based on the LYSO, LuYAG and LuYAP hosts.

References

Fluorozirconate-based glass ceramics activated with europium represent a promising novel class of x-ray scintillators [1, 2]. In contrast to common single-crystal scintillators, glass ceramics can be manufactured easily in any size and shape. The scintillation in these glass ceramics is mainly caused by the typical 5d-4f transition of europium(II) incorporated in barium chloride nanocrystals that are formed in the glass matrix upon appropriate thermal processing. In order to get a better understanding of the scintillation mechanism in europium-activated barium halide nanocrystals in general, an investigation of the processes in the corresponding bulk material is essential.

We investigated single crystals of undoped or europium-doped barium chloride, bromide, and iodide, by x-ray excited luminescence (XL), pulse height and scintillation decay spectra. The Eu$^{2+}$-related x-ray excited luminescence found in the Eu-doped barium halides is at 402, 404, and 425 nm for the chloride, bromide, and iodide, respectively. BaCl$_2$:Eu$^{2+}$ shows the most promising scintillation properties of the systems investigated. The light yield is about 20,000 ± 2,000 photons per MeV of absorbed $\gamma$-ray energy, the energy resolution for the 662 keV photopeak is 9% ± 1%, and the scintillation decay time is (350 ± 35) ns. The influence of the Eu-doping and the anion-cation distance on the scintillation properties of the investigated barium halides is discussed.

References

Point defects and impurities play a major role in optical properties of scintillators, as they can be at the origin of glow emissions which are detrimental for the applications. Spectrally-resolved thermoluminescence is used here to study defects and scintillation properties of LaCl$_3$:Ce and LaBr$_3$:Ce samples grown by Saint-Gobain Crystals. After X-ray irradiation, four glow peaks are observed at 20 K, 65 K, 140 K (when measured at a heating rate of 5 K/s) and at 400 K (when measured at a heating rate of 3 K/s). All these glow peaks exhibit a complex structure. Similarities and differences with previous studies are discussed [1,2]. The recombination centres involved in the thermoluminescence process are characterized and possible thermoluminescence mechanisms are considered, involving Ce$^{3+}$ and self-trapped excitons. Long-term components of the afterglow of irradiated samples are also studied at temperatures around 300 K, where we observe a strong dependence with temperature. Possible explanations and implications of these findings are discussed.

References

SYNTHESIS, STRUCTURE AND THERMOLUMINESCENT PROPERTIES OF NANOCRYSTALLINE ZrO₂ POWDER AND ITS POSSIBLE NEUTRON DOSIMETRY APPLICATIONS

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Synthesis, structural characteristics and thermoluminescence properties of nanocrystalline ZrO₂ powder synthesized by precipitation method have been obtained [1]. X-ray diffraction was used for characterization of the structure and crystalline phase structure. Semiconductor materials with average nanocrystallite sizes ranging from 70–80 nm up to about 140 nm were prepared by precipitation method.

Thermoluminescence (TL) is the emission of light occurring when electrons (or holes) are released from their traps and return to stable states; the escape probability is greatly increased by raising phosphor temperature. Many unresolved problems may appear when TLDs are utilized, in radiotherapy dose level, using radiation fields different from gamma-rays; especially if the linear energy transfer (LET) of the radiation is high. In fact, the thermoluminescent yield of such phosphors may depend on the LET of ionizing particles.

The characteristics of thermoluminescence dosemeters (TLDs) regarding the determination of thermal neutron absorbed doses were investigated in a thermal neutron beam [2]. A simple system consisting of two component thermoluminescent phosphors is proposed to measure a thermal neutron beam. Zirconium oxide (ZrO₂) and lithium fluoride (LiF:Mg,Cu,P), both materials developed in our Mexican laboratories were used in this investigation. Within the experimental uncertainties, these measurements were compared with those obtained using the well known pair dosemeters, gamma rays sensitive TLD-700 (⁷LiF:Mg,Ti) and neutron sensitive TLD-600 (⁶LiF:Mg,Ti).

We concentrate on powders and consider the present trend in the research for developing synthesis procedures for fabrication of high-efficiency luminescent materials consisting of nanocrystalline particles.

References

OThD4

TIME-DEVELOPMENT OF SCINTILLATING RESPONSE AND THE ROLE OF DEFECTS IN Ce or Pr-DOPED CRYSTALS

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Scintillating properties and performance of various high or less efficient inorganic crystals are intensively studied [1,2]. X- or γ-ray spectroscopy is used to investigate their scintillation response and related characteristics as the \( N_{\text{phel}}(E) \) or L.Y.(E) photoelectron or light yields, respectively, scintillation decays, En.Res.(E) energy resolutions, proportionality of the yields, etc. [2]. Modern scintillation detectors and applications need suitable crystals characterized by (i) fast decay, (ii) high light yield, (iii) low afterglow and (iv) appropriate density. Low afterglow is conditioned by suppressed presence of defects or centres responsible for slow scintillation decay processes. An occurrence of thermo-luminescence (TSL) peaks around RT and presence of very slow decay components in the Ce\(^{3+}\) scintillation decay was observed on LuAG:Ce crystal [3]. Trapping levels related to unspecified point defects were found on pure, Ce and (Ce,Si)-doped YAG crystal [4]. Generally, the presence of shallow traps results in slow scintillation decay processes and this should be also reflected in the time-development of scintillating response, e.g. in \( N_{\text{phel}}(E) \) time dependence.

The main goal of this paper is to present and summarize the time-development of scintillating response of the Ce\(^{3+}\) and Pr\(^{3+}\) doping ions in selected fast and efficient inorganic crystals, based on aluminum garnets or perovskites [1,3-6]. Time development of \( N_{\text{phel}}(E) \) yield was measured for fixed values from the time span between 0.25 – 5 µs integration times [1,6]. These measurements were carried out with a special HPMT multiplier [1]. Generally, the highest difference in \( N_{\text{phel}}(E) \) yield between the shortest (0.25 µs) and the longest (5 µs) integration time was observed for the Lu-containing garnet crystals, while that for those with Y was smaller (60 – 70 % against 20 %, respectively). Time dependence of \( N_{\text{phel}}(E) \) yield, presence of slow decay components and possible traps/defects reflected in TSL spectra, correlated on the same crystals, will be presented. An influence of traps and related defects will be discussed.

References

Photonic crystals are periodic dielectric structures in which light can behave much differently than a homogeneous medium. The analysis of such structures closely parallels that of periodic atomic crystals for solid-state physics. Some of the most interesting and challenging problems occur, however, when the periodicity is broken, either by design or by the inevitable fabrication imperfections. This talk presents an overview of some of the interesting properties and applications of these media, from switching in subwavelength microcavities, to slow-light devices, to guiding light in air. We also discuss a few examples of small perturbations that have important effects, from slow-light tapers, to surface-roughness disorder, to quantum effects in highly nonlinear cavities.
The multifaceted polaronic problem in the highly polarizable quantum paraelectric perovskite-like oxides SrTiO$_3$, KTaO$_3$ and related materials is one of the most interesting and discussed questions of the day. On one hand, the very existence of polarons in SrTiO$_3$ and KTaO$_3$ is still under debate. On the other hand, a number of new intriguing observations, such as dielectric relaxation, optical properties, short- and long-range phase transformations in pure and doped perovskite-like ABO$_3$ quantum paraelectrics, have been explained invoking various kind of polarons, formation of polaronic complexes and polaron related effects.

Recently, a new challenge emerged due to the discovery of gigantic UV-light induced dielectric permittivity enhancement and unusual dielectric relaxation in SrTiO$_3$, KTaO$_3$ and CaTiO$_3$ at low temperatures. Various types of possible photo-induced phase transitions with appearance of mesoscopic metallic or polar clusters formed around photocarriers localized as small polarons (which can be treated as “photo-induced defects”) were suggested in attempts to explain such phenomena.

In the present work we review a range of light induced properties and effects observed in KTaO$_3$, KTa$_{1-x}$Nb$_x$O$_3$ and SrTiO$_3$ at low temperatures. The phenomena and our experimental studies fall into following main cases: i) evidence of hole- and electronic UV-light induced polarons in IR optical absorption spectra; ii) photocarrier localization and charge transport features; iii) nature of giant photo-induced dielectric effect; iv) attempts to check for the presence and character of the UV-light induced phase transitions.
The discovery of the “colossal” magnetoresistance (CMR) in the manganites with perovskite structure [1] has stimulated the research of the compounds exhibiting large magnetoresistance. The magnetic and transport properties of La$_{1-x}$Sr$_x$CoO$_3$ cobaltites with perovskite structure and manganites such as La$_{1-x}$Sr$_x$MnO$_3$ have common features [2]. In both systems the substitution of La with divalent ion Sr creates paramagnetic (x < 0.2) to ferromagnetic (x > 0.3) transition as the dopant concentration is increased. The Sr$^{2+}$ and especially Ba$^{2+}$ ionic radiuses is significantly greater than that of the La$^{3+}$ ion, so it is possible to expect stabilization of the intermediate spin state of cobalt ions by substituting Sr$^{2+}$ and especially Ba$^{2+}$ ions for La$^{3+}$ ones. However, at such heterovalent substitution Co$^{4+}$ ions appear, leading to the ferromagnetic metallic ground state [3, 4]. The origin of the ferromagnetic state in metallic cobaltites and manganites has been a subject of discussion for a long time [5]. The majority of researchers suppose that ferromagnetism in cobaltites is caused by “a double exchange”, as in manganites [6]. To prevent the Co$^{3+}$ ion appearance, it is possible to introduce simultaneously Nb [7] ions, which at the presence of Co$^{3+}$ ions will be in oxidizing state 5+. By simultaneously introducing Sr$^{2+}$ and Nb$^{5+}$ the cobalt ions keep their valence state and the electroconductivity of La$_{1-x}$Sr$_x$Co$_{1-x/2}$Nb$_{x/2}$O$_3$ solid solutions decreases with dopant concentration enhancement. Thus, the different nature of ferromagnetic interactions formation in the given systems is obvious [7]. In this work we present extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) of the Co K-edge studies in La$_{1-x}$Sr(Ba)$_x$CoO$_3$ and La$_{1-x}$Sr$_x$Co$_{1-x/2}$Nb$_{x/2}$O$_3$ (x = 0; 0.2; 0.3; 0.5) solid solutions. The sensitivity XANES and EXAFS to chemical composition, local lattice distortion, “chemical pressure” effect and to an overlapping mixture of low (1$^A_1$), intermediate (3$^T_1$) and high spin (3$^T_2$) states of Co$^{3+}$ and Co$^{4+}$ ions in these cobaltites was also considered. Experimental EXAFS and XANES spectra at the cobalt K-edge will be interpreted in terms of detailed theoretical calculations based on multiple-scattering theory (ab initio codes: FDMNES and FEFF8).

Crystal and magnetic structure of these cobaltites were precisely determined by high-resolution X-ray and Neutron diffraction methods. Correlations of the long-range structure parameters with local atomic and electronic structure ones and also with SQUID magnetization measurements was analyzed.

The details of local atomic and electronic structure in cobaltites doped by Sr, Ba and Nb are presented and discussed.

References
Recent experimental data clearly demonstrate that using both femto- and nano-second laser pulses with photon energies tuned to excite particular surface features at the MgO surface, one can achieve a very effective desorption of hyper-thermal atomic O and Mg species. It has also been demonstrated that photo-luminescence of MgO nanocubes with maxima at 3.4 eV and 3.3 eV results from the excitation of 4-fold and 3-fold coordinated anions at 5.4 eV and 4.6 eV. In this presentation we demonstrate a new mechanism responsible for both the desorption of O and Mg atoms and photo-induced radiative and non-radiative processes on low-coordinated sites at the MgO surface.

To model the photon-induced processes in MgO we employ an embedded cluster approach, which combines a quantum-mechanical treatment of a site of interest with a self-consistent classical description of the remaining part of the system. The method is implemented in a computer code GUESS; it allows one to account consistently for the ionic and electronic contributions to the defect-induced lattice polarization and for their effect on the defect itself, and to treat excited states using different ab initio techniques.

We modelled the electronic excitation of 3-coordinated O and Mg corner sites at the MgO surface and developed a three-step mechanism of O and Mg atom desorption. The results of our calculations suggest that the first photon of \( \text{ca. 4.5 eV} \) can induce an optical transition at the oxygen corner site. This first excited state relaxes with a significant displacement of the corner oxygen ion away from its original site. The relaxed state corresponds to a charge transfer exciton configuration \( \text{O}^- \ldots \text{Mg}^+ \). A radiative transition into the ground state is responsible for the photo-luminescence and the calculated value for the maximum of this transition is 3.4 eV. The non-radiative transitions to the lowest triplet and ground state have barriers of \( \text{ca. 0.3 eV} \) and are responsible for the quenching of this luminescence. While the system remains in the excited state, excitation with another photon at about 4.8 eV will ionize the corner creating stable corner O\(^{\text{+}}\) species. Further excitation of O\(^{\text{+}}\) species with photons at \( \text{ca. 4.8 eV} \) transfers an electron from a nearby Mg ion. After this excitation an oxygen atom prefers to leave the surface with the maximum kinetic energy of several tenths on an eV. The surface site relaxes with the formation of a F\(^{\text{+}}\) centre at the corner site previously occupied by the desorbed oxygen atom. We demonstrate that a similar mechanism is responsible for desorption of Mg atoms. The results are in good agreement with the experimental absorption and photo-luminescence energies and kinetic energies of desorbed species.
KThF

DENSITY FUNCTIONAL MODELLING OF IMPURITY-VACANCY CENTRES IN ALKALI HALIDE LATTICES

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Incorporation of aliovalent impurities in principle requires charge compensation. In alkali halides Schottky disorder prevails. Hence, cation or anion vacancies are the most obvious lattice defects through which charge compensation may be accomplished. Such vacancies change the symmetry of the impurity centre, cause a redistribution of electron density and introduce electric field gradients in the crystal. If the centre is paramagnetic, all these effects may be monitored with electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopy. However, vacancies have neither electronic nor nuclear spin, and are therefore not directly detectable with EPR and ENDOR. Their presence can only be inferred from the observed effect on spin Hamiltonian parameters, i.e. \( g \), (super)hyperfine (A) and quadrupole (Q) tensors.

Today’s advances in \textit{ab-initio} modelling using density functional theory make it possible to simulate the effect of charge compensating vacancies on the spin Hamiltonian parameters of paramagnetic impurities and prove (or exclude) their presence in observed centres. However, in order to obtain physically meaningful results, a sufficiently accurate quantum mechanical model of the defect has to be used. Our recent results on chalcogen-doped alkali halides have, e.g., shown that the lattice relaxations and the quantum description of the first shell around the vacancy have a marked influence on the computational results [1].

In this contribution, we present results of DFT calculations on substitutional O− and S− defects in alkali halides, and Rh\(\text{Cl}_6^{4−}\) and Ir\(\text{Cl}_6^{4−}\) complexes in NaCl and AgCl. For the X− centres (X = S, O) the anion vacancy that preserves charge compensation of the X2− precursor centre remains bound to the defect after hole trapping. For Rh\(^{2+}\) centres in NaCl and AgCl it has been found that local charge compensation only occurs via next-nearest neighbour cation vacancies, whereas for Ir\(^{2+}\) complexes no final defect models could be proposed up to now [2]. Total energy calculations for various impurity-vacancy configurations are compared in order to identify the energetically most favourable vacancy position for each type of defect. The results are found to be in agreement with observed defect symmetries. In addition, computed \( g \), A and Q parameters are confronted with results of EPR and ENDOR experiments. Specific aspects of time-efficient modelling of the environment of the impurity ion and the vacancy are discussed.

References

CONCENTRATION-DEPENDENT HYDROGEN DIFFUSION IN VITREOUS SILICA RELATED TO TRAPPING

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An analysis of literature data [1, 2] of transport of hydrogen in vitreous silica strongly points at a contribution of atomic hydrogen to the overall hydrogen transport. Such a contribution explains an extraordinarily high diffusivity and permeability of hydrogen in vitreous silica relative to those of noble gases. In this paper transport of hydrogen through a 0.1 cm thick vitreous silica wall was studied, where different pressures of hydrogen: 70 mbar, 460 mbar, 880 mbar and 1200 mbar were applied at the high-pressure side at 550°C. The steady state flux of permeated hydrogen was found to approximately increase proportionally to the applied hydrogen pressure over the silica wall, while the steady state concentration of hydrogen in the silica wall did not. Therefore, a concentration-dependent diffusivity of hydrogen in vitreous silica has been obtained from multiplying flux by concentration gradient, illustrated by ”experimental value” in Figure 1. An iterative fitting procedure of the experimental data confirmed a concentration-dependant diffusivity of hydrogen, illustrated by ”iterated value” in Figure 1. Knowledge of both flux and concentration at different applied hydrogen pressures is needed for correct calculation of effective diffusivity. The observed extraordinarily high diffusivity and permeability of hydrogen and our observation of a concentration dependent diffusivity are consisted with a situation where a transport of atomic hydrogen is retarded in reversible traps. Since the abundance of traps is finite, it seems reasonable that the fraction of hydrogen retarded in traps decreases when the hydrogen concentration in the material increases. This leads to the situation of concentration-dependant diffusivity.

![Figure 1: The diffusivity of hydrogen in a silica wall at 550°C versus mean concentration of hydrogen.](image)

References

Defects in halide materials have been investigated using atomistic scale computer simulation. These defects are important in controlling a number of key materials properties. Two corresponding issues have been considered in depth. The first issue addressed is the anisotropic dielectric relaxation of lithium doped ZnF₂. The relative energies for the solution of LiF indicate the formation of a split interstitial defect structure. By analysis of the lithium migration and cluster binding energies, the experimentally observed dielectric relaxation processes are better understood [1].

Also considered are rare-earth halides (REX₃ with X= F, Cl, Br, I), which are currently being considered as scintillator hosts [2]. These materials undergo an experimentally observed structural change as a function of RE cation radius. We have reproduced this structural variation with an atomistic model. In order to optimise scintillator properties (fast and bright), the intrinsic defect mechanisms need to be assessed as such defects act as performance limiting trap sites. The predictions made are interpreted as a function of the host cation size in order to reveal structural trends.

References


The detailed understanding of the transport mechanisms in ionic solids is important from both the academic and technological viewpoints. Developing successful models of the migration of ions in solids has provided a rigorous test-bed of the point defect theories. Key applications of ionic solids rely on their ability to perform as solid electrolytes, for example in sensors, batteries and fuel cells, and the knowledge of the transport processes leads to improved performance. The last three decades, the lifetime of the EURODIM conference series, have witnessed continued progress in research in this area and this series has been the major forum for this work. This contribution will review the challenges, progress and future perspectives for research in this field.

The contribution will begin with a brief summary of the status of research in 1973, the time of the meeting in Marseilles. As a result of work on simple ionic crystals, such as the alkali and silver halides, the nature of the basic point defects and their diffusion mechanisms had been established. The next decade saw a number of important developments. These included the use of a wider range of experimental techniques, particularly the application of A.C. impedance spectroscopy and the removal of the requirement of single crystal samples. Computer simulation methods were also established as an important tool in this decade. Interest moved away from the simple binary systems to oxides and more complex materials, starting with the fast-ion conductors and driven further by technological demands in the energy field (i.e. energy storage).

The bulk of the contribution will focus on the current status of the field. This will include the available experimental and computational techniques and will use some case studies as examples. The recent interest in nanomaterials has led to research on nanocrystalline ionic crystals – referred to as nanoionics – with the aim of producing materials with exceptionally high ionic conductivities. An overview will be presented on the research in this field. Finally, the prospects for future developments in transport studies will be presented.
Insulating materials possess peculiar optical properties, like transparency in the visible spectral range, which can be modified and controlled by electronic excitation [1]. Lithium Fluoride (LiF), a radiation sensitive ionic material well known in dosimetry and in the field of tuneable colour centre lasers, can host point and extended defects stable at room temperature. Low penetrating radiations can create high concentrations of primary and aggregate electronic defects, which change the passive and active optical properties of LiF in thin irradiated surface layers [2]. Among them, simultaneous modifications of refractive index [3] and gain properties [4] have been achieved within volume of size comparable with light wavelengths.

The recent developments in laser technologies, electron and particles beam methods, and novel photon sources have led to a wide range of opportunities to locally change the LiF optical properties at a sub-micron scale, with promising applications in the field of photonics [5] and soft X-ray imaging detectors [6].

Combining these opportunities with LiF thin film growth capabilities, interesting developments are under way. An overview of the most significant results will be provided, together with a comparison among different systems and processes, in order to allow better understanding and control of point defects in LiF thin layers.

References

EPR OF Cu$^{2+}$ IN LITHIUM TETRABORATE SINGLE CRYSTALS

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Lithium tetraborate (Li$_2$B$_4$O$_7$) has acousto- and optoelectronic properties, while Cu doped Li$_2$B$_4$O$_7$ is a well-known scintillator and thermoluminescent dosimeter material. Time resolved luminescence studies of Li$_2$B$_4$O$_7$:Cu have recently been extended to low temperatures and higher energies (see abstract of Nagirnyi et al. [1]). However, no impurity EPR studies have been reported up to now due to difficulties in incorporating dopants. While there are two crystallographically different B sites within a compact covalent B-O network with three- and fourfold oxygen coordination, respectively, there is only one Li site, having ionic character. Though all these sites have C$_1$ local symmetry, the Li site is located on a diagonal glide mirror plane of the space group $I4_1d$ belonging to the $C_4v$ point group [2] roughly at half distance between symmetry related B$_4$O$_7$ groups. The aim of the present investigation is to characterize the position and the electronic structure of the Cu impurity in the lattice.

Li$_2$B$_4$O$_7$ single crystals containing, according to an atomic absorption analysis, $\sim 4 \times 10^{-3}$ mol% Cu, have been prepared at the Research Institute for Solid State Physics and Optics, Budapest, Hungary. EPR spectra have been taken using ESP-300 Bruker spectrometers in the X and Q bands. The EPR spectra have been described assuming an $S=1/2$ electron spin and well resolved HF splittings from isotopes with $I=3/2$ nuclear spin. These properties can be attributed to the Cu$^{2+}$ ion with $3d^9$ electronic structure and the two Cu isotopes with natural abundances of 69.2% and 30.8%, both having $I=3/2$ spins. Four different orientations (EPR lines) are observed in general orientations but the lines are pair-wise nearly coinciding in the crystallographical planes. This indicates that the centre has an approximate symmetry, which corresponds to the properties of the Li site. The principal values of the $g$ tensor ($\sim 2.03, \sim 2.22, \sim 2.52$) and the Cu$^{63}$ HF tensor ($\sim 100, \sim -56, \sim 15$, in units of $10^{-4}$ cm$^{-1}$) with nearly coinciding eigenvectors and also the nonaxial character of the $g$ and HF tensors all support the model of an unpaired hole with $d$ character localised on a Cu$^{2+}$ ion at or near to the Li site. The presence and site of possible charge-compensating defects like Li vacancies could not be derived from the spectra.

It will be shown that these data are in accordance with the conclusions of the luminescence measurements of Nagirnyi et al. [1] in particular about the low symmetry of the non-paramagnetic Cu$^{+}$ sites.

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References

ELECTRONIC TRANSITIONS IN Li$_2$B$_4$O$_7$:Cu SINGLE CRYSTALS

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An important advantage of the acousto and optoelectronic crystal, lithium tetraborate (Li$_2$B$_4$O$_7$), is its transparency up to 160 nm, which is remarkable even among other borates often used for non-linear optical applications in the UV region. If doped by small amounts of Cu, Li$_2$B$_4$O$_7$ is a scintillator suited for neutron detection, and can also be used as a tissue-equivalent thermoluminescent dosimeter with outstanding sensitivity. Earlier luminescence studies of Li$_2$B$_4$O$_7$:Cu have been confined to room temperature and a narrow range of excitation energies ($E_{\text{exc}} < 6$ eV) insufficient to reveal the variety of impurity states which might be involved in view of the large energy gap of the material. Here we report on a low-temperature ($T \geq 1.85$ K) study of Li$_2$B$_4$O$_7$:Cu crystals by methods of time-resolved polarization spectroscopy using synchrotron radiation in the 4-20 eV region and microsecond Xe flash lamp pulses. Li$_2$B$_4$O$_7$ single crystals containing $\sim 4 \times 10^{-3}$ mol% Cu have been grown at the Research Institute for Solid State Physics and Optics, Budapest, Hungary.

The emission spectrum of Li$_2$B$_4$O$_7$:Cu at low temperature reveals a relatively narrow strong band peaked at 3.35 eV, which is substantially different from a broad 3.65-eV emission of self-trapped excitons in pure Li$_2$B$_4$O$_7$. The excitation spectrum of the impurity-related 3.35 emission contains two groups of bands at about 5 and 7 eV, the latter situated at the onset of fundamental absorption and obviously distorted on the short-wavelength side due to host absorption. The efficiency of the excitation strongly reduces by 10 eV and then does not significantly change up to 20 eV indicating a non-efficient energy transfer from the crystal matrix to an impurity centre. We assign the excitation bands at 5 eV to the parity- and spin-forbidden $3d^{10} \rightarrow 3d^94s$ transitions and those at 7 eV to the allowed $3d^{10} \rightarrow 3d^94p$ transitions of the Cu$^+$ ion, whereas the latter are observed for the first time in borate systems. Accordingly, the $3d^94s \rightarrow 3d^{10}$ transitions are considered to be responsible for the 3.35 eV emission band. The analysis leads to the assumption that Cu$^+$ ions substitute Li$^+$ at a site of very low (C$_1$) symmetry, and do not enter the covalent B-O network. A time-resolved polarization study of the 3.35 eV emission confirms this suggestion. The decay time of 25 µs at room temperature, which is relatively short for forbidden transitions, is characteristic of a Cu$^+$ ion situated in a low-symmetry or off-centre position. The temperature dependence of the decay time indicates a triplet nature of the relaxed excited states of the Cu$^+$ centres. Two decay components are found at temperatures below 5 K polarised in a different way with respect to the main crystallographic axis. This causes unusual temperature behaviour of the polarization properties of the emission due to the temperature-induced changes in the relative population of the corresponding states. Other phenomena connected with the anisotropy of optical transitions are also reported. The nature of the electronic states responsible for optical properties of Li$_2$B$_4$O$_7$:Cu is discussed.

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DOPED NANOCRYSTALLINE INSULATING MATERIALS: OPTICAL STUDIES OF STRUCTURAL PHASE TRANSITIONS

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Nanocrystalline insulating materials reveal significant effects of size restriction in their optical properties [1,2] and may be of interest for applications. We report the results of optical studies of new RE and TM ions doped nanocrystalline materials which undergo structural phase transitions: SrTiO$_3$:Cr$^{3+}$, SrTiO$_3$:Eu$^{3+}$ and BaTiO$_3$:Eu$^{3+}$. The selection of SrTiO$_3$ was stimulated by its unique physical properties; BaTiO$_3$ is attractive as an extremely well studied material.

Doped nanocrystalline SrTiO$_3$ and BaTiO$_3$ samples were produced by the sol-gel process. The RE and TM ions were added in the course of sol-gel synthesis. The samples structure and crystallite sizes were determined by x-ray scattering methods. The samples consist of the powder clusters built of the 25-50 nm particles (the particles size depends on the annealing temperature).

The Cr$^{3+}$ $^2E - ^4A_2$ and Eu$^{3+}$ $^5D_{0,1} - ^7F_n$ fluorescence spectra were studied at T=10-300 K under the laser and LED excitation. The observed spectra were similar to that of the bulk doped materials [3,4]. The only difference is the additional inhomogeneous line-broadening observed in nanocrystalline samples. The peculiar highly asymmetric shape of inhomogeneously broadened zero-phonon Cr$^{3+}$ $^2E - ^4A_2$ transition was observed in SrTiO$_3$:Cr$^{3+}$.

Fluorescence spectroscopy of the probe Cr$^{3+}$ and Eu$^{3+}$ ions was used to detect the structural phase transitions in nanocrystalline SrTiO$_3$. The D$_{4h}$ – O$_h$ phase transition was observed via its effects on Cr$^{3+}$ $^2E - ^4A_2$ and Eu$^{3+}$ $^5D_1 - ^7F_1$ fluorescence transitions. In nanocrystals the phase transition temperature is shifted by ~40 K to the higher temperatures and this shift is the same for 30 and 45 nm samples. The study of phase transitions in nanocrystalline BaTiO$_3$ is performed with both probe ions spectroscopy and second harmonic generation techniques.

The lifetimes of Cr$^{3+}$ $^2E$ and Eu$^{3+}$ $^5D_{0,1}$ excited levels were studied in the wide temperature range. The differences of the lifetimes in nanocrystalline and bulk materials are discussed taking into account the influence of modified refractive index of the media on radiative transitions and other effects of size restriction.

References

EXTENDED POSITRON-TRAPPING DEFECTS IN INSULATING MgAl₂O₄ SPINEL-TYPE CERAMICS

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A meaningful characterization of positron-trapping defect centres in insulating MgAl₂O₄ spinel-type ceramics extensively studied as one of the most perspective materials for humidity sensors is developed at the basics of positron annihilation lifetime (PAL) measurements.

The investigated samples are prepared from MgO and Al₂O₃ reagents. The above oxides are weighed, mixed with a highly pure acetone, ball-milled during 96 h and dried. The obtained powder is mixed with an organic binder to prepare green body billets. Then, these pellets are sintered in a special regime with maximal temperature of 1250 °C. In the result, we obtained humidity-sensitive ceramics having 51.3 % total porosity. In our experiments with ORTEC spectrometer the full width at half maximum is 0.270 ns and ²²Na isotope (0.74 MBq) was used as a positron source. The obtained spectra were fitted by LT program in terms of mixed single positron trapping and ortho-positronium decay modes. We used a few measured PAL spectra for the investigated pair of samples with a total number of counts in the range of 800000-1200000. Each spectrum was multiply treated owing to slight changes in the number of final channels, background of annihilation and time shift. The best results were selected on the basis of weighted least-squares deviation between experimental points and theoretical curve.

It was established that only three-component fitting procedure with arbitrary PAL parameters can be more or less successfully used to describe correctly the obtained experimental data. The identified extended positron-trapping defects in the insulating MgAl₂O₄ spinel-type ceramics were supposed to be as follows:
- positron trapping defects in the form of individual vacancies and small vacancy-like clusters within ceramics bulk attributed to the shortest PAL component with 0.18-0.20 ns lifetime (along with theoretical para-positronium lifetime of 0.125 ns),
- positron trapping defects in the form of neutral or negatively charged clusters of charge-compensating vacancies located at grain-boundaries, attributed to the middle PAL component with 0.4-0.5 ns lifetime.

In addition, the ortho-positronium pick-off decay mode in free-volume pores of ceramics filled with adsorbed water (presumably, between individual grains due to incomplete intergranual contacts), attributed to the longest PAL component with ~2 ns lifetime was revealed.
INTERACTION OF DEFECTS WITH DOMAIN BOUNDARIES IN FERROELECTRICS AND RELATED MATERIALS

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The interaction of domain boundaries with crystalline lattice defects controls all main properties of these materials, connected with switching processes. In present work the mentioned interaction in ferroelectric-ferroelastic crystals was investigated. It was shown, that in the discussed materials in the process of interaction with charged and elastic defects a modification of a domain wall profile take place, during which the bound electric charges and twinning dislocations appear in the area of the deflected domain wall. And interaction of initial defect with these charges and dislocations actually is effective interaction of the mentioned defects with a domain wall.

Calculations of the defects interaction with domain boundary for a case of a dilatation centre and dislocations with various orientation of a dislocation line concerning a plane of undeflected domain wall were performed. It was shown, that in case of interaction of a domain wall with a centre of dilatation the wall displacement possesses symmetry in a direction perpendicular to spontaneous shift, and is asymmetric along this direction. The energy of the dilatation centre interaction with domain boundary decreases with growth of defect distance from boundary $x_d$ proportionally to $1/x_d^3$.

As well as in the case of interaction with a dilatation centre at the interaction of domain boundary in a ferroelectric - ferroelastic with a dislocation the certain deflection of the boundary removes a part of strains, which are created in crystal by the dislocation, that effectivly means a mutual attraction of the domain wall and initial dislocation. For interaction with ferroelectric-ferroelastic’s domain wall of a screw dislocation, which line is parallel to the initial position of domain boundary and to the spontaneous shift, the coordinate dependence of boundary displacement along the spontaneous polarization direction has the following form:

$$U(z) = -\frac{b}{2\pi\varepsilon_0 (1+\gamma)} \text{arctg} \frac{z}{x_d},$$

$$\gamma = \frac{8\pi P_0^2}{\varepsilon 2\mu\varepsilon_0^2},$$

$\varepsilon = \varepsilon_c = \varepsilon_a$,

where $b$- Burgers vector of dislocation; $\mu$- shift modulus; $P_0$ and $\varepsilon_0$ - spontaneous polarization and spontaneous deformation, respectively; $\varepsilon_c$ and $\varepsilon_a$ - dielectric permittivity of monodomain crystal along and perpendicular to polar axis, respectively.

Influence of the domain-defect interaction on processes of ageing and fatigue in ferroelectrics was investigated. It was shown, that the reasons of ageing and fatigue of ferroelectric crystals are: 1) defects diffusion to the domain walls, which reduces total energy of the crystal, 2) appearance of obstinate domains reducing reversible polarization of ferroelectrics due to compensation of the bound charge and elastic strains on domain boundary by electric and elastic fields of defects and 3) destruction of electrodes material or surface non-ferroelectric layer due to occurrence of mechanical strain in a place of their contact with a switchable material during sustained cycling of a ferroelectric sample.
Fluoride crystals have long presented a challenge for chemists and physicists, because their preparation often requires very specific procedures [1]. In spite of this, fluoride crystals have found many applications as dosimeters, information storage devices, x-ray monochromators, and, in particular, in the field of optics as laser media.

Colour centres are lattice vacancies defects trapping electrons or holes. They are easily created in single crystals at room temperature, by irradiation with ionizing radiation. Recently it was shown that is possible to create, with dimensional control, colour centres with interaction of ultra short pulse laser in crystals and glasses [2]. This action allows the modulation of the material refraction index, creating waveguides or photonics devices [3].

The laser performance of fluoride crystals is dependent upon a number of factors directly related to the crystal growth conditions and laser operation. For example, the presence of oxygen impurities and/or moisture during crystal growth can change considerably the defects formation as well as the optical response of such devices. Moreover, when laser crystals are exposed to high intensities of pumping radiation in the UV-visible spectral regions or ionizing radiation, degradation of their characteristics and performance are implies.

Colour centres are used as a probe to understanding the relevance of laser-degradation process in crystals. In this work, we show that is possible to produce stable colour centres inside fluoride crystals (LiYF₄, BaLiF₃, LiSrAlF₆, LiF) with dimensional control. Besides, high intensity lasers produce colour centre aggregates, that are suitable for laser action. Ti:Sapphire CPA laser system operating at 830nm was used, producing a train of 640 mJ, 60fs pulses at 1kHz, with a peak power of 12.5GW. A comparison between the optical properties of colour centres produced by ultrashort laser irradiation in samples grown by different methods was done, and it was possible to discuss the basic formation mechanisms of these centres. The optical absorption spectra of the produced colour centres was measured.

References

OFrC1

THEORETICAL MODELLING OF THE PHOTOCONVERSION AND AGGREGATION OF OXYGEN CENTRES IN CALCIUM FLUORIDE

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Calcium fluoride is known to be an ultimate optical material for vacuum and deep-ultraviolet spectral regions. At present moment the main limiting factor for its industrial applications is the unavoidable presence of oxygen impurity centres possessing optical absorption (OA) in VUV region. In our previous work [1] we explained the mechanism of oxygen-vacancy dipoles photodissociation taking place under irradiation in 8.4 or 9.2 eV absorption bands of the dipole at temperatures above 200 K. The products of this photodissociation are \( \text{O}^- \) ions as well as \( \text{F}_A(\text{O}_2^-) \) and \( \text{F}_{2\text{A}}^+(\text{O}_2^-) \)-centres, i.e. \( \text{F}^- \) and \( \text{F}_{2}^+ \)-centres perturbed with oxygen ion. Recent measurements confirm the suggested photodissociation scheme but put other questions. After the irradiation of the sample is stopped then the gradual reappearance of oxygen-vacancy dipoles is observed at room temperature together with decrease of \( \text{F}_{2\text{A}}^+(\text{O}_2^-) \)-centres luminescence. In the present work we tried to clarify the nature of this process and to make further characterisation of the aggregation of oxygen-vacancy dipoles, including optical properties of aggregates.

Ab initio study of oxygen centres has been performed in embedded cluster approach with modified B3LYP functional containing 40% of Hartree-Fock exchange in order to reproduce the correct degree of electronic states localisation. We have calculated such defects as isolated \( \text{O}_2^- \) and \( \text{O}^- \) ion, oxygen-vacancy dipole \( \text{O}_2^-\text{-V}_A \) and dimer \( \text{O}_2^-\text{-V}_A^2 \), \( \text{F}_A(\text{O}_2^-) \) and \( \text{F}_{2\text{A}}^+(\text{O}_2^-) \)-centres. The dependence of results on basis set and cluster size has been carefully checked.

Use of optimised basis set allowed us to sufficiently improve our previous result for optical absorption (OA) of oxygen-vacancy dipole. Calculated OA energies of 6.38, 6.48 and 6.63 eV are in good agreement with experimental OA band at 6.7 eV, while calculated transitions at 8.1 and 8.22 eV agree well with OA band at 8.4 eV. The optical absorption of \( \text{O}^- \) ion lies in the same VUV region and has, according to our results, the energy of 6.48 eV and oscillator strength about 0.1. Calculated hyperfine couplings of \( \text{O}^- \) ion are in good agreement with experiment.

Classical MD simulations were undertaken in order to understand in details the processes of reorientation, diffusion and aggregation of oxygen-vacancy dipoles. These simulations confirmed that the reorientation of dipoles goes through intermediate configuration (i.e. \( <100> \leftrightarrow <110> \leftrightarrow <010> \)). Besides the reorientation the jumps \( <100> \leftrightarrow <200> \) can be often observed in MD run. The possible sequences of configurations leading to formation of the dimer from the pair of dipoles were found.

References

The radiation damage of complex fluoride crystals was analyzed from the point of view absorption and luminescence properties deterioration.

Few materials including Ce and Eu doped KMgF₃, LiBaF₃, LiCaAlF₆ and LiSrAlF₆ were chosen to prove different hypotheses based on the crucial role of the intrinsic defects in the energy storage. It is shown that oxygen ion presence changes the energy storage, absorption and emission characteristics of pure and RE doped fluoride compounds.

Besides, the energy storage of Ce³⁺, Pr³⁺ and Eu³⁺ doped LiLuF₄ crystals are discussed in respect to the oxidation-reduction reactions and the RE³⁺ level positions within gap.

The mechanism of Lu dopant influence on emission and coloration of BaF₂ based crystals is considered in the view of charge compensative interstitial fluorine role as well as Lu³⁺ level position slightly above the valence gap.

All examples demonstrate that main reasons for distinctions between materials are the point defect structure, volume and local alignment of compensative defects, RE³⁺ typical redox reaction. If the defect structure explains the efficiency of the charge carrier capture with the following colour centre formation, the activator valence change is the base for the luminescence yield decrease. It is shown that the same host crystal can be modified from the scintillation to dosimetry application by the proper choice of dopants.
COLOUR IN GEMSTONES: A SOLUTION TO THE PUZZLE OF RUBY, EMERALD AND ALEXANDRITE

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Ruby (Al₂O₃;Cr³⁺) and emerald (Be₃Si₆Al₂O₁₈;Cr³⁺) are reference systems in the realm of doped insulating materials and gemstones. Despite they have attracted a great deal of experimental work the origin of the different colour displayed by such gemstones is a fundamental but up to now unsolved problem. Due to the insulating character of host lattices the colour in ruby and emerald has usually been explained on the basis of quasi-octahedral CrO₆⁻⁻ complexes (formed under the Al³⁺→Cr³⁺ substitution) and the ligand field theory [1]. Moreover the difference of the ⁴A₂g (t₂g³) → ⁴T₂g (t₂g²e_g) peak for ruby (2.24eV) and emerald (2.0 eV) has been ascribed to an average Cr³⁺-O²⁻ distance, R, which is higher by 5 pm for emerald than for ruby assuming that 10Dq = KRⁿ (n = 5). Although such an explanation has been considered as reasonable, recent Extended X-ray Absorption Fine Structure (EXAFS) measurements performed on both gemstones [2,3] reveal however that ruby and emerald have the same R = 1.97 Å value within the experimental uncertainty (1 pm).

A simple explanation of this puzzling problem is given in this work where the role played by the electrostatic potential, V_R(r), imposed by the rest of lattice ions on CrO₆⁻⁻ is stressed. Density Functional Theory (DFT) calculations have been performed on CrO₆⁻⁻ complexes in vacuo as well as under the influence of V_R(r) upon localised electrons in the complex. These results clearly demonstrate that when the local symmetry is lowered the electric field associated with V_R(r) leads to a supplementary contribution to 10Dq (not considered within the ligand field theory) which is responsible for the differences in colour between ruby and emerald [4]. This fact can be rationalised through the different local symmetry of CrO₆⁻⁻ units in such gemstones (C₃ in ruby, D₃ in emerald [1,3]) which allows the existence of an electric field around Cr³⁺ in ruby but not in emerald.

Following these ideas attempts have also been made to understand the challenging situation found in alexandrite (BeAl₂O₄;Cr³⁺) [5]. Indeed there are remarkable experimental differences between the ⁴A₂g (t₂g³) → ⁴T₂g (t₂g²e_g) peak energy corresponding to the two available sites: it appears at 2.19eV for the centre m while at 2.53 eV in the case of centre i [5]. DFT calculations on CrO₆⁻⁻ complexes subject to the corresponding V_R(r) are shown to explain again such significant differences.

It should finally be pointed out that the internal electric field due to V_R(r) has much less importance as far as the ²Eₐ (t₂g²) → ⁴A₂g (t₂g³) emission is concerned since the involved states both arise from the same configuration [4]. This reasoning is consistent with the fact that the energy of the emission line in ruby, emerald and alexandrite only differ by 1.8% [5].

References

The rare earth doped fluoride materials are of interest in a range of optical device applications, from IR to UV solid-state lasers [1, 2]. However, determining whether a particular fluoride-dopant combination will have useful optical properties requires considerable experimental effort in synthesis of the doped material and its subsequent characterisation.

In this paper we present a new modelling approach for calculating the optical transitions of any doped material. The method is based on energy minimisation-based calculations of optimal doping sites and lattice relaxation about these sites, followed by crystal field calculations of the optical transitions. Optimal positions for doped rare-earth ions are calculated, with a full treatment of lattice relaxation about the dopant site. The relaxed positions are then used in a crystal field calculation of the optical transitions of the dopant ion. The method represents a refinement of previous approaches, exemplified in [3], in which the dopant ion symmetries were assumed to be the same as the symmetry of the lattice ion being replaced in the doping process.

Applications of the method are presented for rare earth doping in BaY$_2$F$_8$, where comparisons are made with recently determined experimental results [4], and in LaF$_3$, where comparisons are made with the results of the survey presented in [3]. Crystal field parameters (B$_{k_3}$) are reported, which are useful in the analysis of experimental spectra, and spectra have also been calculated, using the SPECTRA code [5].

References

POINT DEFECTS IN GROUP III NITRIDES: COMPUTATIONAL MODELING

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The group III nitrides have great potential for technological device applications. In this context, their defect properties are of particular interest. Here we describe a modelling scheme for point defects in group III nitrides and present detailed examples of results obtained.

The modelling scheme is based on a molecular cluster embedded in a classical crystal: the ICECAP method [1]. The molecular cluster is analyzed on the basis of the unrestricted Hartree-Fock approximation with many-body perturbation theory correlation correction. The embedding classical crystal is represented by the shell model. The Hartree-Fock solution and the polarization and distortion of the embedding crystal are treated self-consistently.

The results emphasize the nitrogen vacancy in AlN in the zinc-blende structure [2]. Three charge states, +1, +2 and +3, are analyzed. Computed properties include optical excitation, charge-state stability, spin state, spin density at nearest-neighbour nuclei, local deformation of the crystal, and breathing-mode force constant. Modelling issues arising from fractional ionic charges are also discussed.

References

Poster Session I
Colloids, nano–crystals, and aggregates
Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} (PMN) is an outstanding ferroelectric material which exhibits a very high dielectric constant, high electrostrictive coefficients and a diffuse and dispersive phase transition over a temperature range near -15°C [1, 2], too low for practical purposes. To increase the Curie temperature, solid solutions of PMN-PT have been reported [3], covering a wide range of applications depending on the amount of PbTiO\textsubscript{3} (PT). PMN-PT solid solutions with PT<40% have the ABO\textsubscript{3} perovskite structure, where different atomic species share the same crystallographic B positions; the relaxor behavior is due to structural heterogeneities consisting in a partial short range 1:1 ordering of B cations in nanometric domains [3, 4]. This ordering results in the formation of a \(2a_0 \times 2a_0 \times 2a_0\) fcc superstructure (\(a_0\) is the perovskite lattice parameter), visible as diffuse spots in the electron diffraction patterns.

We report here a structural and compositional study of a PMN-10%PT ceramic sample by analytical electron microscopy. Although not expected, two crystallographic phases were evidenced: the perovskite and the pyrochlore (Pb\textsubscript{1.86}Mg\textsubscript{0.24}Nb\textsubscript{1.76}O\textsubscript{6.5}). High resolution transmission electron microscopy (HRTEM) images reveal the presence of ordered nanodomains (2-5 nm) in the perovskite phase, observable in two specific orientations, [011] and [112]. However, the visibility and the ordering degree of the nanodomains on the HRTEM images are not at all obvious. By processing the HRTEM images using specialized Fourier filtering routines of the Digital Micrograph\textsuperscript{TM} software, we could clearly reveal the ordered domains in the disordered matrix and calculate their volume fraction. We also demonstrate that, unlike what was thought [4], the nanodomains are not uniformly spread in the disordered matrix. Also, the average size of the ordered domains vary in different regions of the sample, most probably due to non uniform distribution of Ti, as revealed by energy dispersive X-ray spectroscopy (EDS).

Ordered domains in PMN - 10%PT: a) Experimental HRTEM image; b) Filtered HRTEM image

References

PERIODIC NANOSTRUCTURES ON SURFACES OF Ti:Al₂O₃ CRYSTALS BY FEMTOSECOND LASER PLUSES

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Recently, surface ripples [1] and structural changes [2] with a period below the wavelength of incident laser have been observed in some metals and silica glass, respectively, after irradiation by a single femtosecond laser beam. However, until now there have been few studies on surface periodic nanostructure formation in transparent dielectrics by a single laser beam.

We report the observation of the formation of periodic nanostructures of subwavelength gratinglike grooves on surfaces in Ti:Al₂O₃ crystals after irradiation by a focused beam of a femtosecond laser. In our experiments, the laser radiation by a regenerative amplified mode-locked Ti:sapphire laser (800 nm, 130-150fs, 200KHz) and a regenerative Er-fiber pulsed laser (780 nm, 233fs, 1KHz) was focused via microscope objective on the Ti:Al₂O₃ samples. The surfaces of samples after irradiation of laser with linear and circular polarizations were analyzed by AFM. We examined the surface morphology (pattern) throughout irradiated area on linear and circular polarizations of laser. The typical AFM images of a pocket in irradiated spot and a groove in rectilinearly beam-scanned region for linearly polarized laser irradiation are shown in fig.1(a) and (b). The periodic, subwavelength gratinglike grooves (nanograting) are observed in the irradiated spot and line scanned region. The periodic nanostructures of grooves are aligned perpendicular to the laser polarization direction. The period of nanograting structures changes from ~150 nm to ~400 nm by the pulse energy. The grating period and ablation depth increase with increasing pulse energy for a fixed exposure time. The dependence of the observed periodic nanostructures on pulse energy is explained in terms of interference between the incident light field and the electric field of the surface electron plasma wave, resulting in the periodic modulation of electron plasma concentration and ablation change. A typical AFM image for circularly polarized laser irradiation has been also shown in fig.2. A windmill-like periodic nanostructure in the irradiated spot, which reflects circular polarization, was observed.

Fig. 1: AFM images of (a) focal spot and (b) rectilinearly scanned region on Ti:Al₂O₃ surface after linearly polarized laser irradiation. Fig. 2: AFM image of focal spot on Ti:Al₂O₃ surface after circularly polarized laser irradiation.

References

In this paper we present for the first time the method of obtaining the nanoclusters of Sn in KCl crystals using step by step conversion of Sn$^+$ ions by thermal annealing. We performed optical absorption (OA) and transmission electron microscopy (TEM) measurements on the same samples. These studies confirmed that like in the case of KCl:Ag, KCl:Au, KCl:In, KCl:Ga and KCl:Pb [1-3] if the coalescence takes place the nanostructures are spatially arranged. The tin nanoclusters are spatially arranged when the KCl:Sn crystals were codoped with Ca and we obtained isolated spheres in the KCl:Sn crystals, proving that in this last case the coalescence process is missing (Fig. 1).

![Figure 1](image-url)

Figure 1. TEM image of Sn nanoclusters obtained by thermal treatments in (a) KCl:Sn+Ca and (b) KCl:Sn crystals.

Additional, we calculate by the means of modified Mie’s theory [4] the tin nanoparticles dimensions and the values obtained are confirmed by the optical absorption results. The TEM patterns show very clearly that, depending on the temperature of the thermal treatment, the nanoclusters can be obtained either as isolated particles or as spatially arranged nanostructures. The histograms of the particles distributions after different times of annealing show that an increasing of the particles diameters takes place. Moreover, the TEM images prove that the spatial arrangement of the particles is formed by coalescence process.

References

FEATURES OF SOL-GEL SILICA GLASSES AFTER Gd-DOPING

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The incorporation of rare earth (RE) ions in crystalline and amorphous matrices is often investigated due to their key role in scintillation processes. Among the glassy systems, Ce-doped sol-gel silica glasses exhibit excellent scintillation properties [1]. Moreover, different RE ions were doped in a sol-gel silica glass to obtain new scintillation materials. In a previous research, some indications were obtained while comparing Ce and Gd-doped glasses [2].

Several Gd-doped sol-gel silica glasses (in the range 0-8 Gd mol%) were analyzed by: steady state and time resolved photoluminescence (PL), Raman and IR spectroscopies, electron paramagnetic resonance (EPR), and transmission electron microscopy (TEM). No crystalline aggregates were detected within the amorphous matrix, up to 8 Gd mol%, though TEM analyses revealed amorphous clusters for Gd concentration higher than 1 mol%. Moreover, the size of nanoclusters increases by increasing the dopant concentration and by performing a rapid thermal treatment (RTT) procedure at 1800 °C in air, which causes a radiative lifetime shortening, see Fig. 1. After comparing the results obtained with different techniques, an overview is given on Gd dispersion in silica.

![PL time decay measurements on samples with 3 mol% Gd, before and after RTT.](image)

Figure 1: PL time decay measurements on samples with 3 mol% Gd, before and after RTT.

References


Composite materials, consisting of glass matrix with introduced micro/nano-crystallites (called also glass ceramics) could possess properties either of the glass matrix or crystallites, as well as new properties and applications. Fluoride nano-crystals have been obtained recently in fluorozirconate glasses, a novel application of fluorozirconate glass-ceramic has been proposed as an x-ray storage phosphor [1,2]. Less investigated are fluoride crystallites in oxy-fluorides: aluminate [3,4,5] and SiO₂ glasses [6], new interesting properties of so-called up-conversion have been reported [4-6].

In the present work we studied the possibility to obtain oxyfluoride glass ceramics based on a lithium borate glass and lanthanum fluoride. Oxyfluoride glass samples of system B₂O₃ – Li₂O – LaF₃ have been obtained from raw materials B₂O₃, Li₂CO₃, LaF₃, with rare earth activator – CeF₃ (0.2 mol. %). Glasses without lanthanum fluoride are transparent up to 275 nm. In samples with LaF₃ doped with Ce-activator, an additional absorption at about 300 nm and intense photoluminescence could be observed. After x-irradiation, EPR spectrum appears with slightly resolved structure and a thermoluminescence could be observed. We will discuss under which conditions fluoride crystallites could be created in the investigated borate glass matrix.

References

FRACTAL CHARACTERISTICS OF METAL CLUSTERS SELF-ASSEMBLED IN ALKALI HALIDE MATRICES

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In the last several years the researches in the field of nanotechnology showed an increasing momentum because of the possibilities of applications in a large domain, from electronic and communication industry to medicine and life sciences. A crucial aspect is the understanding of self-aggregation phenomena and the model of diffusion limited aggregation (DLA) proved to be especially interesting allowing the approach of processes from the most diverse branches of physics.

Extensive experimental, numerical and theoretical studies [1, 2] have been dedicated to fractal growth processes. The DLA model, in which infinitely diluted concentrations of particles mimic Brownian motion by moving about randomly until attaching upon first contact with a central cluster, is a particularly attractive realization of such a process. Studies on Ag nanoclusters obtained in alkali halide crystals [3, 4] showed that the clusters are obtained in spatially arranged structures of fractal type (Fig. 1).

The paper is presenting our studies concerning the self-aggregation phenomena of colloidal nanoparticles of Ag and Au in matrices of alkali halide crystals (KCl, NaCl and KBr). The study was realized both by specific measurements such as electron microscopy as well as by modelling using the fractal geometry. The fractal character of the structures is proved by their fractal dimensions, $d_f$. The self aggregation of the metallic structures is governed in both cases (Ag and Au) by the DLA mechanism.

References


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OPTICAL PROPERTIES OF LiF CRYSTALS WITH GIVEN CONTENT OF OXYGEN, HYDROXYL AND METAL IMPURITIES

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Optical absorption and luminescence spectra have been studied in LiF crystals containing oxygen, hydroxyl and metal impurities, and coloured with gamma rays at room temperature with doses up to \(10^7\) R \([1,2]\). Measurements of uncoloured crystals, Fig.1 at left, show that the spectra already contain well defined bands, which have been attributed to which are related to various colour centres, but at the same time depend strongly on the impurity content, especially as far as their formation efficiency is concerned.

![Figure 1: Absorption and emission (PL) spectra of blank, left, and colored, right, LiF crystals. The emissions have been excited at 208 and 450 nm, respectively, and normalized, right, at the maximum value.](image1)

The connection among impurities and colour centres will be discussed on the basis of the optical spectra of uncoloured and coloured crystals, and also some annealing results on the latter ones will be considered for their information on discoloration and aggregation of colour centres and aggregation of impurities \([4,5]\).

References

Zinc oxide is promising material for different applications and the investigations of structure defects, excitonic processes and donor-acceptor centers gives rise the great interest. ZnO resolved luminescence spectroscopy. Two excitation sources was used for luminescence excitation: pulsed electron beam (8 ns, 250 keV) and YAG:Nd laser pulse (2 ns, 266 nm). ZnO nanoparticles were obtained a) from wet chemistry reactions using water solution of zinc chloride ZnCl₂ and NaOH as starting precursors, b) by plasma synthesis, c) the vaporization in a solar reactor from the targets of ZnO:Al nanoparticles synthesized by hydrothermal method. The additional testing using SEM images, FTIR spectroscopy and x-ray diffraction analysis was drown out.

The luminescence due to ZnO defect states (red and green luminescence) strongly depends on sample preparation method as well as annealing condition [1,2]. The origin of was under discussion up to now. The luminescence decay was studied over the wide time and intensity range. The examples of decay kinetic for ZnO nanostructured whisker (a) and powder (b) are shown. The decay processes are similar in red and green spectral region and diffusion-controlled process forego recombination.

The exciton and donor-acceptor luminescence (ZnO:Al) was studied at low temperatures and its intensities are estimated for different nanostructured ZnO samples.

Figure 1: Luminescence decay kinetics at RT (266 nm excitation) for ZnO nanostructured whiskers (a) and powder (b)

References
AN AB INITIO STUDY OF IRON WIRES INTERACTING WITH BN NANOTUBES

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A systematic study of Fe wires interacting with zig-zag boron nitride (BN) nanotubes is presented. Spin-polarized total-energy ab initio calculations based on the density functional theory are used to describe the structural, electronic and magnetic properties of all studied systems. For the Fe wires, either outside or inside the nanotube, the most stable configuration is found to be over the centre of the hexagonal site. For all the investigated Fe structures adsorbed on the BN nanotubes, either high-spin or low-spin, the interactions between Fe atoms, between Fe and B and between Fe and N atoms become stronger as the Fe coordination number increases. The resulting magnetic moments for all adsorbed systems are found to be close to their original values for the corresponding free Fe structures. Some special magnetic properties resulting from the interaction between the Fe wires and zig-zag BN nanotubes are found. Our calculations suggest that for applications to spin transport devices, it is desirable to form magnetic nanostructures isolated by a non-magnetic material, i.e., BN walls, could be efficiently used for high-density data storage.
The effect of ion exchange and a post-exchange thermal treatment in a gaseous hydrogen atmosphere upon the optical and structural characteristics has been analysed for phase separated soda lime silicate glass (SLSG) doped with monovalent copper. For these purposes, optical absorption, concentration profiles, and size distribution of the dopant-related species (ions and colloidal nanoparticles, respectively) have been investigated. Transmission electron microscopy (TEM) observations for the extraction replicas and the SAED analysis have been performed for the investigated specimens.

The ion exchange of samples was performed in a molten bath of Cu₂Cl₂ at 723 K for times ranging between 2 and 168 hours, after which the copper concentration on the exchanged surfaces alters from approximately 0.6 to 3.5 wt. %. Subsequent annealing of samples at 773 K for 5 hours in hydrogen induced the formation of metallic copper and semiconducting copper oxide in a near-surface layer.

For the optical absorption measurements and the electron microscopy investigations the plan-parallel sample (with two exchanged layers) has been polished. The exchanged layer was entirely removed from one surface while the other one was polished to a wedge-like shape. Approximately 1 µm of the exchanged layer per 1 mm of the sample-thickness was successively removed. Optical absorption was measured in the range between 250 and 2500 nm by using a Varian (Cary 5) spectrophotometer at room and helium temperatures. The concentration profiles were determined by using the EDX technique.

It has been stated that:
1. for the exchanged specimens, the fundamental absorption edge and the absorption band located at about 800 nm speaks in favour of the presence of cuprous and cupric ions,
2. after hydrogenation metallic copper and semiconducting Cu₂O nanoparticles are formed,
3. the concentration profiles character of the Cu/Na ions exchanging at 723 K is not dependent upon the exchange time, at least up to 168 h,
4. both, the size and the width of the size distribution of copper colloids increase with the penetration depth of the dopant.
AMORPHISATION AND RECRYSTALLISATION STUDY OF ELECTROLYTIC MANGANESE DIOXIDE

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The Electrolytic Manganese Dioxide (EMD) serves as a cathode material in alkaline batteries, and is known to be a disordered random intergrowth of pyrolusite and ramsdellite manganese dioxide polymorphs. It has superior electrochemical discharge properties to other forms of manganese dioxide of similar composition and structure. Experimental methods such as X-ray diffraction and IR spectroscopy, which provide information on the long-range order are not sufficient to characterize EMD materials and hence there has been no efficient method to characterize their structures and thereby no means of relating their atomic scale arrangement with their behaviour in batteries. In this work models of manganese dioxide nanoparticles, with full atomistic detail, have been generated using a simulated amorphisation and recrystallisation strategy. In particular, a 25,000-atom 'cube' of manganese dioxide was amorphised (tension-included) under molecular dynamics (MD). Long-duration MD, applied to this system, results in the sudden evolution of a small crystalline region of pyrolusite-structured manganese dioxide, which acts as a nucleating 'seed' and facilitates the recrystallisation of all surrounding (amorphous) manganese dioxide. The resulting manganese dioxide nanoparticle is about 8nm in diameter, and conforms to the pyrolusite structure (isostructural with rutile titanium dioxide, comprising '1x1'octahedra) and is heavily twinned. In addition, we suggest the presence of ramsdellite ('2x1'octahedra) intergrowths. The calculated radial distances compare reasonably with the experimental results. Bulk structures were also generated and the corresponding radial distances and X-ray diffraction patterns also agree with experimental results. Lithiation of these systems will be discussed.
PHOTOCHEMICAL REACTIONS OF SMALL MIXED ALKALI-METAL PARTICLES IN KCl

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When the alkali-halide crystals colored in alkali-metal vapor are annealed at appropriate high temperatures, the colloidal particles consisting of alkali metal are produced; the absorption bands due to the particles have been widely investigated [1, 2]. Nevertheless, the details of electronic transitions of these alkali-metal particles are still unknown, together with the formation mechanism and the size effect. Recently based on the free-electron model, Okada has calculated the radius of the mixed alkali-metal particles, and estimated the numbers of atoms consisting of these nano-particles [3].

In this work, using the additively colored KCl crystals containing Na⁺ or Li⁺ ions, we have investigated on the photochemical reactions of the alkali-metal particles created by thermally annealing the crystals in dry argon-gas. The band peaking at 1.95 eV after the thermal annealing at 195°C of KCl:Na (0.05 mol %) crystals containing F centers is considered to be absorption originating in the mixed alkali-metal particles consisting of Na⁺ and K⁺ atoms. Subsequently after annealing at higher 360°C, there appear the two bands peaking at 2.21- and 1.69-eV which are caused by F centers and K⁺-metal particles, respectively. From the fact that this position of the F band is coincide with that of the virgin F band for KCl without colloidal particles, it is considered that the F centers and K⁺ metal particles which are produced by the thermal destruction of the mixed Na⁺-K⁺ particles are separately situated each other. This consideration is consistent with the experimental results of ESR. On the other hand, the position of the F band observed in the process of production of the K⁺ particles is different from the virgin position, i.e., 2.21 eV of the F band. It follows that the F centers in the middle process of the colloidal-particle formation are ionized by the thermal energy and that the reproduced F centers presumably aggregate in company with the migration of the trapped-electrons and vacancies.

In addition, we will also report on the size effect of the mixed alkali-metal particles of nano-scales.

References

The investigation of development of nanoparticle colloidal centers in LiF and NaF crystals under pulse electron beams was carried out. LiF and NaF crystals were grown in ambient air by the Kyropoulos method in platinum crucibles at ambient air. It was made in Institute of Physics of National Academy of Science of Kyrgyzstan. The KLAVI-R pulse electron accelerator (\(E_e = 160\,\text{keV},\, j = 150\,\text{A/cm}^2\)) was used for electron irradiation. The pulse cathode luminescence (PCL) spectra were measured for LiF and NaF crystals at different dose of irradiation. The examples of PCL spectra are presented at Fig.1.

At the spectra (Fig. 1) some bands with position correlated with position of known absorption band of nanoparticle Li colloidal centers was observed. So at the PLC spectra the quasi-resonant luminescence of nanoparticle Li colloidal centers was found. For NaF crystals analogue effect is not found.

For explanation of these phenomena the model of development of nanoparticle colloidal centers in LiF and NaF crystals was proposed. This model builds on the base of assumption about ion excitations appeared during irradiation of crystals. Due to these ion excitations moving of ion became possible. It leads to collection ions in local point and creation nanoparticle colloidal centers. However not always ion excitation can provide forming colloidal centers. It is connected with relative dimensional radius ion in crystals. So in LiF crystal the radius of Li ion is smaller than radius of F ion. Opposite in NaF crystal the radius of Na ion is larger than radius of F ion. In frame of proposed model some scheme of nanoparticle colloidal centers forming process in LiF crystals was suggested.
Titanium dioxide, TiO$_2$, is a very important technological material. It is currently being investigated for advanced functional and environmental applications, such as photocatalysis, photovoltaic cells and solid state gas sensing. In the nanocrystalline state, TiO$_2$, like other oxides, can dissolve higher concentrations of impurities than their bulk counterparts as they have an increased density of grain boundaries where considerable amounts of dopants can segregate. This dopant segregation has been found in some cases to improve the catalytic activity and electrical properties. In previous computational work we have studied the influence of the dopants (i.e. Pt, Pd, Ag, and Au) on the optical and structural properties of single crystalline anatase TiO$_2$ using the local spin density approximation (LSDA) within the density functional theory. The results show that doping TiO$_2$ with these precious metals enhances absorption in the visible range (i.e. above 400 nm) with Ag showing the most enhanced absorption. This work also shows that substitutional doping enhances absorption better than the interstitial one. This offers the possibility of considerable improvement in photovoltaic cells.

Experimental information is essential for the verification and ultimate improvement of the simulations and EXAFS experiments are unique in providing this kind of information. For example, the EXAFS can determine the oxidation state of the dopant, the detailed local environment of the dopant (nature of the neighbours, bond distances to neighbours, degree of disorder, etc.) and segregation of the dopant.

In this contribution we report EXAFS studies of precious metal doped nanocrystalline TiO$_2$. 

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Temperature dependent Raman study of NaNO₂ confined within porous glass with a pore size 45 nm has been performed. It is demonstrated that the linewidths and frequencies of the Raman bands as a function of temperature show similar behaviour, but not identical, as those observed for bulk NaNO₂. In particular, the most significant temperature dependence near the para- to ferroelectric phase transition has been noticed for two librational modes observed at 158 and 121 cm⁻¹. This result indicates that the first order phase transition mechanism is only slightly modified by embedding NaNO₂ into the glass with a pore size 45 nm. It seems that formation of “premelted state”, observed just above T_c for NaNO₂ embedded in a porous glass with a pore size 7 nm [1], is not significant in the studied material, at least up to 40-50 K above T_c. At higher temperatures, however, a significant increase of linewidth of the 1326 cm⁻¹ band is observed, which could indicate appearance of “premelted state”. The dielectric measurements are consistent with this view since they show large increase of dielectric permittivity above 490 K, well below the NaNO₂ melting temperature (554 K).

References

Surface enhanced Raman scattering (SERS) is a sensitive spectroscopic technique for identifying ionic and molecular species adsorbed on or near some nano-size metal particles [1].

Colloidal Ag nanoparticles were prepared in aqueous solution following the procedure of Lee and Meisel [2]. The Ag sol prepared in this work was yellow and had absorption maximum at 420 nm. Later, NaCl solutions in different concentrations were prepared and mixed with silver sol. The effect of the addition of NaCl is observed in the Raman spectra of Figure 1A. This Figure shows several Raman bands that in any cases were enhanced in the Raman signal, Fig.1B. In this work, we reported the existence of Raman bands in these mixtures. Moreover, we have found the ideal mix for to evaluate other samples.

On the other hand, we have used this colloidal mixture for to evaluate the SERS spectra of pyridine solutions, which had shown excellent results.

References
There is considerable interest in nanocrystalline materials due to their unusual properties. In the case of ionic solids enhanced ionic conductivity has been reported for nanocrystals. This has potential commercial applications, particularly for oxide ion conductors. However, a detailed knowledge of the microstructure is important in fully understanding the novel properties exhibited by nanocrystalline materials. The final microstructure of a material is dependent on the preparation method used, for example, sol-gel and ball-milling methods are commonly used in the preparation of nanocrystalline oxides. Additionally, there is a problem in maintaining the materials in nanocrystalline form when they are subjected to elevated temperatures. We have been exploring strategies to restrict the growth of nanocrystalline oxides and have found that adding a small amount of an inert material, e.g. silica or alumina, is particularly effective.

We will report XRD and EXAFS studies of nanocrystalline ceria prepared by sol-gel, sol-gel pinned and ball-milling methods and the effect of preparation method on the final microstructure.
LUMINESCENCE OF OXYGEN RELATED DEFECTS IN ZIRCONIA NANOCRYSTALS

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The zirconia (ZrO₂) is known material for sensors, catalysts etc. and the properties of material is strongly controlled by defects in oxygen sublattice. Zirconia nanocrystals for the present experiments were produced by hydrothermal method described in [1].

The different excitation sources were used for zirconia nanocrystals luminescence study: (I) a pulsed electron beam; (II) a pulsed laser beam (4.66 eV); (III) conventional UV light from deuterium lamp. The time-resolved spectra of luminescence, decay kinetics and excitation spectra of luminescence were measured. The luminescence spectra at room temperature shows two overlapping bands peaking at ~2.2 eV and ~2.8 eV. Luminescence decay kinetics for these bands were different, the spectra changes after excitation pulse end. An additional luminescence band peaking at ~4.2 eV was observed at 80K. Excitation of bands at ~2.2 eV and ~2.8 eV within band-gap region is possible, whereas of ~4.2 eV band not. The bands at ~2.2 eV and ~2.8 eV had different excitation spectra and these bands were observed in all zirconia nanocrystals studied. Therefore the intrinsic defects were suggested to be responsible for bands at ~2.2 eV and ~2.8 eV. The luminescence band at ~4.2 eV was due to self-trapped excitons [2]. The tetragonal phase zirconia nanocrystals were used in experiments and it is known the structure of tetragonal phase zirconia is controlled by presence of oxygen vacancies [3]. Thus, the luminescence spectra and decay kinetics were studied for a set of zirconia nanocrystals annealed in oxygen - nitrogen gas mixture with different oxygen content (oxygen content from 2.11% to 23.4% ). The relative intensities of luminescence bands changes in zirconia nanocrystals annealed in different oxygen – nitrogen gas mixtures. The luminescence parameters changes during the zirconia nanocrystals heating up in vacuum also and during the cooling down (in vacuum) the initial parameters did not recover. The results from zirconia nanocrystals annealing experiments and from heating – cooling in vacuum experiments suggested the defects responsible for luminescence are oxygen related. The possible models of defects will be discussed.

References

METALLIC LEAD COLLOIDS OBTAINED IN KCl MATRIX

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In the previous paper [1], were proved for the first time that by electrolytic coloring in KCl:Pb²⁺ crystals with the concentration more than 10¹⁸ ions/cm³, nanoclusters of Pb were formed. If the temperatures of coloration take a place at 550⁰C, the nanoclusters have a spatial arrangement, like a corals. If in the crystals were added Ca²⁺ ions, the samples are coloured at 250-280⁰C, the nanoclusters have form an isolated spherical particles.

In the present paper more detailed studies are proposed, taking into account that in the case of KCl:Ag [2] and KCl:Au [3] electrolytic coloured crystals, at any temperature we obtained only nanocluters with spatial arrangement and, in the cases of KCl:In [4] and KCl:Ga [5], the coloration also at any temperature leads to the formation of separate spherical nanoparticles.

By optical absorption spectra, the band of colloidal Pb nanoclusters appears besides of spatial of isolated nanostructures as in the case of Mie theory conditions. By TEM patterns is strongly demonstrated that in all cases, if the temperature of coloration is above the melting point of impurity (325⁰C for Pb), the nanoclusters are isolated and spherical (figure 1) and if the temperature of coloration is below the melting point, the nanoclusters are in the spatial arrangement. (figure 2)

Figure 1: KCl:Pb coloured at 550⁰C
Figure 2: KCl:Pb+Ca coloured at 250⁰C.

The explanation of these results by the hypothesis that below the melting point of the metal, the kinetics of aggregation take a place in the solid phase and, in the opposite case the superficial tension energy produce isolated and spherically particles.

References

AGGREGATION OF EU-V_{C} DIPOLES INSIDE DISLOCATIONS IN POTASSIUM CHLORIDE CRYSTALS STUDIED BY AFTERGLOW

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In previous studies we have associated the UV induced afterglow (AG) of europium doped potassium chloride at 20K with the emission of Eu related defects (dipoles and aggregates) in dislocations [1]. The AG model that we have used is not based on tunnelling as in other works [2] but on the random migration of H centres through dislocations and the subsequent recombination with F centres near Eu defects. In this work we provide further evidence for this assumption by showing that AG intensity of crystals with a low dislocation density is lower than that of crystals with a high dislocation density (Figure 1). Using the assumption that AG comes exclusively from Eu in dislocations, we have followed the aggregation process of Eu-V_{C} dipoles at 375K in dislocations in samples quenched from 773K to room temperature. It was found that at the beginning of the aggregation process the concentration of dipoles in dislocations grows until it reaches equilibrium after 6h while the aggregation starts slowly and after 6h continues at a constant rate (Figure 2). We discuss a simple kinetic model for the aggregation process in dislocations with which good fittings to our data were obtained.

![Figure 1: AG emission (a) a strained sample with many dislocation lines and (b) an unstrained sample with few dislocation lines.](image1)

![Figure 2: Concentration of (a) dipoles and (b) aggregates in dislocations, during ageing at 375K. The insert shows the emission bands in the AG associated with (a) dipoles and (b) aggregates.](image2)

References


Li-ion conducting organic-inorganic hybrid electrolytes derived from TEOS and methacrylates

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Solid-state electrolytes with high ionic conductivity ambient temperatures have recently potential to be used in rechargeable lithium batteries and the other advanced electrochemical applications. In this study, Li – ion conducting organic-inorganic hybrid electrolytes have been synthesized from tetraethyl orthosilicate TEOS, poly (ethylene oxide), ethyl methacrylate, ethylene glycol dimethacrylate the other minor organic additives and solvents and were doped with lithium perchlorate (LiClO₄, weight fraction – 0.01). Mass fractions of the organic additions in the gels were from 20 to 30 mass %.

The hybrids were obtained as amorphous, transparent or translucent and colourless materials, with the ionic conductivities of $10^{-4} - 10^{-3}$ S cm⁻¹ order of magnitude at room temperatures and they have been revealed to be stable during thermal treatment for 3 hours at temperature of 80 °C. They were investigated for morphology and structural properties by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy SEM/EDS, Fourier - transform infrared spectroscopy (FTIR), nuclear magnetic resonance ²⁹Si MAS NMR. All hybrid materials were successfully applied as solid electrolytes in the WO₃ - based thin film electrochromic cells of the smart window arrangement and electrochemical performance of these systems had been examined for their current - voltage and optical transmission characteristics.

Possible influence of the organic additives and lithium doping on the structural properties had been evaluated from the FTIR and NMR spectra and there have been found variety of structural properties, strongly depended on kinds and combination of organic additions. Li ions introduces a distortion into the hybrid matrix structures. The best poly-condensation ability of the [SiO₄] tetrahedrons for creation inorganic network have been observed for hybrids containing relatively high concentration of TEOS and lower concentration of higher molecular weight organic parts in the precursors sols. The higher polymerisation rate have been observed in sols containing relatively high concentrations of organic polymers can be due to cross-linking process associated the heterogeneous polymerisation.

References

Defects and material preparation technology
POLYCRYSTALLINE FLUORAPATITE DOPED WITH Eu$^{3+}$, OBTAINED FROM AQUEOUS SOLUTION

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Compounds of the apatite type $\text{Me}_{10}(\text{ZO}_4)_6\text{X}_2$ (Me=Ca, Sr, Ba; Z=P, V; X=F, Cl, OH…), doped with rare earth elements (REE) have been widely studied since they can be used for various applications as luminescence materials and phosphors for light converting coatings, ionic exchangers [1,2], as possible laser materials [3], etc. Processes of apatite formation of dispersion system from aqueous solution of mixed composition, namely calcium fluorapatite (FAP), doped with REE are studied. In the present work we studied influence of physical and chemical growth conditions during $\text{Me}_1^{10-x}\text{Me}_2^x(\text{PO}_4)_6\text{F}_2:\text{Eu}^{3+}$ ($\text{Me}_1^I=$Ca; $\text{Me}_2^{II}=$Pb, Mg) formation on its composition, structure and morphology.

Monophase polycrystalline undoped and doped with Eu$^{3+}$ FAP ($\text{C}_{\text{Eu}}^{3+}=1\%$) were formed at $\text{pH}=4.7$ and $\text{T}=80$ °C. Increase of $\text{pH}$ value from 4.7 to 6.5 and decrease temperature of solution to 20 °C leads to appearance of additional phase CaF$_2$. Presence of Pb$^{2+}$ in samples ($\text{C}_{\text{Pb}}^{2+}=1\%-20\%$) leads to multicomponent system. SEM micrographs of samples shows that particles of FAP:Eu$^{3+}$ form conglomerates, which consists of complex spherical particles. The typical dimension of spherical particles was from 5 to 20 µm. It was found that Pb$^{2+}$ promotes growth of FAP in needle-like form. Size of these particles is above 1 µm. XRD results show that a particle consists of nanocrystalline blocks (FAP coherent scattering fields for obtained samples were determinate to be of $L=21-43$ nm). Increase of Pb$^{2+}$ concentrations leads to linear increase of FAP crystal lattice parameters. It was found that as-grown undoped and doped FAP samples do not emit. Luminescence of Eu$^{3+}$ was detected only in annealed samples. Spectroscopic properties of $\text{Me}_1^{10-x}\text{Me}_2^x(\text{PO}_4)_6\text{X}_2:\text{Eu}^{3+}$, ($x=0.1, 0.3, 0.5, 1, 2$) are discussed.

References

Positron annihilation lifetime (PAL) spectroscopy is one of the most suitable and powerful tools for experimental study of extended open-volume defects in solids at different levels of their structural hierarchy. However, in respect to powder and fine-grained ceramic materials this method has been rarely applied because of high complications in correct interpretation of the obtained PAL data.

The main aim of this work is to develop a meaningful interpretation of PAL characteristics for functional ceramics at the example of mixed transition-metal manganites within quaternary MnCo$_2$O$_4$-NiMn$_2$O$_4$-CuMn$_2$O$_4$ system and humidity-sensitive MgAl$_2$O$_4$ spinel-type ceramics.

The experimental PAL measurements (the LT computer program of J. Kansy) are performed with an ORTEC spectrometer, using a source placed between two identical sandwiched samples. The methodological possibilities of PAL spectroscopy technique in application to the investigated disordered materials is checked at the example of different fitting procedures with arbitrary and fixed PAL parameters.

Taking into account that a total number of simultaneously distinguished PAL components does not exceed typically 4-5, the following cases of mathematical fitting procedures are considered in order to develop correctly the alternative phenomenological model for multi-channel positron annihilation in the investigated ceramics: two-component fitting procedure with arbitrary PAL parameters, three- and four-component fitting procedures with arbitrary and with fixed (0.125 ns) PAL parameters.

It was established that in all cases under consideration, the three-component fitting procedure is the best one, it being analysed in term of mixed discrete positron trapping and ortho-positronium decay modes. The middle positron trapping component with lifetime at the level of 0.3-0.5 ns is attributed to extended free-volume defects revealed themselves as neutral or negatively-charged clusters of charge-compensating vacancies located near the grain-boundaries within ceramics bulk.
Some new information about forming of condensed substance on the surface of fibre crystals during their growth by Micro Pulling Down method is presented. The LiF, NaF and BGO (Bi$_4$Ge$_3$O$_{12}$) $\mu$-PD fibre crystals was investigated. These crystals were grown by Micro Pulling Down method in platinum crucible at the ambient air. It was made at Physics-Chemistry Laboratory of Luminescence Materials (director – Ch. Pedrini) at Lyon 1 University (Lion, France) by K. Lebbou, B. Hautefeuille, D. Perrodin, B.V. Shulgin, T.S. Koroleva and A.N. Tcherepanov.

The investigation of surface of LiF, NaF and BGO $\mu$-PD fibre crystals was made by optical and raster electron microscopy methods. It was made at Ural State Technical University (Ekaterinburg, Russia) by R.M. Kadushnikov and at Institute of High temperature electrochemistry of Ural Division of RAS (Ekaterinburg, Russia) by V.B. Malkov. Examples of imaging of LiF and BGO fibre crystals are shown at Fig.1.

It was found that different types of surface are observed. In particular the smooth or dendrites surface was shown depending on chemical compounds and parameters of grown processes. Model for explanation this phenomenon is proposed. This model take into account possible gas–solid transitions appeared during Micro Pulling Down growth process at the ambient air. Additionally our model allowed to into account the possibility of nanoparticles crystals developing in ambient air. In the frame of this model it is possible to find the distributions of pressure of gases ($p(x)$) and temperature of fibres ($T(x)$) along length of fibres. The formulas of model were verified on experimental data for investigated fibres.
RAMAN AND IR SPECTROSCOPIC CHARACTERIZATION OF
LiNbO₃ CRYSTALS GROWN FROM ALKALI METAL OXIDE
SOLVENTS

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Several methods exist for the preparation of stoichiometric LiNbO₃ single crystals. The one which yields the composition closest to 50% Li₂O is the high temperature top seeded solution growth (HTTSSG) method from the K₂O-Li₂O-Nb₂O₅ ternary mixture [1]. Other alkali ion oxides (Na₂O, Rb₂O, and Cs₂O) can also be used as solvents for the growth of LiNbO₃ single crystals. While K₂O, Rb₂O and Cs₂O behave as ideal solvents, since they do not enter the crystal, Na₂O builds into the lattice as concluded from analytical measurements [2]. For the determination of the composition (Li₂O content) of the crystals – grown from the starting solution with Li/Nb = 1 and 10 mol% alkali metal oxide – our previous UV absorption edge calibration has been used [3]. In the present work we have systematically applied two further non-destructive methods as the IR absorption spectroscopy of OH ions and the Raman spectroscopy of the lattice vibrations.

In the nearly stoichiometric LiNbO₃ crystals (Li₂O ≈ 49.6 – 50 mol%), such as those grown from K₂O, Rb₂O and Cs₂O solvents two OH⁻ stretching vibrational band components appear at about 3465 and 3480 cm⁻¹ [1]. Their intensity ratio R = I₃₄₈₀/I₃₄₆₅ measured some days after crystal growth decreases almost linearly with increasing Li₂O content reaching R = 0 at c(Li₂O) = 50 mol %. It has been shown earlier that there is a redistribution of hydroxyl ions among the different defect sites even at room temperature changing the intensity ratio as a function of time [4]. In fact, half a year later the slope of R vs. c(Li₂O) becomes about twice as much than that observed immediately after crystal growth. For the crystal grown from Na₂O solvent a characteristic broad OH⁻ band appears at about 3473 cm⁻¹ attributed to some kind of Na-OH defect due to the incorporation of Na ions into the crystal. The change of the band shape as a function of time has also been observed in this crystal.

The frequency and the full width at half maximum of the A₁(TO₁), A₁(TO₂) and E(TO₁) Raman modes are also changing with the composition of the LiNbO₃ crystals [5]. The Li₂O content has been determined for the nearly stoichiometric crystals grown from K₂O, Rb₂O and Cs₂O solvents using the calibrations described in [5, 6]. A relatively good agreement has been found with the results obtained from the UV absorption edge measurements. In the case of Na₂O solvent, however, the Raman spectra were different from the others; some of the peaks were shifted and broadened. The increase of the intensity of the A₁(TO₂) mode indicates that the Na ions are built in on Li sites.

References
Double fluoride crystals with perovskite structure ABF$_3$ (A = Ba, Cs, B = Ca, Li) are very interesting because they are convenient model systems for studying the magneto-optical properties of impurity dopant ions. In principle, in these matrices it is possible to substitute two various cations being inequivalent positions. This enables one to carry out investigations of impurity dopant ions in sixfold or uncommon twelvefold coordinations. CsCaF$_3$ and BaLiF$_3$ crystals were mainly studied when doped with iron group ions. The physical properties of rare-earth ions in these compounds are not sufficiently studied. The introduction of three-charge rare-earth ions is hampered because of heterovalent substitution and the essential difference in the ionic radii of rare-earth ions and lattice cations. Previously we presented results on the study of Nd$^{3+}$, Ce$^{3+}$, Sm$^{3+}$ and Yb$^{3+}$ in KMgF$_3$ and KZnF$_3$ and Yb$^{3+}$ in CsCaF$_3$ crystals [1-5]. This report is concerned with the further investigation of impurity paramagnetic centers (IPC) formed by Nd$^{3+}$, Ce$^{3+}$, and Yb$^{3+}$ ions in CsCaF$_3$ and Nd$^{3+}$, Ce$^{3+}$, and Yb$^{3+}$ in BaLiF$_3$ single crystals.

The crystals were grown using the Bridgman-Stockbarger method. The concentration of the impurity ions was 0.1-1.0 w %. A wide variety of IPC is the characteristic feature of the studied crystals. In dopant crystals new types of IPC are discovered. For CsCaF$_3$ : Yb several types of IPC with tetragonal symmetry were investigated. In BaLiF$_3$ : Nd under certain conditions of synthesis an unusual IPC was discovered. The optical spectra confirm the presence of a wide variety of IPC types in synthesized crystals.

The parameters of the corresponding spin Hamiltonians, the ground states and their wave functions were determined. Structural models of the observed complexes were proposed. The analysis of the obtained results as compared to those obtained for the same paramagnetic ions in other hosts was carried out.

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References

Recent investigations have shown that certain types of telephone cards containing microchips have the potential to be used for retrospective dosimetry (Göksu 2003, Marthur 2006). It has been observed that a certain type of telephone chip-card can be used as radiation detectors for individuals exposed to external gamma doses. The radiation dose responses of more than 200 chip-cards, produced by various companies since 1990, were investigated using infrared stimulated luminescence (IRSL). The radiation dose responses of some of the chip-cards were found to be linear with radiation dose over 250 mGy to 5 Gy and stable at ambient temperature, which allows the use of such chip-cards for reconstruction of doses for individuals. In order to determine the source of radiation induced signal, we have investigated the chip cards produced by INFINEON at various stage of production. The initial investigations show that radiation induced signal mainly come from the layer that is used for protection chip cards from the environmental effects. In order to improve the radiation dose response and detection limits of the cards, various type of artificial phosphors are added to protecting layer of the chip cards The variation of the dose response and the detection limit with respect to the amount and the type of the phosphor is investigated using various luminescence techniques. Feasibility of production of such cards in industrial scale will be discussed.
Femtosecond laser processing is considered a promising technique for manufacturing two or three-dimensional photonic elements such as gratings, waveguides, microholes and microchannels in different type of transparent materials [1]. Multiphoton absorption, avalanche ionisation and optical breakdown are the mechanisms leading to ablation or local refractive index variations in glass. In transparent ferroelectric crystals, beside the previously mentioned phenomena, also the role of photorefractivity in the formation of surface defects should be considered deserving further investigation.

We report on the effects of femtosecond laser irradiation on Lithium Niobate (LN) substrates. LN is a key material for device application in force of the outstanding acoustooptic, electrooptic and nonlinear optical properties [2]. Two different sources of femtosecond pulses at the wavelength of 810 nm are used: either a low energy high repetition rate Ti:Sapphire oscillator (20 nJ, 82 MHz, 130fs), or a high energy low repetition rate amplified Ti:Sapphire laser system (1 mJ, 1 kHz, 130 fs). The laser beam is focused on the crystal by microscope objective lenses with a magnification of 20x up to 60x. At the focus region either refractive index changes or material removal were observed by varying the irradiation conditions. The induced defects are investigated by optical polarizing microscopy, and microRaman spectroscopy [3]. We also explored the possibility to better characterize through electron paramagnetic resonance the electronic centres, which can play a role in the charge accumulation processes induced by fs laser pulses. In the illuminated regions the mapping of Raman spectrum shows the insurgence of Raman modes, forbidden in the used scattering geometry. This phenomenon increases gradually by approaching the ablation region where niobium oxides and Li-deficient surfaces are formed for the low energy and high repetition rate pulses from the Ti:Sapphire oscillator, while amorphous surfaces are obtained for the high energy and low repetition rate pulses from the amplified Ti:Sapphire laser system.

Our results suggest that surface ablation was mediated through photorefractive-like charge accumulation in the high repetition rate irradiation regime, whereas the photorefractive response appears not to be relevant in the low repetition rate regime.

References

The effect of vacancies on the electronic transport in the ZnCr$_{2-x}$Ni$_x$Se$_4$ antiferromagnetic single crystals is considered. For this purpose the electrical conductivity and the thermoelectric power measurements and the calculations of the vacancy model [1] parameters were used. The electrical measurements have been done in <001> direction and in the temperature range from 290 to 520 K for single crystals with x=0.001, 0.05 and 0.065. The above investigations showed that: 1) at room temperature the electrical conductivity decreases with increasing Ni concentration, 2) for single crystal with x=0.001 a temperature induced change in the sign of the temperature coefficient of resistivity ($\alpha_{TCR}$) at 426 K is observed, 3) the thermoelectric power increases for all single crystals with increasing temperature, 4) for single crystals with x=0.05 and x=0.065 the n-p phase transitions at 336 and 311 K are observed, respectively, 5) all single crystals show the hole electrical conductivity above 336 K, and 6) with increasing Ni content $x$, the ion packing coefficients both in the tetra- ($P_t$) and octahedral ($P_o$) sites and the volume fulfilment coefficient $\alpha$ were nearly constant, whereas the vacancy parameter $\beta$ of about 11 % have slowly decreased.

Smaller values of $P_t$ in comparison with $P_o$ suggest larger ion distances and thus smaller overlap of the cation $s$ orbitals and of the anion $p$ orbitals in the octahedral sites. It means that the ionic bond is stronger in the octahedral sites than in the tetrahedral ones suggesting an excess of cation vacancies in the tetrahedral sites. On the other hand, the observed n-p phase transitions for samples with higher nickel content $x$ suggest that the anion vacancies can exist in this case, too, because the vacancy parameter $\beta$ remains almost constant and the substituted nickel ion instead chromium one has smaller ion radius [2].

It was also observed that the thermoelectric power can be explained concerning only the diffusion component (which varies linearly with temperature) for the single crystal with x=0.001. For the remaining samples the temperature dependence of thermoelectric power is more complex, as a competition between a hole and electron conductivities at lower temperatures is observed. These effects are explained in terms of a polaron mechanism of the electrical conductivity including structural and spin defects. It is well known, that band semiconductor transport characteristically has carriers with high mobility and low concentration while small polarons have high concentration and low mobility [3]. In our case a polaron mechanism of the electrical conductivity is observed, because the carriers which come from excitations do contribute to the thermopower and they are activated to polaronic states at the Fermi level giving a linear dependence between the thermopower ($S$) and the electrical resistivity ($ln\rho$) [4]. One can conclude that the substituting Ni ions play a reducing role in the case of the chromium vacancies (spin defects) causing an occurrence a certain number of anion vacancies, an increase of a sample resistivity and finally a polaron conductivity.

References
PMo30

SPECTROSCOPIC METHODS FOR THE DETERMINATION OF THE COMPOSITION OF POTASSIUM LITHIUM NIOBATE CRYSTALS

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Potassium lithium niobate (K₃Li₂Nb₅O₁₅, KLN) with tungsten bronze-type structure is a useful material for applications in nonlinear optics, electro-optic and piezoelectric devices [1]. However, the applications of KLN crystals are limited by cracks and compositional variations due to incongruent melting [2]. The variations in the chemical composition of the crystal modify significantly its physical properties like lattice constants, Curie temperature (Tc), refractive indices etc. [3]. Our aim was to find a method for the determination of the real composition of KLN crystals.

In the present work we investigated the composition dependence of some spectroscopic properties of the KLN crystals grown from melts with 46.5 mol% Nb₂O₅ and 29-34 mol% K₂O content. Beside the optical spectra in the UV-VIS and IR regions recorded by a JASCO V550 and a BRUKER IFS 66/v type Fourier-transform spectrometer, respectively, the ferroelectric Curie temperature of the crystals was determined from the temperature dependence of the dielectric constant.

The UV absorption edge of the crystals changes in the range of 383-372 nm (at α = 20 cm⁻¹), but it does not depend on the K/Li ratio of the melt, only on the crystallized fraction. The shift of the UV edge to lower wavelength from the top to the bottom of the crystals shows a decreasing amount of antisite Nb (niobium occupying Li sites). Similarly, the shift of the UV edge as a function of composition in LiNbO₃ crystals has also been attributed to the decreasing amount of Nb on the Li sites [4].

The presence of hydroxyl ions has been observed in as-grown KLN crystals. A complex absorption band of the OH⁻ vibrations with two components at about 3440 cm⁻¹ and 3520 cm⁻¹ was observed for IR light polarized along the ferroelectric c-axis, accordingly to ref. [5]. We noticed that the ratio of the absorption bands depends not only on the Nb content of the crystals, but on the K/Li ratio, too.

The ferroelectric phase transition temperatures of ceramic samples were measured and compared to those of crystals grown from melts with different K/Li/Nb ratios. The Curie temperature of the crystals and ceramics depends considerably on the Nb content, and slightly on the K/Li ratio. However, the real crystal composition (the ratios of the three cations) cannot be obtained from the Tc measurement itself. For lack of high precision chemical analytical measurements the three methods mentioned above can be combined to determine the composition of KLN crystals.

References

Based on A₄B₆ and A₂B₆ solid solutions single crystals widely used in IR- technique as constituent of heterostructures, solid-state lasers, γ – sensors etc. High degree of the single crystals perfection is one of main desires for guaranteeing of such structures and devices sufficient parameters.

The A₄B₆ and A₂B₆ solid solutions single-crystals growth was performed by modified Lo [1] and Tamari [2] methods. The crystal microstructure was studied by optical and electron microscopy, X-ray diffraction. Besides, the selective chemical etching was carried out to determine the structure defects content and nature on the (111) and (110) surfaces prepared from crystals wafers. The inclusions nature was determined on elemental analysis data obtained using an electron beam microscope (JEOL).

Research of factors, which influence on appearance, development and morphology of single crystals volume defects, in particular, inclusions, microvoids, L-voids, second phase precipitations was performed in this paper. The correlations between the parameters of growing processes and structural properties of single crystals were studied. The interconnection between microvoids density and boundary grains are determined.

It was obtained, that the reason of formation of microcavities in most cases is aerosil which appeared in a quartz container at its sealing under vacuum. The aerosil particles coagulation as separate microobject arises from the vapour stream concretion on the growing crystal surface or by convective streams in a melt. A model of the microvoids forming during the single crystals growth was developed on the researches basis.

The factors which promoted the aerosil amount considerable increase in the grown crystals were also studied. It was concluded that chalcogen particles adhesion on the ampoule surface stimulates the intensive aerosil evolution during the next ampoule sealing operation. In addition, intensity of aerosil evolution depends on the chalcogen chemical activity. Sulphur and Selenium multiply the aerosol presence in a crystal more then an order in comparison with Tellurium.

One of the principal reasons of the second and fourth group chalcogenides microvoids formation during growth of the single crystals isthe aerosil particles ingress on the growing surface (crystallization front) of the crystals.

Thermoplastic deformations which arise up as a result of temperature vibrations more then 0.5 K, that are typical for the process of the proportional – integral - differential temperature regulation, promote the L-voids formation in the single crystals.

The volume defects free crystals with dislocations density less than 10⁴ cm⁻² are obtained. The recommendations for the structurally perfect A₄B₆ and A₂B₆ crystals growth conditions optimization are proposed.

References.

INTERNAL STRESSES AND THEIR RELAXATION AT HIGH-TEMPERATURE DEFORMATION OF ALKALI-HALIDE SINGLE CRYSTALS

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The results of experimental researches of occurrence and a relaxation of average internal back stresses are submitted during creep of single crystals KCl with initial density of dislocations $\rho_0 \sim 10^9 \text{ m}^{-2}$. Samples as rectangular parallelepipeds $4 \times 6 \times 10 \text{ mm}^3$ are deformed by uniaxial compression in an interval of temperatures $0.83T_{melt} \leq T \leq 0.92T_{melt}$ ($T_{melt}$ – melting temperature) at a level of external stresses $\sigma > \sigma^*$, where $\sigma^*$ – the stresses necessary for multiplication of dislocations. Single crystals KCl of two orientations: $<100>$ and $<111>$ are investigated. In the first case orientation factor $\alpha$ in four systems of easy sliding in these crystals $\{110\} <110>$ is equal 0.5, and in the second case in all systems of easy sliding $\alpha = 0$. Nonlinear dependence of creep rate on value of external stresses for crystals of both orientations is established and effective activation energy of creep process is determined. Observable anisotropy of creep rate is put in interrelation with change of the mentioned above system of easy sliding to system of sliding $\{100\} <110>$.

Measurement of average internal stresses $\sigma_{int}$ is carried out by a technique similar [1]. Dependence $\sigma_{int}$ on a level of external stresses, temperatures and orientations of a crystal in relation to external stresses is determined. It is found out, that the higher level of $\sigma_{ext}$, the higher $\sigma_{int}$ at all investigated temperatures. $\sigma_{int}$ decreases with growth of temperature. Dependence of a level $\sigma_{int}$, time (total deformation of a crystal) and number crystal loads are analyzed at $\sigma = \text{const}$. To determine the value $\sigma_{int}$ during all annealing time it is cyclically applied strain transient dip tests technique. Results of experiment show the change of value of average internal back stresses with deformation.

Creep kinetics and change laws of average internal stresses are compared to dislocation structures change of single crystals (density of single dislocations and the size of subgrains) during high-temperature deformation.

References

The single crystals with garnet structure, in particular, substituted Gd$_3$Ga$_5$O$_{12}$ (GGG) ones are used as scintillation and laser materials. The main advantage of the single crystal garnet films properly grown is more perfect crystalline structure and, as consequence, lower concentration defects, impurities and other irregularities of garnets structure. The main difference between the epitaxial films and single crystals consists in the incorporation of impurity ions from the flux melt into the film. The concentration of these impurity ions is the highest in the transient surface layer with the thickness less than 100 µm.

In the present paper the influence of growth conditions of epitaxial GGG single crystal films on the optical absorption and luminescence spectra is investigated. It is believed that the differences of these spectra are connected with the defects, impurities and other irregularities of garnets structure.

The films were grown on GGG substrates by liquid phase epitaxy technique from the supercooled flux melts based on PbO – B$_2$O$_3$ or Bi$_2$O$_3$ – B$_2$O$_3$. The luminescence was exited by UV and $\gamma$ radiation.

It is occurred that the optical absorption spectra of the films which are consequently grown at the same conditions from the same flux melt are strongly different between each other. This, in particular, is displayed in the different film colour. The different concentration of defects, impurities and other irregularities in the GGG films grown at different growth conditions leads to the change of the additional optical absorption in visible and infrared spectral region more than on three orders of value.

In the luminescence spectra of the GGG films as well as GGG substrates the bands at the wavelength $\lambda = 382, 415 \text{ and } 438$ nm are the most intensive. The corresponding $I_{382}$, $I_{415}$ and $I_{438}$ values of the luminescence intensities are changed on two orders of value depending on the film growth conditions.

We are proposed to use the intensities of optical absorption and luminescence exited by UV and $\gamma$ radiation as the quantitative characteristics of the irregularities of optical materials.
The crystals of yttrium fluoride are solid state laser material. The melting point is at about 1160°C. But the growing problem of this material is existence of phase transition at about 1080°C known as the α-β transition from rhombohedral to orthorhombic symmetry. However, it possible to decrease of melting point temperature below the phase transition by LiF doping. The temperature amounted at about 800°C at the 20% LiF doping. The growth of YF₃ single crystals accomplished by the Czochralski method with platinum crucible in a helium atmosphere. The used technology of growth allows producing more expensive LuF₃ crystals. The crystals of LuF₃ are perspective material for PET tomography excelling high density.

The solid solution CaF₂-(YF₃)₄ is new and promising optical material. The CaF₂-(YF₃)₄ crystals have been grown by the Stokbarger method in vacuum in the graphite crucible with system of traps. The raw materials were CaF₂ and YF₃ in the ratio of ¼ mol %, respectively. The crystallize temperature of this system at about 1150°C. The speed of crystallization varied in region 3-6 mm/hour, the temperature gradient was 20-30 degrees/cm. The solid-phase synthesis has been executed at 900°C during 4 hour. The samples of dimensions of 60x20 have been produced. The control of solid solution structure cared out by X-ray methods.
Stimulated Raman scattering (SRS) is a very interesting nonlinear optical phenomena. Recently it was shown, that PbMoO$_4$:Nd crystals are very attractive for design of Raman laser due to high Raman scattering cross section [1]. SRS needs very high laser pump power density to achieve threshold conditions that requires high optical quality of Raman crystals.

In the present work author report Nd and Yb doped lead molybdate single crystals growth and their properties. PbMoO$_4$:Nd and PbMoO$_4$:Yb single crystals were obtained by the Czochralski method in the automated set up “Analog” from Pt crucibles. The starting charge of molybdenum and lead oxides was prepared by the ceramic method. Single crystals with different activator concentrations were grown along the crystallographic directions [001] and [100] at temperature gradients 50 deg./cm, the pulling rate 2.5 mm/h and the rotation 20-30 min$^{-1}$.

Taking into account the method of activation, the crystal structure peculiarities were established. Optical properties and damage threshold of doped crystals were measured. The morphology of PbMoO$_4$: (Nd, Yb) crystals damage under the laser beam is studied. The dependences of damage threshold upon activator concentration were investigated and discussed.

References

PMo36

INFLUENCE OF ELECTRICAL ACTIVE DEFECTS ON DIELECTRIC PROPERTIES OF COMPLEX OXIDE CRYSTALS

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Complex oxide crystals Ca$_3$Ga$_2$Ge$_4$O$_{14}$ (acentric Ca-gallogermanate-structure) (CGG), Ca$_3$Ga$_2$Ge$_3$O$_{12}$ (garnet-structure) (CGGG), PbWO$_4$ (sheelite-structure) (PWO), and CdWO$_4$ (wolframite-structure) (CWO) has important technical characteristics and widely used in modern physics and devices. However the physical properties of above crystals in particular, electrical and dielectric properties, also as relaxation processes caused by forming of polarization and electrical active defects are investigated insufficiently. Our preliminary results of electrical and dielectric investigations of PWO crystals are published in [1–3] and CGG in [4].

In this paper CGG, CGGG, PWO, and CWO single crystals grown by the Czochralsky method are studied. Here the results of the investigations are presented in the temperature range 200–550 K. Dielectric constant and conductivity in frequency range 10–10$^6$ Hz are studied. The results interpreted in frame of small-polarons theory and of electrons (holes) hopping in process of charge transfer what realized with variable length of hopping.

Dielectric constant of PWO crystal increases with increasing temperature and peaked about 320 K. In this case the value of dielectric constant at room temperature is up 25 to 30. After polarization influence of direct external electric field about 350 K the value of dielectric constant is up 150 to 300 in maximum of experimental dielectric constant temperature dependence. In CGG and CGGG crystals this effect increasing of dielectric constant after polarization is absent. The influence of crystals growth conditions, disordering of crystals lattice and forming of dipolar defects (dipolons) [2] to dielectric and electrical properties of crystals with theirs structural features are considered.

References

PHASE COMPOSITION AND CRYSTALLINITY OF THIN FERROELECTRIC LEAD TITANATE FILMS

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It is well known that phase composition and crystallinity essentially determine an existence of domains and ferroelectric properties of thin ferroelectric films. Thin ferroelectric films on basis of lead titanate are intensively studied due to their application in microelectronic. Therefore the aim of the present work was the investigation of microstructure and ferroelectric properties of thin lead titanate films depending on the obtaining conditions, such as lead and titanium Pb/Ti ratio in the initial components and the annealing regime of as-deposited structures.

Lead titanate films on substrates of polycor (Al₂O₃) were synthesized by plasma-enhanced magnetron sputtering of pure metals – titanium Ti and lead Pb – layer by layer in an argon environment. The obtained structures were annealed in an oxygen atmosphere. The film thickness was about 1 micron. The choice a polycor as a substrate was caused by its chemical inertness [1]. An optimal annealing regime was chosen accordingly to the most appropriate phase composition (there was perovskite phase predominant and weren’t unreacted metals and metal oxides) and temperature stability of ferroelectric properties. Continuous annealing of synthesized structures under increase of temperature from the room temperature up to 700°C for one hour proved to be optimal one [1]. Phase composition was controlled by the X-ray diffraction analysis. Atomic force microscopy was used for microstructure measurements.

The Pb/Ti ratio was varied from 1.0 to 1.3 in order to compensate for lead evaporation [2]. It was found experimentally that polycrystalline films with a stoichiometric phase composition and the highest ferroelectric properties were obtained when the ratio of lead and titanium in the original components was equal Pb/Ti=1.25. The most narrow peak of dielectric permittivity about the phase transition point and the transition temperature the closest to that of bulk PbTiO₃ samples were observed. Values of doubled spontaneous polarization 2Pₛ and doubled coercive field 2E_c were estimated as 32 microC/cm² and 240 kV/cm, respectively.

Investigations of morphology of a film surface revealed that films, which were synthesized with lead excess, had more homogeneous polycrystalline structure and larger sizes of crystallites. For films corresponding to Pb/Ti=1.25 in the initial components, the crystallite size was equal 400-600 nm.

References


Germanium glasses containing Bi$_2$O$_3$ are intensely investigated due to their applications in optical devices as active medium for Raman fibre and optical amplifiers [1]. Amorphous bismuth germanates have also attracted for their scintillations properties [2]. The bismuth oxide is known as unconventional glass network former, differently from conventional formers such as SiO$_2$, B$_2$O$_3$, P$_2$O$_5$, GeO$_2$. However, its high polarisability and low field strengths result in the possibility to act in certain systems as glass network former. Crystalline structures, such as Bi$_{12}$GeO$_{20}$ sillenite and Bi$_4$Ge$_3$O$_{12}$ eulytite, are interesting for applications in optical memories, holography or optical phase conjugation devices.

Bi$_2$O$_3$-rich glasses belonging to the system $x$Gd$_2$O$_3$·(1-x)[0.875Bi$_2$O$_3$0.125GeO$_2$] with 0.005 < x < 0.1 were obtained by quickly undercooling of the melts from 1250°C to room temperature. This heavy metal glass system was studied in order to elucidate its structural characteristics and the competition of Gd$_2$O$_3$ and Bi$_2$O$_3$ in the formation of the glass network. The glasses were crystallized by heat treatment. Vitreous and polycrystalline samples of the same composition were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), electron paramagnetic resonance (EPR) and infrared spectroscopic (IR) measurements.

The heat treatment temperature was estimated from DTA analysis, in agreement with the crystallization temperature recorded around 575°C. Bi$_{12}$GeO$_{20}$ and Bi$_{24}$GeO$_{38}$ crystalline phases were identified by XRD after the heat treatment applied to the glass samples. The EPR results give information on the local order around the resonant Gd$^{3+}$ ions and on their magnetic interactions [3]. For glass samples is recorded a typical spectrum for Gd$^{3+}$ ions in disordered systems, that consists of lines at g ~ 5.9; 2.85; and 2.0 and with resonance line at g ~ 4.8 with unusual intensity for vitreous sample. The EPR structural data are supported by the results obtained from IR spectral investigations. The shape and parameters of Gd$^{3+}$ EPR spectra are changed by crystallization. For heat treated samples the lines become narrower and the distribution of Gd$^{3+}$ ions on sites of certain crystal fields is changed. In the IR spectra of the heat treated samples are also evidenced changes, including the appearance of new absorption bands. The main structural units identified in the studied samples are [GeO$_4$], [BiO$_4$] and [BiO$_6$] groups.

References:
Zinc oxide is a versatile functional material that exhibits piezoelectric, semiconducting and scintillation properties. Recently, ZnO crystal has attracted much attention due to its potential applications in ultra violet (UV) and blue light-emitting devices \cite{1,2}. However, ZnO crystal is difficult to grow from its congruent melt due to its strong polar surfaces and volatilization at higher temperatures \cite{3}. In the present work, ZnO crystals were grown by a novel growth technique.

The crystal growth was carried out in a modified vertical Bridgman furnace. A gas-cooling system was assembled at the bottom of platinum crucible to induce single nucleation. ZnO crystal up to 1 inch in diameter has been obtained. However, as-grown ZnO crystal was easy to crack because of large thermal stress. Some inclusions were found at the edge of the crystal near the crucible. As-grown crystal shows pale-brown colour, which was attributed to the absence of oxygen during the growth. Annealing experiments were carried out in air.

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Electronic excitations, excited state dynamics, radiative and non-radiative relaxations
MAGNETIC FIELD DEPENDENCE ON TRIPLET STATE IN IRIDIUM COMPLEX PHOSPHOR

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The organometallic phosphors, such as tris (2-phenylpyridine) iridium; Ir(ppy)$_3$, have attracted remarkable attention as emitters of high efficient electro-phosphorescent devices [1]. Strong spin-orbit coupling due to heavy ion effect leads to the efficient phosphorescence even at room temperature. Up to now, details of basic photo-physics of the phosphorescence are still remained as opened question.

We have investigated the decay dynamics of photo-luminescence and its temperature dependence in the Ir(ppy)$_3$ centre dispersed in CBP or PMMA matrix [2]. The decay curves were decomposed into three exponential components ($\tau_1$: 30 $\mu$s, $\tau_2$: 10 $\mu$s, $\tau_3$: 2 $\mu$s at 5 K.) and a trace of faster component, corresponding to luminescence from the sub-levels of the triplet state and a singlet state. From detail analysis of the temperature dependence of these components, it has been revealed that population transfer is thermally activated from each sub-level of triplet state to a higher lying singlet state [2].

In this work, we present the magnetic field dependence of phosphorescent spectrum and of its decay profiles in Ir(ppy)$_3$ in PMMA matrix. Upon applying magnetic field from 0 to 6 T, remarkable change of luminescent spectrum and decrease of the intensity were observed as shown in Fig.1. The spectral decrease was in coincident with shortening of lifetimes of the sub-levels. It might be caused by a modification of the spin-orbit interaction by applying magnetic field. We will discuss the structure of the lowest excited states and the dynamics of luminescence.

Figure 1: Luminescent spectra in Ir(ppy)$_3$ in PMMA at 5K excited by 3.81eV light under magnetic field strength at 0, 1, 2, 3, 4, 5, 6 T and a difference spectrum between luminescent spectra at 0 T and 6 T. Inset shows the integrated intensity of the spectra versus magnetic field strength.

Excitation, emission and time resolved experiments were performed in LiNbO$_3$:Tb,Eu single crystals at RT and 12K. An effective energy transfer between the Tb$\rightarrow$Eu ions has been identified and the results are presented and discussed in this paper. Lithium niobate (LN) crystals are well known as technologically important material and have been widely used in laser and opto-electronic technologies. Many of these applications are strongly dependent on the incorporation of optically active ions. Recently, solid-state materials containing Eu [1,2] or Tb [3] ions have attracted much attention because of their potential applications in laser and optical data storage. For the purpose of this paper, high optical quality single crystals of LN:Tb,Eu were grown in congruent composition in the Research Institute for Solid State Physics and Optics in Budapest, Hungary. Then, a systematic study on the optical properties of our double doped single crystals was performed. In the luminescent spectra, all the samples present the characteristic transitions $^5D_4 \rightarrow ^7F_J$ of Tb ions and $^5D_0 \rightarrow ^7F_J$ of Eu ions. Figure 1 shows the 12K emission spectrum of our LN:Tb,Eu sample under excitation at 485nm corresponding to the Tb $^7F_6 \rightarrow ^5D_4$ absorption transition. At this excitation wavelength no emission from the Eu ions is expected to occur. However, from the data portrayed in this figure is clear that, though an active energy transfer mechanism, the emissions from the $^5D_0$ levels of the europium ions are also present in the emission spectrum. Tb $\rightarrow$ Eu energy transfer can be explained from our data due to the fact that the $^5D_4 \rightarrow ^7F_4$ Tb emission overlaps the $^7F_0 \rightarrow ^5D_0$ Eu absorption.

References
NATIVE AND RADIATION-INDUCED TWO-FOLD COORDINATED SITES IN NANOSTRUCTURED SnO$_2$:SiO$_2$

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Oxygen vacancies are surely the key defect-configurations responsible for defect-related processes in SiO$_2$, many of them with a demonstrated technological relevance. Oxygen vacancy defects play an important role in several optical applications of silica, such as in photorefractive writing of optical waveguides and in vacuum ultraviolet (VUV) photolithography [1-3]. Nevertheless, the attribution of the optical features arising from point-defects are still debated [4,5].

We have analyzed a particular system, constituted by a silica matrix with tin-dioxide nanoclusters thermally grown from an oversaturated Sn-doped silica xerogel. The resulting glassy network around the crystalline SnO$_2$ clusters contains several oxygen vacancies in a configuration never observed up to now. Fig.1 shows a photoluminescence spectrum of this material, with features similar to the optical activity previously observed in neutron irradiated pure silica but with excitation features typical of Ge-doped SiO$_2$, although the present material is not irradiated nor doped with Ge atoms. These results point out the crucial role of the environment of native defects, more relevant in some case than impurity effects, as previously proposed [6].

![Photoluminescence spectrum](image)

Figure 1: Photoluminescence excitation spectrum of 300 nm emission (inset) of oxygen defects in nanostructured SiO$_2$:SnO$_2$

References

Tm$^{3+}$ is an attractive laser ion for operation in the visible and NIR regions [1, 2]. Its absorption band at about 800 nm ($^3H_4 \leftrightarrow ^3H_6$ transition) allows pumping by means of commercial laser diodes, making it suitable for the development of compact solid state laser devices. In this paper we present the results of our investigations on Tm$^{3+}$-doped YAl$_3$(BO$_3$)$_4$ (Tm:YAB). This crystal is a very promising host for laser ions in order to develop self-frequency doubling and self-frequency-sum solid state lasers [3, 4]. It presents a high nonlinear coefficient, allows for high doping level, and shows high optical quality, good mechanical strength, good thermal conductivity, and absence of photorefractive damage [5]. In particular, it is interesting to verify the possibility of combining the emission properties of the Tm$^{3+}$ ion with the nonlinear optical properties of YAB in order to generate new laser channels. This requires a detailed knowledge of the energy level scheme and of the excited state dynamics of the material. We have measured polarised absorption spectra of Tm:YAB in the 400-2000 nm range and the emission spectra and the fluorescence decay curves of crystals with different doping levels in the 400-1600 nm range. All measurements have been carried out at 10 and 298 K. The room temperature absorption spectra have been analysed using the Judd-Ofelt approach and the $\Omega_2$, $\Omega_4$ and $\Omega_6$ intensity parameters have been evaluated and used to calculate the spontaneous emission probabilities, the branching ratios and the radiative lifetimes of the most important emitting levels. Finally, these values have been compared with the experimental decay times in order to estimate the efficiency of the non-radiative processes in this material.

References

The intrinsic electronic excitations play an important role in the energy transfer processes. The intrinsic luminescence of Sc$_2$SiO$_5$ crystals was reported in [1] as the two broad emission bands with the Stokes shifts more than 2 eV ($E_g \approx 7$ eV). The purpose of the present work was to compare the features of intrinsic luminescence bands of the Sc$_2$SiO$_5$ crystals at the selective VUV- and inner-shell excitation. For obtaining information about the spectral properties of the system under investigation we recorded time-resolved emission (2-6 eV) and excitation spectra as well as luminescence decays of Sc$_2$SiO$_5$ crystals at T=8.5 K and 300 K using the possibilities of the SUPERLUMI station (4-40 eV) and the BW3 channel (50-600 eV) of HASYLAB at DESY in Hamburg.

The intrinsic emission band of the Sc$_2$SiO$_5$ crystals at T=8.5 K consists of two components peaking at 3.6 eV and 4.3 eV (Figure 1). Both components of intrinsic emission were not excited in the transparency region of crystal, but their excitation spectra differ significantly in the VUV- and soft X-ray region (see Figure 2).

It was found that the 3.6 eV luminescence in Sc$_2$SiO$_5$ crystal shows slowly decaying phosphorescence, which is very similar to that of the 3.6 eV emission in Sc$_2$O$_3$ crystal [2]. The tunnel recombination of the spatially correlated self-trapped d-electrons with the p-holes is responsible for the appearance of 3.6 eV emission in Sc$_2$O$_3$ [2]. The UV emission peaked at 4.3 eV has no direct analog of the luminescence in Sc$_2$O$_3$ and we suggest tentatively that the appearance of the Si s-orbitals in the conduction band of the Sc$_2$SiO$_5$ crystals leads to the formation of the metastable self-trapped exciton in contrast to the Sc$_2$O$_3$ crystals.

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References

DECAY COURSE OF SLOW EMISSION COMPONENT FOR THALLIUM AND LEAD CENTERS IN SOME ALKALI HALIDE CRYSTALS

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TI or Pb doped alkali halide crystals belong now to the textbook examples illustrating the manifestation of dynamical Jahn Teller (JT) effect in optical spectra. Despite the large number of papers devoted to these systems there are still many open questions provoked by performed experiments. In our contribution we focus on rather general question – what is the course of decay in the case of excited state subjected to dynamical Jahn-Teller effect. The common feature of octahedral thallium and lead impurity centres is the presence of radiative and metastable levels in the lowest excited triplet state with characteristic lifetime of ns and ms, respectively (determined by induced dipole matrix element between the excited and ground states).

We have observed that for some crystals (e.g. KBr:Pb, KI:Pb and KI:Tl) the slow component of emission excited in the A absorption band clearly deviates from expected exponential shape. A deviation of the slow (ms) emission component needs to have some temporal emission with microsecond characteristic time. So far proposed explanations are slightly contradictory. One is based on tunnelling between different kinds of minima in the excited-state potential energy surface [1, 2]. This picture concerns all processes inside a model octahedral quasimolecular ion composed by an impurity ion and six neighbouring anions. Our explanation is based on conserving a part of energy dissipated during relaxation of an excited state in the form of new vibrational mode called soliton or breather [3, 4]. This mode is spatially leeched onto the impurity centre and affects the coupling between the radiative and metastable levels. In our model the process covers the lattice response to the excitation of impurity centre and a necessity to create new equilibrated interionic distances. The decay function of slow emission component is then not sum of exponentials.

To go further in this discussion and to find a new support for one of the above mentioned approach we revised the measurement of emission kinetics of NaCl, KCl and KBr doped with thallium or lead with the particular attention to the precision of slow component mapping. We also monitor the influence of symmetry lowering of the nearest neighbour anion coordination in KCl:Br:Tl and KCl:Br:Pb systems on the observed decay curves. As it is possible with high accuracy to approximate any curve by sum of several exponentials we checked the suitability of fitted function to the experimental data by sophisticated statistical methods. On the other hand we discuss the reasonability of consideration some additional energy levels participating in the decay process being either from the same JT minimum or from another one.

References

THE THERMOSTIMULATED EXOELECTRON EMISSION OF AlN:Y₂O₃ CERAMICS AFTER ELECTRON BEAM IRRADIATION


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The high sensitivity to radiation of AlN:Y₂O₃ ceramics which have been proposed for application as TLD sensor [1] and scintillator [2] encouraged the new additional study of exoemission properties of this specimens. The thermostimulated exoelectron emission (TSEE) of AlN:Y₂O₃ ceramics after electron beam irradiation (fluence 10¹²–10¹⁴ cm⁻²) have been investigated at the temperature region 20–400°C. The ceramic specimens of AlN:Y₂O₃ (2 vol.%) have been developed in nitrogen atmosphere in a graphite crucible at 1800–1850°C during 1 hour. Grown AlN:Y₂O₃ ceramic samples had gray colour and were cut up on disks with diameter 15 mm and thickness 1–2 mm. The peaks of TSEE have been found at temperatures 78, 108, 141, 174 and 282°C. The main peak of TSEE is situated at 70–110°C.

On the base of AlN:Y₂O₃ ceramics the new working substance for TSEE dosimetry have been proposed [3]. Some problems and new possibilities of TSEE dosimetry are discussed. The AlN:Y₂O₃ compound is perspective for electron and gamma-rays dosimetry and as antifire (peak TSEE at 78°C) sensor.

References

LIGHT-INDUCED POLARONS IN LITHIUM-NIOBATE ON THE FEMTOSECOND TIME SCALE

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Light pulses of 240 fs duration and a wavelength of 388 nm generate in LiNbO\textsubscript{3} single crystals transient absorption that we attribute to small bound polarons because of the temporal, spectral and polarization fingerprints. Light-induced absorption changes are observed with delayed femtosecond pulses of 776 nm wavelength and with continuous-wave light at 785 nm over 10 decades from 400 fs up to 10 s after the pump pulse illumination. The decay is well described by one stretched-exponential function over the entire range. With an intensity of 250 GW/cm\textsuperscript{2} a polaron concentration of about $5 \times 10^{18}$ cm\textsuperscript{-3} is achieved.

Using pulses of 4 ns the wavelength dependence of the light-induced absorption confirms the generation of the small bound Nb\textsubscript{Li}\textsuperscript{4+} electron polarons, formed on niobium at a lithium position in the disordered congruent LiNbO\textsubscript{3} crystal. They show an absorption maximum at 740 nm [1,2]. These well known paramagnetic polarons are intensively studied by ESR [3]. The temperature dependence of the decay time reveals two activation energies of 0.14 eV for low temperatures and 0.38 eV for high temperatures, separated at $T = 280$ K, indicating two different kinds of hopping processes.

![Fig. 1: Decay of light-induced absorptions $\alpha_0$ in LiNbO$_3$ after excitation with a 200-femtosecond laser pulse](image)

References

Excitons, impurities, and defects I
Structural inhomogeneity of amorphous silicon dioxide (a-SiO2) influences the spectral properties of point defects of the material [1]. One of these defects, usually named B-type centre, is associated to the presence of Ge impurities and is relevant for the photosensitivity of a-SiO2. This defect is characterized by an optical absorption band peaked at ~5.2 eV and two related photoluminescence (PL) bands peaked at ~3.2 eV and ~4.3 eV [2]. Many works have been devoted to investigate the effects of inhomogeneity on the emission properties of the B-type centre mainly by stationary PL measurements.

We report here a study of the PL time decay of B-type centres in sol-gel Ge-doped a-SiO2 under excitation by synchrotron radiation. Measurements were carried out by excitation in uv and in vacuum-uv (v-uv), and were performed both at 300 K and at 8 K in order to isolate the effects of the intersystem-crossing process, proposed to link the two emission bands of the centre. Repeating the time decay measurement at several emission energies falling inside the 4.3 eV band, we observed a variation of the decay lifetime with spectral position (Fig. 1). The estimated lifetime decreases by more than 25% on increasing excitation energy both at high and at low T. The results are interpreted as a fingerprint of the inhomogeneity in the centres environment. Our findings suggest a direct tool to probe the inhomogeneity effects of the material.

![Figure 1: PL time decay at T=8 K under excitation at 5.0 eV studied at various emission energies around 4.3 eV.](image)

References


The thermoluminescence (TL) properties of a uranium-rich natural fluorite from Vendee uranium district of France have been investigated. The natural TL of the phosphor showed a prominent peak around 325°C with two shoulders around 300°C and 375°C. However, for the annealed sample artificially irradiated to gamma doses, three TL glow peaks are observed around 125°C, 220°C and 325°C, with a shoulder still appearing at 375°C. These differences between the glow curves from naturally and artificially irradiated samples are discussed. Fading of TL signals of the three major peaks over 3 months was carried out. The highest loss of signal as expected was recorded for the peak around 125°C. For the other two peaks no appreciable loss of signal was recorded. For possible use of this phosphor in dating, the peak around 325°C should be preferred because it is present both in the naturally and artificially irradiated samples. The glow peak temperatures were observed not to shift with change in dose. Linearity of dose-response of the three peaks was also investigated.

References

PMo50

LIGHT-INDUCED LUMINESCENCE PROCESSES IN AlN: MACROSI
ZED AND NANOMATERIALS

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AlN is one of wide band gap (E_g ~ 6.2 eV) materials, which properties such as high
hardness, thermal conductivity and some optical properties are promising for applications. Optical
properties of each material highly depend on its structure and defects present in it. Therefore
spectral investigations based on luminescence can give rich information about the defects and
light-induced processes characteristic for the material. Besides there are sintered different types of
nanomaterials during the last decade, which properties can differ from those of macro-sized ones.

The aim of this report is analysis and comparison of spectral properties of different types of
AlN in order to reveal the luminescence processes, their mechanism and defect structure
responsible for luminescence. Photoluminescence (PL) spectra together with its excitation (PLE)
spectra are studied. The original results obtained by authors on AlN ceramics, macro-sized powder,
nanopowder and nanotips are analysed together with those of AlN single crystals [1] and other
literature data.

It is observed that at room temperature (RT) the complex PL spectrum of AlN consists of
several broad and overlapping main bands with maxima at ~390 nm (3.18 eV), ~ 470 nm (2.64
eV) and ~600 nm (2.07 eV) characterized with their own PLE. The same PL bands are observed in
different types of AlN when the material size is reduced from macro-size (AlN ceramics and
macropowder) to nanomaterial (AlN nanopowder and nanotips) and no new band appears, but in
the same time the ratio of intensity of various PL bands is different. The main PL bands can be
excited not only in their own PLE bands but also through the host material excitation caused by
band-to-band transitions or exciton creation. In AlN single crystals [1] and nanotips the
luminescence of excitons is also observed.

The results observed allow reveal some defect types responsible for the PL bands mentioned
above. The 390 nm PL is caused by oxygen-related defects in a bulk material shown by
Youngman and Harris [2]. Subsequent investigations allowed to reveal the structure of acting
defects and to propose the recombination luminescence mechanism [3]. The 470 nm luminescence
is proposed to be related to surface defects. A nature of 600 nm luminescence is discussed.

References

The SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ is one of the persistent luminescent materials, which preserves its luminescence visible in the dark more than 10 hours after irradiation. The luminescence process in SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ is quite different from "standard" intra-ion luminescence due to transition of electrons from Eu$^{2+}$ excited state to traps (photo-charging effect) [1]. In this work we report the behaviour of luminescence stimulated with visible and UV light at room temperature as well as at elevated temperatures up to 650 K.

The typical photo-charging and AG curves are shown in Figure 1. After switch-on of irradiation luminescence increases sharply up to initial intensity (intra-ion photoluminescence), goes up to saturation and decays after termination of irradiation. Increasing of irradiation temperature leads to exponential decreasing of luminescence intensity and AG decay time. The kinetic equations based on the mechanism of persistence luminescence proposed by Dorenbos [2] were used for description of obtained photo-charging and AG curves. The mechanism supposes excitation of the 5d state of Eu$^{2+}$ with subsequent thermal activation of excite electron to the conduction band and formation of Eu$^{3+}$. Next, free electrons can be trapped in Dy$^{3+}$ forming Dy$^{2+}$ or return to Eu$^{3+}$ forming Eu$^{2+}$ in excited state. The luminescence arise from deexcitation of the 5d state of Eu$^{2+}$, the occupancy of which is determined by direct excitation of the Eu$^{2+}$ and the trapping rate of free electrons by Eu$^{3+}$.

References

OPTICAL SPECTROSCOPY OF LEAD TUNGSTATE CRYSTALS DOPED WITH EUROPIUM IONS

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Improvement of scintillation characteristics of the lead tungstate crystals PbWO₄ (PWO), in particular, decreasing of decay time of scintillation response is known to be achieved by special implantation of the crystals with impurity ions of rare earth (RE) elements. These impurities also significantly improve such characteristics the PWO as transmission in the near UV region and radiation hardness [1]. Various impurities of RE ions lead to the same changes in spectral properties of own matrix emission of the PWO crystals [2]. In this paper we carried out detail investigation of spectral-luminescent properties of the PWO crystals doped with the Eu³⁺ ions as well-known luminescence probe.

The spectra were investigated in a wide temperature range at different excitation and registration wave length. They consist of both weak wide nonstructural bands of the matrix emission and narrow spectral lines caused by inner f-f electron transitions in the impurity Eu³⁺ ions. The complex character of the observed changes in the emission and excitation spectra of the Eu³⁺ ions as a function of the temperature and excitation wavelength and the carried out analysis and interpretation of observed spectral lines due to the electron transitions actual in excitation and luminescence of the Eu³⁺ ions allow us to made assumption about formation of two different types of luminescent centres on the basis of the Eu³⁺ ions in the PbWO₄ crystals. Redistribution of the relative intensities of the spectral lines as a function of the excitation wavelength is caused by various contributions of the two types of centres in the total spectra under various excitation wavelengths.

Origin and structure of these centres are studied. The first type of the RE centres is formed, when RE ions occupy Pb positions in the crystal lattice. In the case of lead deficiency the impurity RE ions can fill cation vacancies and, therefore, decrease a number of cation vacancy related emission centres. Another type of the RE centres in the PWO crystals was proposed, where RE ions occupy W positions. The described structures of the both types of centres, where the Eu³⁺ ions are incorporated in the Pb and W positions, should some differences in spectral properties of their emission, because Pb and W atoms have different oxygen surrounding in the PWO crystal lattice having the octagonal and tetragonal coordination, respectively. Analysis of spectral positions of Stark components allows to estimate crystal field force and symmetry for the both types of centres and to prove the made assumption about structure of two types of the Eu³⁺ centres in the PWO lattice.

References

LUMINESCENCE OF NANOPOROUS C12A7 COMPOUND

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12CaO·7Al2O3 (C12A7) compound has received considerable attention due to several unique properties and good prospects in optoelectronic applications [1]. The unit cell of the C12A7 includes two molecules and twelve cages having a free space of ~0.4 nm in diameter. Such free space provides a great flexibility for doping of the C12A7 with unusual impurity ions (e.g. Au [2]). Another important feature of this cage is a mean effective charge of +1/3 (+4 charge/12 cages), which makes one in six cages hosting extra-framework O2- ions. The diffusive exchange of these ions with framework ones plays the decisive role in the stability of C12A7 lattice under ion beam irradiation [3].

Polycrystalline samples were sintered by self-propagating combustion method [4] followed by crystallization at 1000 °C in oxygen gas flow. Preliminary characterization of reaction products was made by the XRD method.

Excitation spectra of luminescence were measured at SUPERLUMI station of HASYLAB and BL52 of MAX-lab at 10 K in the VUV spectral range, which covers the intrinsic absorption range of C12A7. These data enabled us to define the framework energy gap of C12A7 as $E_g=6.5$ eV (see Fig. 1), which is in a good agreement with calculations [5]. Cathodoluminescence, long lasting afterglow and spectrally resolved thermostimulated luminescence after irradiation by means of 15 keV, 50 nA electron beam were measured, which gave information regarding shallow trap levels caused by impurity/defect centres in C12A7. Based on data obtained the electronic excitations of C12A7 and their relaxation will be discussed.

This work was supported by the European Community Research Infrastructure Action under the FP6 "Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”) and Estonian Science Foundation (grant no. 6538). The authors would like also to thank Dr. V. Nagirnyi for his kind support.

![Figure 1: Luminescence data for C12A7.](image_url)

References

YAl₃(BO₃)₄ (YAB) is prospective representative of self-frequency doubling laser hosts due to its far UV transparency (down to 200 nm), good incorporation of the rare earth ions, and large nonlinear optical coefficients. Although the difficulties of crystal growth limit its availability, the spectroscopic properties of several rare-earth dopants have been investigated in YAB [see reviews 1,2], including the absorption spectra of Er³⁺ [e.g. 3,4]. Er³⁺ related luminescence spectra were only presented in double doped YAB where the excitation is efficient [5,6].

Single crystals of Er-doped YAB were grown by the top-seeded flux method (for these experiments with 1, 12 and 50% Er in respect to Y). Excitation at the specific Er-absorption lines in the 365-521 nm range (⁴G₉/₂, ⁴G₁₁/₂, ²H₉/₂, ⁴F₃/₂, ⁴F₅/₂, ⁴F₇/₂ and ²H₁₁/₂ levels) resulted in dominantly the ⁴S₃/₂ - ⁴I₁₅/₂ emission. At given excitations traces of the ⁴F₇/₂ - ⁴I₁₅/₂, ²H₁₁/₂ - ⁴I₁₅/₂, and ⁴I₉/₂ - ⁴I₁₅/₂ emission were also detectable. The 488 nm laser excitation made it possible to analyse the fine structure of the ⁴S₃/₂ - ⁴I₁₅/₂ emission. The ground state Stark components are in good matching with those derived from the high resolution absorption spectra [3]. The decay time of the luminescence and its temperature dependence were followed by pulsed OPO laser excitation to the ²H₁₁/₂ level. The decay kinetics suggests phonon-assisted non-radiative energy loss starting around 100K. The low temperature decay time was dependent on the Er-concentration, reflecting Er-Er interactions at higher Er contents.

References

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YAG:Eu nanopowder, a perspective material for red phosphors, was synthesized by a nitrate-citrate sol-gel method [1]. The morphologic modifications produced by the thermal treatments at various temperatures (900÷1400°C) were monitored by a series of parameters obtained from the optical fluorescence spectroscopy: intensity ratio $R_2$ of the transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$, the maximum splitting $\Delta E$ of the $^7F_1$ level, and the linewidth of some fluorescence transitions. An abrupt decrease of these parameters at the amorphous-crystalline transition temperature, followed by a slow decrease, is observed. As an example, in Fig. 1 we show the dependence of the ratio $R_2$ on the annealing temperature.

![Figure 1: Dependence of $R_2$ on the annealing temperature.](image)

The maximum splitting $\Delta E$ of the $^7F_1$ level (a measure of the crystal field intensity [2]), and the linewidth of the fluorescent transitions show a similar behaviour. We could link this behaviour with the decrease of the surface / volume ratio produced by the thermal treatment (by the increase of crystallites’ size). The lower size nanocrystals have more sites with lower symmetry located near surface (yielding higher $R_2$ and $\Delta E$) and are therefore more disordered (wider spectral lines). Nevertheless, an inspection of the fluorescence spectrum of the YAG:Eu powders immediately after the amorphous-crystalline phase transition shows that the local symmetry is close to $D_2$: the fluorescence spectrum is typical for the YAG phase and the transition $^5D_0 \rightarrow ^7F_0$ is absent.

References

TEMPERATURE DEPENDENCE OF THE POLARON PHOTOLUMINESCENCE LIFETIME IN LiNbO$_3$

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Lithium niobate (LiNbO$_3$, LN) is of great interest for optical applications owing to its large electro-optic and non-linear optical coefficients. Several physical properties involved in device operation are sensitive to the concentration of point defects and to the chemical reduction degree of the material – i.e. the concentration of electrons trapped in the forbidden band gap. For instance, in nominally-pure LN, both the Li/Nb ratio and the position of the Fermi level are thought to have major influence on the electrical conductivity and on the light-induced absorption (LIA), two properties of great importance in electro-optical devices such as integrated Mach-Zehnder interferometers. LIA related to intrinsic defects in Fe-doped LN also plays a major role in two-color photorefractive effects used for holographic storage [1].

The defect structure of LiNbO$_3$ is attributed in particularly to the presence of Nb in the lithium site (so called niobium antisite). This is the origin of photoluminescence; it is likely that niobium antisite defects Nb$_{Li}^{5+}$ are able to trap an electron on an energy level below the conduction band, giving a single polaron Nb$_{Li}^{4+}$.

Polaron photoluminescence PL is thus a two-photon process: a first photon is required, either to dissociate a bipolaron or to transfer an electron from a deep centre (for doped LN) to the polaron antisite level Nb$_{Li}^{4+/5+}$, then a second photon excites the polaron, which gives the PL band at slightly large wavelength (700-1200 nm).

In this work, we present a study of the IR photoluminescence band in lithium niobate below room temperature. The results are consistent with a simple model involving the two energy states of the polaron defect coupled to the conduction states of the crystal.

Temperature and excitation intensity dependence of the small polaron have been measured:

It is found that the integrated area of the main peaks remains nearly constant at low temperature then decreases sharply with an activation energy of about 0.12 eV above 200 K. The limit between the two regimes is thought to correspond to the crossing point between the radiative and non-radiative lifetimes of the polaron excited state. Temperature dependence of PL decay lifetime has also been investigated.

References

Zoisite, of chemical formula $\text{Ca}_2(\text{Al}_{1.5}\text{OH})\text{Al}_2(\text{SiO}_4)_3$ is found in Minas Gerais State, Brazil as natural mineral of silicate, member of the epidote group. $\text{SiO}_2$ (53.8 % mol), $\text{Al}_2\text{O}_3$ (17.3 % mol), $\text{MgO}$ (2.25 % mol), $\text{Na}_2\text{O}$ (5.94 % mol), $\text{CaO}$ (11.9 % mol), $\text{Fe}_2\text{O}_3$ (7.68 % mol) are basic components of the crystal. Other elements are present in smaller concentration. Its glow curve is composed of one broad TL peak from 50 to 250 °C. The peak position seems to be around 130-150 °C. The TL intensity grows superlinearly as function of the radiation of the radiation dose up 200 Gy. On the other hand, samples heavily irradiates from 2 kGy up the 100 kGy reveal a TL peak around 350 °C, which is very small compared to 140 °C peak. In the region of 1 kGy to 100 kGy, the TL intensity become constant. It is very interesting to note that, the peak position shifts from 148 to 130 °C as function of dose.

The EPR spectrum shores a strong $\text{Fe}^{3+}$ line around 1100 – 1300 Gauss and the typical $\text{Mn}^{2+}$ six lines in the region of 3300 – 3600 Gauss. No radiation effects were observed concerning EPR intensity.
The electro-optical properties of OD⁻ defects in some alkali-halide crystals are atypical: in contrast to free molecules, their vibrational spectrum demonstrates a disparate distribution of intensities between harmonics, such that the ratio of intensity of the second harmonic (first vibrational overtone band) to that of the fundamental vibrational transition is 2.3 for NaBr, 7.5 for KF and 16 for NaI [1]. Such a distribution for an OD⁻ diatomic defect in these crystalline environments is inexplicable in terms of only mechanical anharmonicity, likely arising instead through anomalous electro-optical anharmonicity.

Using experimental data for intensities of OD⁻ in NaBr, KF and NaI vibrational transitions, we generated the radial functions for electric dipolar moment. According to our calculations, for all crystal systems the magnitude of the first derivative $d'$ of this moment is less than that of the second derivative $d''$. For instance, for OD⁻ in NaI the ratio $d'' / d'$ is approximately ten. Thus the first derivative of the permanent dipolar moment and that induced by the moment of the crystalline field are expected to have opposite signs. On replacing OH⁻ by its isotopic counterpart OD⁻, this observed effect becomes stronger, because the intensity of the first harmonic decreases. Measurements performed at decreased temperatures, with improved resolution and with increased concentrations of molecular defects require further investigation, but our phenomenological model of diatomic defects describes the anomalous distribution of intensities in infrared absorption spectra of OD⁻ in alkali-halide crystals.

References

TUNNELLING RECOMBINATION PROCESSES IN PbWO₄

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Lead tungstate crystals are intensively studied as fast and heavy scintillators for the high-energy physics experiments. In many works (see, e.g., [1] and references therein), besides the fast (ns) process, much slower processes were observed in the photoluminescence decay kinetics at RT, which influence also scintillation characteristics of PbWO₄ crystals. The contribution of the slow processes is especially high in the green spectral region. The aim of the present work was to clarify the origin of the defects and processes responsible for the slow decay of the green emission in PbWO₄ crystals.

For that, time-resolved emission spectra and decay kinetics were studied at 160-300 K at 308 nm (4.02 eV) XeCl pulsed excimer laser excitation for the PbWO₄ crystal grown by the Bridgman method and annealed at 600 °C in air. In this crystal, containing the isolated oxygen vacancies of the type of WO₃, the green 2.5 eV emission appears at T>150 K and reaches maximum at 220 K, in accordance with [2]. The narrow excitation band of this emission, located at 4.07 eV, coincides with the creation spectrum of the electron centres produced at the photo-thermally stimulated decay of localized exciton states. The activation energy for the localized exciton decay (0.18 eV) coincides with that obtained from the rise of the 2.5 eV emission intensity at T>150 K. Decay curve of the 2.5 eV emission can be approximated by the formula \( I(t) \sim t^{-\alpha} \). In the log I (log t) coordinates the decay curve is a straight line with a slope \( \alpha \sim 1 \) which is independent of temperature. Dependence of the emission intensity on the irradiation dose is linear at small doses and then becomes sublinear. No superlinear dose dependence is observed, and the slope \( \alpha \) does not depend on the irradiation dose. The features observed are characteristic for tunneling recombination processes occurring between isolated (genetic) pairs of electron and hole centres (see, e.g., [3]).

We conclude that under excitation in the exciton absorption region at T>150 K, the genetic pairs of electron centres (e.g., of the type of \{Pb⁺-WO₃\}) and WO₃-related hole centres are produced as a result of the photo-thermally stimulated decay of localized excitons. The 2.5 eV emission appears at the tunneling recombination of these centres. The same emission appears at the recombination of electrons, thermally released from the electron centres, with the hole centres. The dose dependence of the emission intensity indicates that the photo-thermally stimulated decay of localized excitons is not accompanied with the release of electrons into the conduction band. Just the 2.5 eV emission is responsible for a slow luminescence decay at room temperatures. This emission can be removed by doping with trivalent ions (e.g., Ce³⁺ [1]) which results in a drastic reduction of the WO₃-type oxygen vacancies content in the PbWO₄ crystal lattice.

References

In view of high transparency, these glasses are considered very good materials for hosting lasing rare-earth ions since they provide low phonon energy environment to minimize non-radiative losses. Photoluminescence study in ZnO-B₂O₃-ZnF₂ glass system has been carried out. ZnO is thermally stable, sublime and appreciably covalent in character. Er³⁺ ion has a number of strong absorption bands, as a consequence, the emission spectrum exhibits fluorescent peaks in blue, green and red in visible region. The present paper throws light on trends observed in the photoluminescence and IR spectra keeping in view the effect of mixed borate glasses.
NON EMPIRICAL CALCULATIONS OF CROSS-LUMINESCENCE SPECTRUM OF BAF$_2$

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It is known that in the crystals BaF$_2$ doped with La-impurity interstitial ions of fluorine are formed as compensators of excess charge of trivalent La$^{3+}$. These interstitial ions form level inside the band gap of the crystal. It was assumed that radiative transitions just from interstitial ions of fluorine cause appearance of luminescence band at 7.5 eV. This high-energy band was observed in X-rays excited spectrum of La-doped crystal of BaF$_2$ in addition to self trapped exciton luminescence (4 eV) and cross-luminescence (5.7, 6.3, 7.1 eV) [1]. This work presents a theoretical calculations of cross-luminescence spectrum in crystals of barium fluoride with interstitial ions of fluorine.

In the previous work we calculated the cross-luminescence spectrum of pure crystals BaF$_2$ in cluster [Ba5F8] in embedded cluster approach [2]. The calculated spectrum confirmed well with experimental data [2]. In this work theoretical calculations of the core hole electronic and spatial structure and cross-luminescence spectrum were performed in the [Ba6F12] cluster. This cluster contains interstitial ion of fluorine, which is surrounded by five ions of Ba$^{2+}$. The equilibrium geometry of clusters, which contain core hole and interstitial ion of fluorine, were calculated both with Hartree-Fock method and with density functional method. Applicability of these methods for the correct description core hole and interstitial ion of fluorine are discussed.

In the case of using Hartree-Fock method the calculated luminescence spectrum of La-doped BaF$_2$ crystal shows cross-luminescence band with main maximum at 7 eV and high-energy band at 11.7 eV, i.e. the results of Hartree-Fock method calculation differ from experimental data on ~2 eV. In the other case (density functional method) the calculation of transitions from interstitial ions shows the band with maximum 7.5 eV and this result agrees well with experimental data.

The present results confirm the assumption that the 7.5 eV emission is due to radiative transitions between the electron state of interstitial ions and outermost core band of BaF$_2$ crystal.

References

LUMINESCENCE STUDY OF CHARGE CARRIER TRAPS IN Sn$_2$P$_2$S$_6$ CRYSTALS

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Tin hypotiodiphosphate Sn$_2$P$_2$S$_6$ is promising uniaxial semiconductor ferroelectrics with favourable photorefractive properties in the red and near-infrared spectral regions and with pronounced photoconductivity. Photorefractive properties of brown tinted Sn$_2$P$_2$S$_6$ crystals were improved by modified growth conditions in comparison to conventional orange tinted crystals. However, the nature of photorefractive centres was not satisfactorily explained up to now. Moreover, Sn$_2$P$_2$S$_6$ crystals exhibit low temperature photoluminescence (PL) in the red and near-infrared spectral regions [1]. At steady-state excitation with light with the wavelength shorter than 710 nm, the changes of PL intensity were observed with crystal exposure time at temperatures lower than 110 K. Since the analysis of these photoinduced changes can provide valuable information about defect energy levels within the band gap, which influence photorefractive properties and photoconductivity, the dependence of PL intensity on exposure time was studied on four nominally pure Sn$_2$P$_2$S$_6$ crystals as a function of temperature (12 – 300 K) and excitation wavelength (300 – 800 nm).

The PL intensity of the Sn$_2$P$_2$S$_6$ crystals cooled in the dark decreased with time of steady-state excitation with monochromatic light with the wavelength shorter than 510 nm at 12 K. The position of the absorption edge of the Sn$_2$P$_2$S$_6$ crystals at 2.5 eV (496 nm) at the temperature of 10 K indicates that PL is excited via fundamental crystal lattice absorption in this spectral region. The decrease of PL intensity was sample-dependent under the given conditions. The strongest decrease was observed in the case of brown tinted crystal exposed to 490 nm light where the saturated value of integral PL intensity was approximately four times lower than the initial one. Contrariwise steady-state excitation via defect absorption for wavelength longer than 510 nm increased PL intensity. Heating of the crystal to suitable higher temperature partially or fully restored the initial PL intensity at a given temperature. Annealing of the orange tinted crystal in vacuum at 300 °C caused increase of crystal photosensitivity and its brown coloration. The model of energy levels within the band gap of Sn$_2$P$_2$S$_6$ crystal was suggested for explanation of observed photoinduced changes of PL intensity. The activation energies of thermal ionisation of considered charge carrier traps were determined by analysis of temperature behaviour of the PL intensity dependences on crystal exposure time. The performed study of photoinduced changes of PL intensity also enabled to reconstruct and quantitatively analyse the real temperature dependences of Sn$_2$P$_2$S$_6$ emission band intensities. Since the inspection of the chemical composition by the PIXE method did not detect any impurities in the crystals, the possible assignment of revealed charge carrier traps to intrinsic lattice defects is suggested and discussed.

References

Hydrogen related defects in anhydrous “dry”, hydrated “wet” and hydrogen implanted amorphous silicon dioxide (α-SiO₂) layers are investigated using cathodoluminescence (CL) technique in a wavelength range 200–800 nm at specimen temperatures between room and liquid nitrogen temperature. Particular defect centres have been identified including the non-bridging oxygen hole centre (NBOHC) associated with the red luminescence at 650 nm (1.9 eV) and the oxygen deficient centres (ODCs) with the blue (460 nm; 2.7 eV) and UV band (295 nm; 4.2 eV) [1, 2]. An additional luminescence band Y in the green-yellow region has been clearly detected in hydrogen-implanted as well as in oxygen-deficient samples.

The red luminescence shows quite different CL dose behaviour in wet and hydrogen-treated samples due to dissociation and re-association of mobile hydrogen and oxygen from and to the NBOHC. The yellow luminescence at 575 nm (2.15 eV) is discussed in terms of radiolytic water dissociation [2] as well as of ODC’s in form of small silicon aggregates in the silica matrix [3,4].

Figure 1: Initial CL spectra measured at room temperature (RT) of thermally post-annealed dry and hydrogen implanted wet SiO₂ layers at different annealing temperatures (T_a) for 30 min in vacuum.

References
CATHODOLUMINESCENCE FROM MIXED KTaO$_3$-KTaNbO$_3$ CRYSTALS

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Cathodoluminescence spectra have been recorded at room and low temperature for a sequence of crystals within the composition range from KTaO$_3$ to KTaNbO$_3$. The pattern of luminescence emission bands is broadly similar across the wavelength spectrum from 250 to 850 nm, although the details as to the relative importance of the component bands are sensitive to composition, temperature and selection via excited state lifetime. For example, the presence of a UV band near 330 nm is only well resolved in some compositions, as is a line type feature near 725 nm. The latter component has a long lifetime and is detectable with DC recording but with a lock-in amplifier only modulation frequencies below ~90 Hz respond to the signal. The roles of defect sites which provide the composition and lifetime sensitivity are considered.
The 220 nm and 300 nm intrinsic emission in the multi-sub-lattice oxides with perovskite structure was analysed at the undoped single crystal (SC) and single crystalline films (SCF) of YAlO₃ (YAP) using time-resolved luminescence spectroscopy under the excitation by synchrotron radiation (SR). Due to low growth temperature when using the Liquid Phase Epitaxy (LPE) the YAP SCF with respect to bulk SC is characterised by much lower concentration of the anti-site (AD) of the YAl type and vacancy-type defects which contributes to the intrinsic emission of YAP SC.

The STE-like emission band peaking at 220 nm was observed in the YAP SC and SCF at 10 K, under the excitation by SR in the main excitation bands at 7.9-7.885 eV in the exciton range [1]. Much larger intensity of the 220 nm STE band and increase of its light yield from 8 K up to 160 K in the YAP SC as compared with SCF testify that this emission centre in SC also contains (or is perturbed by) a defect which is typical for the SC of perovskites grown from the melt. Due to very low intensity of this band in YAP SCF we concluded that such a defect in YAP SC is most probably the YAl AD. The 220 nm emission band in YAP SC can thus appear as a result of preferable de-excitation of STE-like state stabilised by the nearest AD (denote as STEAD) in contrast to YAP SCF where the regular STE is formed at the unperturbed sites of the perovskite lattice. This assumption is also supported both by the similar decay kinetics with the fast (few ns) and main slow (0.1 µs) components and temperature dependence of this emission to STEAD emission in other complex oxides, namely in SC of LuAG and YAG garnets [2].

The intrinsic emission of YAP SC and SCF in the bands near 300 nm corresponds to the luminescence of localized excitons (LE) around the defects or impurity centres. The radiative de-excitation of LE in YAP SC predominantly takes place near the defects of vacancy types (F⁺ or F-centres) [3]. This assumption is supported by the significantly higher intensity of LE emission at 300 nm in YAP SC, as compared to SCF, and by the difference in their position (340 nm) in the spectra of slow components of emission to that for YAP SCF as well as by closer positions of the excitation maxima of LE luminescence (7.595 eV) and F⁺-centers emission (7.41 eV) in YAP SC [3].

For the YAP SCF we assumed that the radiative decay of LE in the band peaking near 300 nm takes place in the vicinity of the main trace impurity – Pb²⁺ ions originated from the Pb-based flux components used for the LPE growth. This assumption also correlates with the presence of Pb²⁺ luminescence in the spectra of the slow components of emission in YAP SCF and location of maximum of LE (Pb) emission band in the SCF at higher energy region (295 nm) with respect to YAP SC. The above mentioned conclusion about the exciton-like nature of this emission is also supported by the spectral location of the main excitation band peaking at 7.64 eV in the exciton range, shifted at least by 0.8 eV from the threshold of band-to-band transitions, and by the fast (5.2 ns) lifetime of the main component of emission.

References

Radiation effects I
The study of colour centres is nowadays a timely research matter because the very relevant role that these defects have in the realization of miniaturized optical devices as well as in different applications with new and unusual properties particularly at nanoscale dimension. In the field of x-ray imagining detectors for digital radiographic based on the optical stimulated luminescence (OSL), the participation of colour centres has been undoubted showed in spite of the mechanisms for OSL is still under debate. Very recently, the OSL of F₂ and F₃⁺ centres in LiF films have been used in a novel X-ray microscopy and micro-radiography detecting systems [1]. Among the radiation sensitive materials, KCl:Eu²⁺ has showed to have a high OSL signal that combined with high spatial resolution could be a potential photostimulable detector for low dimensional applications.

In this contribution, defect creation by electron and X-ray irradiated KCl:Eu²⁺ polycrystalline films of micron grain sizes have been studied by thermoluminescence (TL) and photostimulated luminescence (TSL) measurements. TL glow peaks at 50-170 °C (A), 150-250 °C (B), and 250-320 °C (C) regions are clearly distinguished. As in X- and UV-irradiated KCl:Eu²⁺ crystals [2], we tentatively ascribed glow peaks at A and B regions as F₂ and F centres, respectively. By thermal bleaching methods and defect photostimulation with light on the F₂ and F₃ centres related absorption bands, we were capable to regenerate the previously bleached glow peaks on A and B regions. In this process the glow peaks intensities at C decreased simultaneously. In addition, the low temperature PSL in the near infrared spectral region (1100-1400 nm) shows the typical emission due to F₂ and F₃ centres. These results suggest the glow peaks at C could be ascribed to F centres aggregates, very possible to F₂ and F₃ defects. Finally, TL curves reveal the preferable formation of F₂ and F centres aggregates in electron and X-ray irradiated KCl:Eu²⁺ films instead of insulated F centres as it is the case in x-irradiated KCl:Eu²⁺ crystals [2] and in low energy electron irradiated KCl:LiF multilayer films [3].

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References

THE DIRECT CLUSTERING OF POINT DEFECTS IN DEPOSITED THIN LiF/Si(111) FILMS UNDER LOW ENERGY ELECTRON BOMBARDMENT

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The formation of point defects and their clusters in LiF/Si(111) 200 Å thin films in situ and post room temperature UHV deposition under low energy E<30 eV bombardment at fluences D=10^{14}-10^{15} electron/cm² are investigated. The total current spectrometry for identification and intensity measuring of defects peaks 5,0 eV- F₁; 4,5 eV- X; 4,0 eV-F₃; 3,6 eV-F₃; 2,7 eV-F₂ and colloid; 2,0 eV-F₂⁺; 1,2 eV-F₂⁻ and Li₄ for T<273 K are used (Fig.1). The energy dependencies of electron bombardment shown threshold E=Eₙ =14 eV of radiation induced formation of F₂ and F₃ centres. The post annealing temperature dependencies shown the optimal temperature for F₂⁻-centre- T>573 K and optimal temperature Tₖ=250 K for coalescence of point defects into metallic clusters. The exponential law damage formations versus fluence of electron irradiation are shown [1].

Figure 1: Total current spectra of irradiated thin film LiF/Si (111)
1-RT deposition ,annealing at 473 K, 15 min
2-electron irradiation E=20 eV, D=10^{14} e/cm²
3-electron irradiation E=20 eV, D=10^{15} e/cm²
4-annealing at 573 K,10min after irradiation
5-annealing at 673 K,10 min after irradiation

References

In the present work, Optical Absorption (OA), Electron Paramagnetic Resonance (EPR) and Thermally Stimulated Depolarization Currents (TSDC) techniques were applied to study the effects of irradiation and thermal treatments in the formation, aggregation and destruction processes of dipole defects in MgAl$_2$O$_4$ spinel. Exposure of MgAl$_2$O$_4$ crystals to 10 kGy of gamma rays produces two broad OA bands centred near 3.4 eV and 5.1 eV, one EPR band at $g=2.011$ and one TSDC band at 245K. All these bands, created after gamma irradiation, are completely destroyed for thermal treatments above 500K.

The broad OA band centred near 3.4 eV and attributed to V-type centres [1], increase with the irradiation-dose and stabilizes its maximum height for doses near 10 kGy. This same band decays when the sample is maintained at room temperature reaching a constant value after a few weeks.

The MgAl$_2$O$_4$ EPR spectrum is composed by two superimposed bands, a wide structureless one and another one, which is a set of 16 sharp lines associated with hyperfine interactions attributed by Ibarra et al. [2] to V$_{o}^{2-}$ and V$_{t}^{-}$ centres. Each band behaves in a different way thus indicating that they are associated with two different defects. This conclusion is supported by gamma dose dependence, by thermal treatments between 370K and 500K and by the thermal decay of the two bands at room temperature.

TSDC spectra present dipole peaks at 120K and 160K that do not change after thermal treatments and gamma irradiation [3]. Nevertheless the peak position in temperature of the 245K TSDC band shifts with dose and also increases in height with the gamma dose. When the sample is maintained a few weeks at room temperature, a shift in the position in temperature of the band is observed from 245K to 290K remaining in this position. The dependence of the TSDC band with the polarization temperature $T_P$ allows us to conclude that the band is in fact formed from at least two peaks, one of dipole origin at 290K and another complex band centred at 245K.

References

Protons affect the polymers mainly through scission and crosslinking of macromolecule chains. Ionization processes at proton non-elastic scattering define these effects. One of the most important problems of radiation physics and chemistry of polymers is the dependence of radiation effects in polymers on the kind of ionizing radiation or the problem of LET (Linear Energy Transfer) effect. Analyze of such dependence for protons and some other kinds of radiation is presented. A detailed examination of 100 MeV proton collisions in polyethylene terephthalate (PETP, trade mark Mylar) on the base of the sample heat conductivity behaviour revealed an important role of atom displacements resulting from elastic nuclear scattering of nuclear reaction products. Similar results were obtained for polymethylmethacrylate (PMMA) irradiated by low energy protons. It is necessary also to take into account the establishing clusters of displaced atoms. Such damage of polymer molecules was not obtained for other examined types of radiation, in particular, for recoil nuclei at reactor neutron irradiation and for $^{60}\text{Co}$ - gamma radiation.

Such different energy proton effects on Mylar and PMMA can be used for modification of their operating properties (particularly, thermal and optical ones). It also emphasizes the importance of low energy protons interaction with space materials.
TL, ESR AND PHOTOREFLECTANCE IN NATURAL DIOPSIDE CRYSTAL

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A natural diopside sample from Minas Gerias, Brazil was studied using thermoluminescence (TL), electron spin resonance (ESR) and photoreflectance (PR) techniques. The impurities contained in the samples were analyzed using X-ray fluorescence (XRF). It was found high concentrations of Fe$_2$O$_3$, Al$_2$O$_3$, MnO, TiO$_2$, K$_2$O (in % mol) as well as smaller concentrations of Cr, Ni, Sr, V, Zn, Zr etc (in ppm).

TL of natural sample has shown four principal glow peaks at 160, 270, 360 and 450°C. A laboratory irradiation between 0.005 to 50 kGy using a $\gamma$-ray source produce a fast increment in the intensity of the first peak compared to those others. The sample annealed at 500°C during one hour and then irradiated with the same doses as above presented two other new peaks locate at 205 and 240°C.

The behaviour of the principal peak intensities as function of the dose are similar, it is sublinear up to $\sim$1kGy and saturates for high doses.

UV irradiation of annealed sample produces only three TL peaks at 90, 160 and 450°C which are different from the results of gamma irradiation. The intensity of these peaks increases with the light exposure time.

Samples heat treated at high temperatures, 500, 600, 700, 800 and 900°C and irradiated at 1kGy afterward produce an increase in the intensity of the glow peaks. The effect is longer for the low temperature peaks.

ESR measurements of powder samples were done at room temperature. Hyperfine signals between 2500 and 4500G characteristics of Mn$^{2+}$ were observed. The irradiation or thermal treatment doesn’t change considerably the shape of the signals.

Since natural diopside samples are not transparent photoreflectance (PR) measurements were carried out using slabs $\sim$10×10×3 mm$^3$ cut randomly in the region between 2500 and 250 nm. Bands due to OH molecules (2500-1300 nm) and due to Fe$^{2+}$ (1200 nm) were observed. The irradiation with $\gamma$-ray source at the same doses as in TL measurements doesn’t change the photoreflectance spectra. The thermal treatment at 500, 600, 700, 800 and 900°C induces an increment in the band intensity due to Fe$^{2+}$. 
We review our work on the thermoluminescent properties of LiF and NaCl crystals relevant to their use as dosimeter crystals. In alkali halides, TL is thought to be due to the recombination of trapped electrons (F and F aggregate colour centres) and interstitial halogen atoms (H centres) produced during irradiation. Some dopants enhance the TL response of NaCl and LiF crystals by a significant amount. The role of impurities and their effect on glow curves is considered. We show that the TL behaviour of LiF and NaCl is remarkably similar in several respects. In particular, a spectral analysis of light emitted at glow peaks suggests some common processes active in the two materials. We find that certain activating impurities enhance a dosimeter peak, which emits at the same peak wavelength in both host crystals. This may be related to the presence of impurity – vacancy dipoles in a form which favours TL emission. Structures of some possible aggregates which have been identified are discussed.
EFFECT OF DEEP TRAPS ON THE OPTICAL PROPERTIES OF Tb$^{3+}$ DOPED SOL-GEL SILICA

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Rare-earths doped silica obtained by the sol-gel technique has proved to be a scintillating material of promising characteristics [1]. In this study we investigate the role of traps on radio (RL) and photo-luminescence (PL) properties of terbium doped silica. We focus on those phenomena that can be responsible for problematic properties such as the instability of radio-luminescence intensity following repeated irradiations.

A set of terbium doped silica densified at 1050 °C in oxidizing atmosphere has been prepared by the sol-gel technique. The nominal concentration of the dopant ranges from 0.001 to 10 mol%. The effect of a post-densification rapid thermal treatment (RTT) has been also considered.

As expected, the PL emission spectra evidence a cross relaxation process between Tb ions. In fact, the ratio between the emission intensities due to $^5D_4-^7F_J$ and $^5D_3-^7F_J$ transitions is progressively reduced as the dopant concentration increases.

The effect of X-ray irradiation on RL and PL intensities has been studied. The RL emission intensity increases as a function of the imparted dose while the PL signal is only slightly affected by this procedure. In order to further investigate this phenomenon, thermo-stimulated luminescence (TSL) measurements have been performed; the results are discussed in the framework of a competition process between Tb$^{3+}$ luminescence centres and deep traps acting as killer centres.

![Figure 1: Effect of X-ray irradiation on the PL and RL intensity of a SiO$_2$:0.03 mol% Tb.](image)

References

PHOTOINDUCED ELECTRIC DIPOLE RELAXATION IN ALEXANDRITE

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We have investigated the electric dipole formation in natural and synthetic alexandrite (BeAl₂O₄:Cr³⁺ - chromium doped Chrysoberyl) by using the thermally stimulated depolarization current (TSDC) technique [1]. Alexandrite is a rare and precious material, which has become technologically important from 1974, when the synthetic form became available through Czochralsky growth method. Chrysoberyl (BeAl₂O₄) presents structure approximately hexagonal with compact arrangement of oxygen ions, with Al³⁺ and Be²⁺ ions placed at octahedral and tetrahedral sites respectively. Distortion of a perfect hcp structure of oxygen ions, which are shifted from c axis, leads to two distinct sites octahedrally coordinated: Al₁, located at an inversion site and Al₂, located in a reflection plane [2]. By measuring TSDC on a standard procedure, it was recorded a broad band centered at 179K for the synthetic sample and about 188 to 196K for natural samples from different stones [3]. TSDC bands have been attributed to impurity-vacancy dipoles, which have been analyzed by Havriliak-Negami method. From this data fitting, it was concluded that the observed bands are best-fitted by a continuous distribution of relaxation parameters: activation energy and relaxation time constant (pre-exponential factor). Besides, Alexandrite presents optical absorption bands in the visible range, centred about 420 and 590nm [4] and in the ultraviolet, centred about 265 nm, which are attributed to Cr³⁺ ions substituting for Al³⁺ on the two sites of different symmetries (A₁ and A₂). Assuming that dipole relaxation phenomena in this material is related to Cr³⁺ ions, one can expect photoexcitation of these ions will influence the relaxation. Thus, in this work, we have performed TSDC on a non-standard procedure, where monochromatic light from a Kr⁺ laser, with lines in the 337.5 nm to 676.4 nm range is irradiated onto the sample along with biasing electric field. This procedure allows the observation of a light effect on electric dipole formation and dipole destruction in natural and synthetic alexandrite. For the synthetic sample, TSDC bands can be observed when the biased sample is photo-excited at 77 K. The central position of the band is strongly dependent on wavelength of irradiation source. By the other hand, light irradiated on natural samples allows only the observation of a tendency of dipole formation, without being possible the band recording. This effect may be related to light scattering on irregular faces of natural alexandrite samples, when compared to synthetic sample. Electrical characterization of alexandrite by TSDC was complemented by optical absorption and photoluminescence measurements, which are being analyzed [5], and help interpretation of TSDC data. Financial support: Fapesp, Fundunesp.

References

INVESTIGATION OF QUENCHING PROCESSES IN Yb:YAG FOR THIN DISK LASER APPLICATIONS

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The pursuit of efficient high power lasers has led to the development of the thin disk laser set-up. This architecture demands an active medium with high doping levels so that sufficient absorption can be achieved within a thin layer. Crystalline Yb:YAG is an attractive choice of medium for this application due to the unlimited doping potential, the host’s superior thermo-physical properties and the simple energy level scheme of the Yb3+-ion. However, Yb:YAG thin disk lasers suffer decay processes that generate heat. These processes are known to be dependent on the excitation density, resulting in the suppression of laser operation for crystals with a doping concentration of over 15at% [1].

Yb:YAG crystals grown using powder-metallurgical Re-crucibles under reducing conditions present strong Yb2+-formation. However, the as-grown samples show strong quenching, which cannot be attributed to only the cooperative energy transfer from two excited Yb3+-ions to a single Yb2+-ion [2]. It is suggested that additional quenching takes place due to a colour centre composed of Si2+ charge-compensated by an oxygen vacancy with one electron (F+). The presence of F+ in non-annealed YAG crystals containing Si has been confirmed by ESR measurements. Furthermore, an ENDOR analysis identified the quenching centre to be a local Si2+-F+ complex. Since Si is an inherent impurity in the raw materials used, its presence in the crystal cannot be eliminated and so the formation of the colour centre itself must be prevented. Typically therefore, Yb:YAG laser crystals are annealed in air at around 1000°C for several hours to eliminate the oxygen vacancies. However, in the case of thin disk laser operation it is possible that the high power pumping optically induces the formation of temporary or even permanent colour centres, which may involve the aforementioned complex centres.

The aim of this research is to identify the loss processes that occur in Yb:YAG thin disk lasers and their origin. Extensive spectroscopic investigations of samples with different doping concentrations are performed, including excited-state absorption measurements as well as examination of the temperature and excitation-energy dependency of the fluorescence lifetime. The pinhole-method is used to avoid radiation trapping effects in the lifetime measurements [3].

References

NEW RADIATION INDUCED DEFECTS IN TRIS-(8-HYDROXYQUINOLINE)ALUMINUM (Alq3)

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Results of X-band cw-EPR study of the induced paramagnetic defects in thermally treated and irradiated polycrystalline tris-(8-hydroxiquinoline)aluminum (Alq3) samples are reported.

Alq3 is one of the most used materials in organic light emitting diodes, OLEDs. It is an octahedral coordinated chelate complex, where the aluminum ion is surrounded by three identical quinolinolate anions. Crystallographically several phases have been identified depending on the preparation technique and thermal treatments [1, 2].

In the paper we focus attention on sublimated crystalline Alq3 phases which were γ/β-irradiated with a 20 kGy dose at room temperature. Besides the centres already observed [3], new paramagnetic, very stable, defect centres are induced in the irradiated annealed samples. Their spectra depend on the applied thermal treatment. The EPR spectrum, shown in Figure 1, has a poorly resolved complex structure which made its analysis very difficult. A relatively better resolved hyperfine structure due to the interactions with N and H nuclei could be obtained using a model evaluation procedure - a resolution enhancement algorithm [4]. Using this procedure at least two different centres are identified; their spin Hamiltonian parameters are determined and tentative models are proposed. Comparison with paramagnetic centres in similar materials is made supporting the proposed models.

![EPR spectrum for e-irradiated Alq3 annealed at 400°C](image)

Figure 1: EPR spectrum for e-irradiated Alq3 annealed at 400°C

References
The dipole defects formation in γ-irradiated CsI-CO$_3$(SO$_4$) crystals ($D=10^4\div5\cdot10^6$ Gy) has been studied by different methods: the ionic thermocurrent (ITC), electrical conductivity, optical spectroscopy and computer modelling. The physical and mathematical models of dipole relaxation processes have been proposed.

The dependence of defects formation efficiency in CsI single crystals on the type of oxygen containing impurities and the value of absorbed irradiation dose was studied earlier [1]. The peculiarities of defects formation in γ-irradiated CsI-CO$_3$(SO$_4$) crystals consist in the impurity-vacancy (IV) dipoles generation at the initial irradiation stage ($D<10^6$ Gy). The intensive decay of IV dipoles and the formation of F-colour centres and their aggregates takes place at the higher irradiation dose ($D>10^6$ Gy). These processes are caused by the peculiarities of electron-hole (e$^-$, e$^+$) mechanism of F, H-centres formation in CsI-CO$_3$(SO$_4$) crystals under the γ-quantum irradiation ($E_{hv}=1.25$ MeV) at the room temperature. The dipoles induced by the γ-irradiation were identified.

Computer modelling was applied for calculating the dose and temperature dependences of dipoles and vacancies concentration. The mathematical model of dipole relaxation processes is based on a kinetic equation:

$$\frac{\partial n(T,t)}{\partial t} = n(T,t) \cdot \sigma \cdot e\left(\frac{E_a}{kT}\right) + \frac{N}{\tau} = 0,$$

where $n(T,t)$ – the dependence of dipole concentration on temperature $T$ and time $t$; $E_a$ – activation energy of dipole reorientation; $\sigma$ – frequency factor; $N$ – initial dipoles concentration; $\tau$ – time of dipole relaxation.

For solving of this equation the difference method have been used. The numerical values and characteristic dependences of dipoles and vacancies concentration on the irradiation dose and temperature have been obtained. The theoretical and experimental results are correlated well.

References

THE THERMOSTIMULATED EXOELECTRON EMISSION OF NaF:U,Me COMPOUNDS AFTER ELECTRON BEAM IRRADIATION

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The thermostimulated exoelectron emission (TSEE) of NaF:U,Me bulk, planar, fiber and nanocrystals and their radiation stability after electron beam irradiation (fluence \(10^{12} - 10^{14} \text{ cm}^{-2}\)) have been investigated at the temperature region 300-780 K. Some TSEE peaks (9–13 peaks) have been found (Fig. 1). For example 11 peaks of TSEE have been found for nanocrystals at temperature (K): 328, 366, 412, 466, 510, 548, 594, 620, 644, ~700 and 736 (Fig. 1b). The electron traps connected with these peaks have energy of activation 0.70, 0.79, 0.89, 0.96, 1.10, 1.18, 1.28, 1.34, 1.39, 1.52 and 1.60 eV respectively. The nature of TSEE curves for nanocrystals is discussed in comparison with data for TSEE bulk single crystals of NaF:U,Me. It was supposed that thermoactivated process in NaF:U,Me nanocrystals as in bulk NaF:U,Me single crystals can be connected with destruction of F\(^3+\), F\(^2\) and F colour centres and with next recombination of electron with H-centres or with more complicated hole centres. It was found that the radiation stability of NaF:U,Me nanocrystals is less than radiation stability for bulk single crystals. The problems of high temperature TSEE dosimetry are discussed.

![Figure 1: TSEE curve of NaF:U,Cr bulk crystal (a) and NaF:U nanocrystal (b).](image)

References

INVESTIGATION OF MgO CERAMICS, IRRADIATED IN THE DIFFERENT REACTORS

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One of the problems of ecological (including the radiation) safety is the necessity for reliable detection of ionizing radiation in environment. In this connection, along with the improvement of the known detectors the new effective dosimetric detectors are investigated and developed.

As a new material for dosimetric detector, we used the samples of ceramic magnesium oxide, the results of complex investigation of which are presented in the given work. The complex investigation includes a registration of high temperature luminescence (TSL), optical (electronic and vibrational) and paramagnetic spectra.

The investigated thin samples (10x5x0.7 mm³) were cut from a transparent block of magnesium oxide, contained 0.2 weight % LiF. By measuring EPR spectra the presence of bivalent manganese (\(\text{Mn}^{2+}\)) was detected in the amount not exceed 10 ppm. According to IR absorption spectra the amount of \(\text{OH}^-\) was determined and it was not more than 5.6x10¹⁶ cm⁻³.

The irradiation was carried out by mixed \((n,\gamma)\)-radiation in the channels of IBR-2 (4.1x10¹¹ n/cm².s, in Dubna) and WWR-SM (2.5x10¹³ n/cm².s, in Tashkent) reactors. It was shown that TSL peak about 615 K is due to the neutrons and may be used as a dosimetric characteristic of flux of fast neutrons in mixed fields of radiation. This conclusion is evidenced by linear dependence of the intensity of peak 615 K on neutron dose (curve on the left in Fig.). This figure shows also the dependence of concentration of \((F^+ + F^-)\)-centres, according to optical absorption spectra in irradiated ceramic MgO samples on dose of radiation (curve on the right). It is seen that these dependences are in good correlation with each other, i.e. the TSL intensity of irradiated sample increases with the increase of concentrations of indicated colour centres.

Independent of the degree of destruction of MgO:LiF ceramic samples irradiated in different reactors the dependence of concentration of \(F^+\) (F-centres) on the fast flux is maintained. As a result, the dosimetric information from irradiated ceramic MgO samples can be read out not only by TSL, but also by means of EPR, as well as by spectrophotometric methods.

The work was supported by ISTC grant G-646.
Single crystal of yttrium aluminum perovskite, YAlO$_3$ (YAP), is well-established host both for the solid-state lasers (YAP: Nd) or cathode-ray detectors and x-ray based tomography techniques (YAP: Ce). Especially the latter scintillator applications of YAP: Ce appears more significant during last years. In single crystal scintillators, point defects and trace impurities are often a key point in the energy transfer and storage processes and may influence the material performance significantly. However, apart from the detailed reports on luminescence and scintillator characteristics of both the pure and Ce-doped YAP, the nature and role of various intrinsic defects in the processes of energy transfer and storage are still poorly understood. While the hole traps were identified more than 30 years ago (Schirmer et al., Phys. Rev. B 11, 4201 (1975)) as due to the O$^-$ bond small polarons formed at oxygen lattice sites, the origin of intrinsic electron traps is still not clear.

Using the ESR method, in the present report we show that one possible electron trap can be related to oxygen vacancies that form the F$^+$ or F$_A^-$$^+_*$ centres. In this trap the electron density is essentially shifted to the nearest Y and Al cations. It is found from the analysis of the g-factors ($g = 1.65 – 1.90$), which are typical for the d$^1$ electron orbital, and further supported by the superhyperfine interaction with the Al nuclei. Trapped electron is stable at an oxygen vacancy up to 260-280 K. The antisyte positions of the Y and Al cations as a possible perturbation for the electron trapped at oxygen vacancy were considered as well. The ESR data obtained are compared with thermally stimulated luminescence characteristics and similar data observed in some other oxide crystals.
Coloration of pure and doped CaF$_2$ crystals using various methods has been extensively studied [1 – 4].

In this paper some optical properties of various concentrations PbF$_2$ – doped calcium fluoride crystals have been studied. The crystals have been grown using vertical Bridgman method [5].

The absorption and luminescence spectra of these crystals have been studied and the dependence of the absorption coefficient on the dopant concentration has been established (figure 1).

In order to study the optical properties, the crystals have been irradiated with x-rays and high-energy electrons at room temperature. The coloration of the Pb$^{2+}$-doped CaF$_2$ crystals has been made also by electrolytic method. The absorption and luminescence spectra of the crystals coloured by different methods have been obtained (figure 2). The thermoluminescence spectra of the x-rays irradiated crystals have also been studied. In order to explain the obtain results, some assumption have been presented.

References

Interaction of ions and carbon nanotubes (CNT) now is intensively investigated both as experimental and numerical methods [1-3]. Ion beams are an effective tool of properties modification both separate CNT and their complexes and it opens an opportunity of their application in nanotechnologies. Time scales of processes, which happen at the irradiation, are differ on some orders of magnitude, and the irradiated area contains hundreds atoms and thousand electrons that impedes detailed simulation of processes in nuclear and electronic subsystems. However, average time between incoming particles in used focused ion beam is the greatest from their. Therefore, dynamics of properties change of irradiated CNT and their complexes can be studied within the framework of coupled rate equations describing the evolution of defect densities.

Dynamics of structure defects accumulation especially links between CNT walls in multi-walled CNT, bundles, ropes, mats and similar system under focused ion beams irradiation has been investigated within the framework of this approach. Three mechanisms of links creation are taken into account: 1) 2+2-cycloaddition, 2) by vacancy assistance, 3) by interstitial atom assistance. Also the sputtering of the target and defects appeared as not hexagonal rings after vacancies relaxation were considered. Formation of new links and defects, recombination of vacancies and interstitial atoms were taken into account during relaxation of the struck areas. For low energy (several keV) carbon ions excitation and ionization of atoms are negligible and the first mechanism is ungeared, therefore processes are described by system of six bounded nonlinear differential first-order equations for number of vacancies, interstitial and sputtered atoms, defects and two types of links.

It has been found, that at low radiation doses number of new links between walls of system linearly proportionally to the ions dose with a coefficient depends on energy of the beam (mean cross section of defect formation and temperature of the target) and dominant mechanisms of relaxation (mean lifetimes of various excited states). With the dose increasing the number of defects attains maximal saturation but number of links vanishes. Experimental data are agreed with behaviour of the received curves. It allows us to choice exactly unknown parameters of relaxation processes (lifetimes) in such a way that they can be used for prime analytical estimations and numerical calculations of integral characteristics of irradiated array of the systems by ion beams. From the other side, these parameters give us information about dominate relaxation process in system under ion irradiation.

The proposed model of links accumulation created between CNT by ion irradiation can be used for theoretical investigation of the crosslinking dynamics and for technological applications. This work was supported by the “Dnipro” Program.

References

OPTICAL ABSORPTION INDUCED BY UV LASER RADIATION IN GE-DOPED AMORPHOUS SILICA PROBED BY IN SITU ABSORPTION SPECTROSCOPY

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Many studies have evidenced that laser exposure of Ge-doped silica is able to induce transparency loss, photosensitivity and optical nonlinearity in the material, related to generation and conversion of point defects triggered by laser light and highly interesting from an applicative point of view [1-2]. These processes have been extensively studied with multiple spectroscopic techniques, such as optical absorption (OA) and electron spin resonance (ESR) but many questions still remain open; in particular, their kinetics during and after laser irradiation has not been sufficiently investigated, due to the lack of appropriate \textit{in situ} spectroscopic techniques.

We studied the OA induced by 4\(^{th}\) harmonic Nd:YAG (4.7eV) pulsed (5ns) laser radiation on Ge-doped amorphous silica samples synthesized by a sol-gel technique. OA spectra in the UV (3-6eV) were measured during and after the end of irradiation with an \textit{in situ} technique. Experimental data evidence the growth of an absorption signal whose profile is characterized by at least two bands peaked near 4.5eV and 5.8eV (Fig. 1) and the partial bleaching of the native 5.1eV absorption. The kinetics of this signal is measured during and after the end of irradiation, showing a time dependence of the overall profile. Finally, ESR measurements performed \textit{ex situ} a few hours after the end of exposure permit to complete the information acquired by OA by detection of the paramagnetic Ge(1) (GeO\(_4\))\(~\) and Ge-E\(^{'}\) (=Ge\(^{•}\) centres laser-induced in the samples.

![Figure 1: Time evolution of OA induced by 4.7eV laser irradiation on Ge-doped sol-gel silica, measured \textit{in situ} during exposure.](image)

References


The optical absorption spectra of two samples of grossular have been measured at room temperature. An intense charge transfer band (UVCT) of iron extends to the visible and near infrared region. Some peaks associated to Fe$^{3+}$ ions in tetrahedral and octahedral positions have been identified and their energy levels were computed. Mn$^{2+}$ and Fe$^{2+}$ ions are responsible for some bands and probably these ions occupy dodecahedral positions. Not change in intensity were found with gamma dose, but only the 505nm band decreases with irradiation.

The OH spectra, consisting of OH overtones at 2750nm and asymmetric OH bands in the near infrared region were observed in the two samples. The heat treatment produces Fe$^{2+}$→Fe$^{3+}$ and Mn$^{2+}$→Mn$^{3+}$ by oxidation. This last was observed in sample II only.

References

RADIATION EFFECT ON THE STRUCTURE AND VIBRATIONAL SPECTRA OF THE MULTI-WALLED CARBON NANOTUBE-POLYMER COMPOSITE


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The modification of polymers by carbon nanotubes (CNT) must contribute to the creation of the donor-acceptor bonds, whose number it is easy to regulate by the introduction of radiation defects with the bombardment by the high-energy electrons and ions, capable of overcoming the threshold energy of atomic displacement [1-2]. The samples of the polypropylene polymers with the multi-walled CNT were obtained via the thermal diffusion with the subsequent preheating of granules under the pressure. The influence of CNT on the conformation of the molecules of polypropylene was studied by the X-ray diffraction method with a study of changes in the supermolecular structure. Furthermore, the Raman scattering from the vibrational modes of the polymer molecules depending on the content of CNT and the dose of electron and ion (Ar+) irradiation was investigated in detail. It was found the complex behaviour of the frequencies of the vibrational modes, their relative intensities, that testify about the removal of degeneration as the consequence of the appearance of additional intermolecular interactions caused by the exchange of the charges between the polymer molecules and CNT, which influence the radiation defects generated by the atomic displacement.

This work was partly support by the “Dnipro” programme.

References

LUMINESCENCE OF RADIATION DEFECTS IN LiBaF₃:Fe

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Optical properties of undoped LiBaF₃ crystals have been studied over the last two decades. In the majority of both non-purified and non-doped as-grown LiBaF₃ crystals a complex blue luminescence band is present. In previous works the band has been related to oxygen, which is believed to be a widespread impurity in complex fluorides [1, 2]. Radiation defects in the undoped LiBaF₃ crystals have been studied and main intrinsic structure defects have been recognized.

Here we present studies on optical properties of defects created by an x-ray irradiation of LiBaF₃ crystals doped with Fe. After the x-ray irradiation performed at different temperatures several dose sensitive luminescence bands appear in the visible and infrared spectral regions for the all doped samples. The spectral composition of the luminescence signal depends on the x-ray irradiation temperature. The defects responsible for the infrared luminescence band can be created only after the x-ray irradiation at 290 K though the luminescence itself at room temperature is thermally quenched while the other luminescence band in the visible part of the spectrum can be observed in a broad temperature region. All the photoluminescence bands can be seen in charge recombination processes under electron beam excitation and in thermostimulated luminescence spectra.

Fe role in the radiation defect creation and interaction in LiBaF₃ crystals is discussed.

References


The absorption and luminescence spectra for irradiated NaF:Eu, NaF:Sr, NaF:Sc, NaF:Cu, NaF:U, NaF:Ti, NaF:U,Cr, LiF:Na, LiF:Sc, LiF:U single crystals have been measured. The irradiation has been made by reactor neutron with fluencies $10^{16}$ and $10^{18}$ neutron/cm$^2$.

The position of absorption and luminescence band in optical spectra of neutron irradiated NaF and LiF compounds have been measured. Creation of F and $F_2$, $F_3^+$, $F_2^-$ types of aggregate colour centres in the anion sublattice and their evolution have been investigated. The example of luminescence spectra of neutron irradiated (fluence $10^{16}$ cm$^{-2}$) of LiF:U specimen is presented on Fig.1. After irradiation the luminescence bands of $F_2$ and $F_3^+$ colour centres (540 and 650 nm) are developed. The nature of induced defects is discussed.

For comparison the same spectra for NaF:U,Me and LiF:U,Me single crystals after their irradiation by $N^{3+}$ ion cyclotron beam (16 MeV, fluence $10^{10}$–$10^{16}$ cm$^{-2}$) and by electron microtron beam (10 MeV, fluence $10^{14}$ cm$^{-2}$) have been measured. After neutron and $N^{3+}$ ion irradiation the $F_2$ centres are dominated. After electron irradiation F centres are dominated. The methods of management of optical absorption and luminescence properties of investigated crystals are discussed.
THE ORDER-DISORDER PHASE TRANSFORMATION IN ION-IRRADIATED RARE EARTH SESQUIOXIDES

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In this presentation, we examine an ion-irradiation-induced order-disorder phase transformation in polycrystalline pellets of the rare earth sesquioxides Dy₂O₃ and Er₂O₃ using grazing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). These sesquioxides are characterized by a cubic C-type rare earth structure known as bixbyite. Samples were irradiated with heavy ion Kr⁺⁺ (300 keV) and light ion Ne⁺ (150 keV) at cryogenic temperature. GIXRD and cross-sectional TEM observations reveal that the ordered body-centred cubic bixbyite structure transforms to a disordered (anion deficient) fluorite structure in these irradiated sesquioxides. This observation is consistent with a radiation-induced disordering process in which the oxygen superlattice associated with the bixbyite structure is destroyed and the materials adopt an anion disordered fluorite structure as evidenced by the disappearance of characteristic GIXRD diffraction peaks resulting from ordering of the oxygen superlattice, and similar electron diffraction pattern features.
The interest in radiolysis of NaCl, which leads to the formation of sodium colloids and chlorine bubbles, is stimulated by the fact that rock salt is a prominent candidate medium for storage of high-level radioactive waste [1,2]. Recent experimental studies on radiation damage in NaCl crystals, irradiated with electrons of moderate energies (e.g. ~ 1 MeV) have shown that changes in the irradiation temperature dramatically affect the evolution of size distributions of sodium colloids and chlorine bubbles. Samples of NaCl, doped with 300 ppm KBF₄, have been irradiated initially to a dose equal to 320 GRad at 100 °C, subsequently the irradiation was continued at low temperature (18 °C). Differential scanning calorimetry has shown that the latent heat of melting (LHM) of sodium colloids decreases during low temperature irradiation in the second stage, whereas the stored energy (SE) continues to increase slowly. The experimental results are discussed within the framework of a model formulated to describe the nucleation kinetics and the evolution of the size distribution of chlorine precipitates and sodium colloids in NaCl under high dose irradiation as a function of the temperature. The decrease of the LHM is explained in terms of dissolution of large colloids, whereas the small increase of the SE indicates that the process of radiolysis continues (fig. 1).

Figure 1: Comparison of simulation results and experimental data. 
(a) the LHM (experiment) and the simulated volume fraction of large colloids (R >1 nm). 
(b) the ratio of the SE and the LHM of sodium (experiment) and the ratio of the total amount of radiolytic Na and the amount of Na in large colloids (R >1 nm).

References


Some investigations of defect evolution in LiF and NaF crystals under cyclotron ion radiation (He\textsuperscript{+} ion beam, 4.6 MeV) are presented. For irradiation the R-7M cyclotron of Ural State Technical University was used.

The absorption spectra for LiF and NaF crystals irradiated with different fluences and currents of beam were measured for investigation of defect evolution. It was found that different aggregation colour centre developed into LiF and NaF crystals depending on fluences and currents of ion beams. Moreover it was found that different aggregation colour centre can be developed into LiF and NaF crystals at same fluences and currents of ion beams depending on previous defect state of crystals. It can be determined by previous irradiation. This phenomenon looks like memory because equal input action (equal type of irradiation) gives different output reaction (development of different types of colour centre). Therefore this new phenomenon was called by us “memory of previous defect state” (or MPDS for short). The MPDS phenomenon influences on excitation evolution in LiF and NaF crystals. The spectra of ionoluminescence for LiF and NaF crystals were measured for investigation of excitation evolution. Appearances of blue (420 nm) or red (600 nm) bands in spectra of ionoluminescence were found at same fluences and currents of ion beams depending on previous defect state of crystals (see Fig.1). The previous defect state was managed by type of previous irradiation.

Model for explanation of MPDS phenomenon was proposed. The essence of this model concludes in application of known model of dynamic of population for defect evolution. In frame of proposed model the processes of interconversion and competition between different types of defects are considered. It was shown that influence of previous defect state to defect evolution. Additionally the phenomena of surface electric discharge and surface heating appeared during ion irradiation and its influence upon defect evolution are considered.
POWER THRESHOLDS, CRITERIA, KINETICS AND MECHANISMS OF IGNITION OF EXPLOSIVES UNDER LASER PULSES AND PULSED ELECTRON BEAMS

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It is necessary to understand values of energy $W_{0.5}$ as power thresholds of ignition (PTI), density of energy $H_{0.5}$, capacities $I_{0.5}$ and density of capacity $q_{0.5}$, corresponding to 50% of a level on a probability curve of initiation. Which of these parameters is most informative depends that is criterion of ignition in different experimental situation.

PTI is complex function of many parameters (duration of an influencing pulse $\tau_p$, characteristic relaxation time of external excitation $t_r$, diameter of a beam $d_p$, refraction $n_0$, absorption $\mu$ and dispersion $\beta$ coefficients of explosives, density of substance, dispersivity of explosive powders, pressure of molding and mass molding of explosive powders) and this circumstance is the reason of strongly difference in value of thresholds of various authors in experiences. In turn, criteria of ignition are determined by ratio between space-time parameters of an external influencing pulse and space-time scales of relaxation, which are typical for investigated sample in concrete conditions of experience.

Authors of the given work carry out the analysis of applicability frameworks of various criteria of ignition for modeling representatives of initiating of explosives, secondary explosives and pyrotechnic structures. It is established, that criterion of ignition is energy of a pulse at short time $\tau_p$ ($\tau_p < t_r$) and the small sizes of beam on surface of explosives (the size of excited area less than characteristic size of ignition - $d_c$), and density of energy at great values of $d_p$ ($d_p > d_c$). The criterion of ignition of explosives is capacity or density of capacity accordingly in the field of long duration ($\tau_p > t_r$).

It is suggested to insert additional parameter for more detail understanding of the nature of ignition – threshold cubic density of energy $\omega_{0.5}$ [1](cubic density of capacity $i_{0.5}$), which characterize the minimal size absorbed energy (capacity) in unit of volume of substance result in ignition or explosive decomposition of substance.

The opportunity of use of the suggested parameter of $\omega_{0.5}$ for identification of the nature and mechanisms of initiating of explosives is discussed. It is underlined, that such approach sharply limits opportunities of modelling representations from positions of the chain nature (model of chain duplication of zoned carriers of a charge – electrons and holes [2]).

The important information on the nature of explosive decomposition under pulse of external influence can be received from the analysis of kinetic characteristics of ignition and especially during initial stages of process. Synchronous multiparameter measurements of kinetics with the high time resolution in this connection are of interest.

The opportunity and mechanisms of explosive decomposition from the thermal micro-fireplaces for explosives of various classes are discussed at various ways of external pulse influence. It is concluded in favour of thermal fireplace nature of initiation of explosive decomposition under laser and electron beam pulse irradiation.

References

INFLUENCE OF REDUCING/OXIDIZING HIGH-TEMPERATURE THERMAL TREATMENTS ON THERMOLUMINESCENT PROPERTIES OF YAlO$_3$:Mn CRYSTALS

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Mn-doped YAlO$_3$ crystals became of interest during last years after it was shown a high application potential of the crystal for holographic recording and optical data storage [1] as well as for thermoluminescent dosimetry of ionizing radiation [2,3].

Our previous thermoluminescent (TL) studies of YAlO$_3$:Mn crystals [2] have shown that besides ionization of Mn$^{4+}$ ions (Mn$^{4+} \rightarrow$ Mn$^{5+} + e^-$), ionizing irradiation of the crystals causes recharging of Mn$^{2+}$ ions (most likely the Mn$^{2+} \rightarrow$ Mn$^{3+} + e^-$ ionization) that occupy dodecahedral (Y$^{3+}$) positions in the crystal. The electrons released from both Mn$^{2+}$ and Mn$^{4+}$ ions are captured on deep traps available in the host. During warming of the irradiated crystals from room temperature up to about 650 K, when electrons are released from the traps, the opposite recharging processes take place that become apparent in red (Mn$^{4+}$ ions, transition $^2$E$\rightarrow^4$A$_2$) and yellow-green (Mn$^{2+}$ ions, transition $^4$T$_1$$\rightarrow$$^6$A$_1$) TL emissions. The yellow-green TL emission has been used as a TL signal for detecting of ionizing radiation [3].

The present work represents a continuation of our previous studies [2,3] and includes obtaining of Mn-doped YAlO$_3$ crystals and their characterization by means of optical spectroscopy and thermoluminescence measurements. In particular, influence of after-growth high-temperature thermal treatments of the crystals in oxidizing and reducing atmosphere (T=1300 K) as well as the effect of co-doping with Si$^{4+}$ on TL properties of the crystals have been studied. The studies have been performed from the point of view of possible optimization of the crystals properties for the TL dosimetry application.

References

Radiological imaging and detection, scintillators, and dosimeters
ADAPTATION OF THE ORGANIC POROUS SCINTILLATORS FOR THE α-EMITTERS DETERMINATION


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The toxicology of transuranic elements is rather complicated due to double-sided nature of biological effects of uranium upon organism [1]. In many cases low concentrations of the detected element on the background of high concentration of the matrix components is an obstacle to its direct determination. Consequently, the analysis must be preceded by various procedures of separation and concentration of the detected element.

Recently, detection of radionuclides in water media using porous scintillators has been proposed [2]. These porous scintillators are organic matrices with through pores, on the surface of which a selective complex-forming substance is fixed. The structure of the material allows the analyzed liquid to penetrate through it. The detected element is accumulated in the scintillator volume, which ensures both concentration of the radionuclides and 4π -geometry of radiation detection.

In our work the ability of the porous scintillators application for the detection of α -nuclides in environmental waters has been shown by the example of the selective determination 239Pu.

A selective sorbent has been chosen for concentration of transuranic elements – a strongly basic anionite VP-1Ap, and its properties have been studied. It has been shown that the degree of sorption of α-emitters by the anionite is close to 100% in a broad pH range; an optimum pH range for sorption (6-10) has been determined.

Technological procedures for preparation of porous scintillators have been improved. Mixing of the component mixture in a ball mill before pressure compaction has been proposed, as well as treatment of the sorbent by a surfactant solution.

To improve the detection accuracy at low activities of transuranic elements, we used 241Am (α-particles with $E_\alpha=5.4$ MeV, photons of γ-radiation with $E_\gamma=59.6$ keV).

The results obtained showed the ability of qualitative determination of 239Pu in water with measurement error 30%.

References

Thermoluminescence (TL) is the emission of light occurring when electrons (or holes) are released from the traps and return to stable states; the escape probability is greatly increased by raising phosphor temperature. Thermoluminescent dosimeter (TLD) is a thermoluminescent phosphor in which ionizing radiation deposits its energy and causes some effects in the crystal structure due to lattice defects. Many unresolved problems may appear when TLDs are utilized, in radiotherapy dose level using radiation fields different from gamma rays.

The studied phosphors have been grown, in form of single crystals; these crystals were crushed and sieved to select polycrystalline powder with grain sizes between 200 and 300 µm. ZrO₂ powder was obtained using the sol-gel evaporation method from a solution consisting of a mixture of zirconium (IV) prop oxide.

Zirconium dioxide (ZrO₂) was investigated for gamma radiation dosimetry purposes. Samples were obtained using precipitation technique. Samples of ZrO₂ were exposed to ¹³⁷Cs gamma radiation source at a dose rate of 1.26 Gy/min at room temperature. Thermoluminescent (TL) glow curve for ZrO₂ were recorded and the energy of the localized states for as-deposited and gamma irradiated samples were calculated. It was found that the TL intensity values were increased as the radiation dose was increased.

Samples of ZrO₂ showed a linear increasing in TL intensity with the increase in radiation dose up to a certain dose level. The observed changes in TL properties suggest that ZrO₂ powder could be considered as an effective material for room temperature gamma radiation dosimetry.
THERMOLUMINESCENT CHARACTERISTICS OF ACTINOLITE-TEFLON COMPOSITES FOR GAMMA HIGH-DOSES

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The continuous progress of the use of ionizing radiations in processes associated to medical, industrial and research applications has been motivating the development of new thermoluminescent materials applied to high-dose dosimetry. Many materials as glasses, ceramics and crystals have thermoluminescent properties; however, they need to combine characteristics that limit their use in the radiations dosimetry [1]. The silicates represent 92% of the whole percentage volume of the minerals of the earth crust [2], but studies about high-dose dosimetry are still scarce. The dosimetric properties of Jade were already studied using the thermoluminescent technique, showing its potential use for high-dose dosimetry[3]. The objective of this work was to study the dosimetric properties of actinolite:Ca₂(Mg,Fe)₅(Si₈O₂₂)(OH)₂ (a Brazilian silicate of the Jade family) for gamma high-doses. The sample was received in the form of rude mineral, and grains were obtained with diameter between 0.074 and 0.177mm. Its chemical and mineralogical composition were obtained through analyses using the neutron activation and X-rays techniques. Pellets of Actinolite-Teflon (50mg) were prepared in the proportion of 2(Teflon):1(actinolite). For reutilization and to avoid residual TL, the pellets were thermally treated at 300°C/1h. The samples were irradiated with ⁶⁰Co and X-rays. The TL glow curves were obtained for doses from 0.5Gy to 20kGy, using a Harshaw TL reader of Nuclear Instruments Systems, model 2000 A/B; the data acquisition was performed using a virtual instrument (ADC-212 Pico Technology Ltd.) and a personal microcomputer. The glow curves present two peaks at 110°C and 220°C. The TL response repeatability presented a maximum coefficient of variation of 4.8%. The calibration curve is linear between 0.5Gy and 100Gy. Results about energy dependence and minimum detection limits will be presented too. The preliminary results show that the material presents usefulness for high-dose dosimetry.

References

Strontium tetraborate SrB$_4$O$_7$ (SBO) is a promising nonlinear optical material. Recently SBO activated with rare earth ions has been intensively studied as a storage phosphor [1, 2]. In [3] we have reported photo- and thermoluminescent (TL) properties of polycrystalline powders of strontium tetraborate, activated with different concentration of europium ions (SBO:Eu$^{2+}$). However, there is no information about TL characteristics of SBO:Eu$^{2+}$ single crystals.

In this work photo- and TL characteristics of SBO:Eu$^{2+}$ (0.033 at. %) single crystals irradiated by X-ray and $\gamma$-ray have been studied. SBO:Eu$^{2+}$ single crystals have been grown from the melt using Czochralski method. At the photo-, X-ray excitation SBO:Eu$^{2+}$ single crystals display wide emission band with a maximum at $\lambda$=367 nm, corresponding to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transitions of Eu$^{2+}$ ions. TSL of SBO:Eu$^{2+}$ single crystals is presented by the three peaks in the $T=300-500$ K temperature range. The most intensive peak is observed at $T=418$ K. Energy storage efficiency of SBO:Eu$^{2+}$ single crystal is one order of magnitude higher than in to polycrystalline sample, and 45 times higher compared to the LiF:Mg,Ti (TLD-100) industrial dosimeter. Trap parameters of main TSL peak of SBO:Eu$^{2+}$ single crystals have been determined. The TSL spectrum corresponds to Eu$^{2+}$ emission. TSL dose response and fading of SBO:Eu$^{2+}$ single crystal sample have been determined and compared with polycrystalline one. High TSL yield in conjunction with non-hygroscopicity allows one to consider SBO:Eu$^{2+}$ single crystals as a promising material for dosimetry of ionizing radiation.

References

NEW SCINTILLATION MATERIALS AND SYSTEM FOR REGISTRATION OF RADIATION

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Scintillation method is still one of the main used for registration ionizing radiations. Advantages of scintillation method are enlarged by the possibility of its using as scintillation indicators and screens. In this connection single crystals, fibre crystals, films scintillation and combine scintillation detectors are widely used in nuclear physics, physics of high energies, geophysics, biophysics, biochemistry, radiochemistry, medical radiation, for equipment and industrial complexes of nondestructive radiation control as well as in these ones of radio ecological monitoring of areas, water and territories. Some of scintillation detectors and systems have been developed at Ural State Technical University (USTU). For example, RUS-patents №№ 2065614, 2066464, 2088952, 2094823, 2142147, 2143711, 2154290, 2158011, 2189057, 2190240.

During the last 2005 year at USTU some new scintillation detectors and systems for registration gamma-rays, beta-particles, electrons and neutrons have been developed on the level of inventions. The review of these inventions [1–10] is presented in this report with examples of invention with collaborators from France and Kyrgyzstan [3–9].

References

X-ray storage phosphors are materials capable to store the energy of incident radiation in the form of stable electron and hole pairs. X-ray storage phosphors [1] are alternatives to conventional silver-based film for industrial and medical radiography. Information in X-ray storage phosphor screens is stored in the form of electron and hole trap centres stable at room temperature. Upon photo-stimulation of the electron trap centres, the electron recombines with the hole trap centres resulting in luminescence (PSL) at a nearby activator which is usually a rare-earth dopant ion. The most commonly used X-ray storage phosphors are BaFX:Eu\(^{2+}\)(X=Br, Cl).

Thermally activated recombination processes of radiation defects in undoped and Eu\(^{2+}\)-doped BaFCl polycrystalline powders X-ray irradiated at room temperature have been studied by using thermoluminescence (TL), diffused reflectance and photostimulated luminescence (PSL) measurements and X-ray excited luminescence (XL).

The glow recorded in undoped samples shows two dominant peaks at 375K and 422K, which are attributed to F centre recombination [1], accompanied by two weaker ones at 500K and 670K. In the Eu\(^{2+}\)-doped samples the glow curve presents several TL peaks at 365K, 410K, 472K, \(\sim\)520K and a very strong peak at 645K; TL spectra have shown the Eu\(^{2+}\) 4f-5d broad band luminescence from 385nm.

Diffuse reflectance and PSL stimulation spectra have shown the well known peaks from 450nm and 550nm attributed to the photostimulable F centres [2]. The PSL measurements performed after subsequent thermal bleaching of each of the TL peaks have shown that the PSL is stable up to higher temperatures and decrease completely after the thermal bleaching of the 646K TL peak.

After the optical bleaching of the PSL with 550nm light, the diffuse reflectance peaks decrease almost completely and all the TL maxima partially decrease except the 646K which is completely bleached.

Experimental results indicate that the TL originates from several types of trapped charge populations, the Eu\(^{2+}\)-trapped hole centres playing the role of recombination centres. However only the deep traps associated to the 646K are directly related to the PSL effect. By analogy with the “aggregate model” of the PSL effect [3] we associate this peak with the thermally activated inside the triple aggregates (Eu\(^{2+}\) - hole centres - centres). The same model is used to discuss the recombination mechanisms responsible for the other TL peaks.

References
SIMULATION OF OPTICALLY-STIMULATED LUMINESCENCE OF ZIRCON

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Mineral zircon, ZrSiO₄, is a candidate material for optical dating, because it exhibits luminescence due to a significant content of radioactive uranium and thorium. In view of the high internal dose rate, it is expected that zircon dating will not be affected by eventual problems of small signal to noise ratios. For this reason optical dating based on zircon might be particularly useful for dating of ultra-young samples, which could make zircon dating a reliable tool in environmental investigations and forensic examinations.

From experimental point of view, optically-stimulated luminescence (OSL) of zircon has not been studied systematically. Therefore, the objective of this communication is to investigate by computer simulation (i) what might be expected from zircon during real experiments and (ii) which type of experiments should be administered. The kinetic model of zircon thermally-stimulated luminescence (TL) developed earlier [1] has been modified and used to investigate various aspect of zircon OSL optically-stimulated luminescence (OSL) of zircon. Both selective (in a narrow trap depth interval) and broadband optical excitation of filled electron traps have been considered. Usually luminescence-dating methods involve, as a necessary step, laboratory irradiation at dose rates much higher than the dose rate of natural radioactivity. Even in the simple case of selective excitation simulation of zircon OSL has revealed significant and complicated dose-rate effects [2], which can not be removed by a simple preheat, as used frequently in dating routines. The numerical model suggests that the problem of dose rate effects can be solved by laboratory irradiation at elevated temperatures followed by a preheat. The applicability of the single-aliquot regenerative-dose (SAR) method for dating with zircon has been studied by means of computer simulations using the set of zircon parameters obtained in earlier TL studies. The successive steps of the SAR protocol has been simulated in order to determine the most vulnerable parts of the procedure, which influence the accuracy of the dating experiments. In the standard SAR method laboratory irradiation is performed at room temperature. We have investigated the possibility to irradiate samples at elevated temperatures. The reason is that in our previous studies of TL we have established that laboratory irradiation (high dose rates) at elevated temperatures leads to more equilibrated systems of filled and empty electron/hole traps, which are nearly identical to the systems of filled and empty electron/hole traps formed under natural conditions (low dose rates). Simulation results show that a significant improvement in accuracy of the equivalent dose determination by the SAR procedure can be obtained by combining laboratory irradiation at elevated temperatures with a preheat at a special temperature.

References

Thin films and low-dimensional systems
COMPOSITION-GRADIENT BST FILMS: TECHNOLOGY AND PROPERTIES

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Due to development and optimization of modern technology, the composition-graded materials became recently an object of a great interest for both general science and practical application. Prospective pyroelectric properties have been recently discovered in hetero- and composition graded FE materials [1-6]. For example, in conventional pyroelectric detectors the pyroelectric coefficient is of the order $p \sim 10^{-8}$ C/cm$^2$K. For most sensitive hybrid structures based on Ba$_{1-x}$Sr$_x$TiO$_3$ single crystals $p \approx 2.3 \times 10^{-5}$ C/cm$^2$K, but such structures appeared to be expensive. At the same time rather cheap and composition graded FE structures (e.g. FE film) under the action of periodic electric field demonstrate effective temperature dependent charge pumping phenomenon with an effective pyroelectric coefficient of $p_{\text{eff}} \sim 5 \times 10^{-6}$ and even $6 \times 10^{-5}$ C/cm$^2$K. Both general science tasks and practical application development require additional research focused on the discovery of the nature of this phenomenon, which is still unclear. Complex investigation of these materials will also help to improve the composition-graded materials preparation technology and will allow the fabrication of graded structures with a-priori given well-controlled gradient.

In this work, an experimental study and technology details of BaSrTiO$_3$ (BST) gradient films are presented. BST films were fabricated with low pressure plasma jet system which allows the variation of the Ba/Sr ratio during the deposition process. Structural properties, surface morphology, optical properties (including the depth profiles of refractive index) and electro-physical properties were investigated for a deeper understanding of the origin of the giant pyroeffect and other phenomena in composition-graded films.

References

Er-doped SiO₂ has attracted much attention as a possible pathway to the realization of Si-based optoelectronic devices. Of particular interest is how the presence of silicon nanocrystals affects the Er emission in this host material. We investigated thermally grown oxide layers that were ion implanted first with Si and annealed to form nanocrystals of 3-4nm size. Subsequently the samples were implanted with Er and annealed at different temperatures. In such samples, there are three types of principally different environments for the Er defect to be considered: (1) within, (2) near, and (3) far away from silicon nanocrystals; each environment having the possibility for clustered and isolated Er ions. We present site-selective photoluminescence results for various excitation and emission channels. With the intention to identify the nanocrystal related Er-sites (1) and (2), we compared samples containing nanocrystals with samples that don’t. Despite our good site-selectivity, we were unable to find any special signature of those defect types, suggesting that their local environment is similar to that of isolated Er ions in SiO₂ and excluding type (1) as a main contributor to the emission.

In both types of samples, we observed Er clustering sites which become dominant as the Er activation anneal temperature is increased (Fig. 1). This Er clustering site emission is decreased in the samples containing nanocrystals, indicating that the excess silicon is beneficial and inhibits the formation of the clusters similar to Al in SiO₂ glass.

Figure 1: Image and contour plots of excitation/emission data for Er-doped SiO₂ (without nanocrystals) across a range of Er activation anneal temperatures. Clustering sites indicated by the dotted white line.

We further investigated thermally grown oxides for which the Er doping was performed by ion implantation in the Si prior to the oxide growth. Preliminary results indicate that Er ions are indeed present in the oxide layer and are optically active, but that clustering is prevalent due to the high oxidation temperature (1100°C).

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Lithium niobate LiNbO$_3$ was prepared as a thin film layered structure deposited on stainless steel substrate using e-gun evaporation. The Li doping was provided for by the formation of Li-Nb-O/Li/LiNb-O sandwich structure and annealing at about 250 °C [1]. AC impedance spectroscopy measurements were performed on the samples at temperatures from the interval between 28 and 165 °C and in a frequency range of $10^{-3}$ to $10^6$ Hz. Using the values $Z'$ and $Z''$ at different frequencies, the dielectric parameters – parts of the complex permittivity $\varepsilon'$ and $\varepsilon''$ and loss tangent $\tan \delta$ were calculated.

From the frequency behavior of $\tan \delta$ in Fig. 1, an occurrence of two polarization processes can be seen. The first process decreases its relaxation time with temperature. The maximum of $\tan \delta$ appears at the lower frequency comparing with the second relaxation process. On the other hand, the maximum of $\tan \delta$ belonging to the second relaxation process is shifted down from the range of higher frequencies. The two maxima merge at temperature of about 120 °C. The results prove validity of the proposed equivalent circuit where the first RC element represents the bulk of material and the second RC element belongs to the double layer at the metal interface.

References

PHOTOLUMINESCENCE AND OPTICAL ABSORPTION OF THIN NANODIAMOND FILMS

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Nanocrystalline diamond (NCD) films can become a preferred diamond form for many future applications. They exhibit excellent optical and electromechanical properties, low surface roughness, and can be deposited at low cost over large area by microwave plasma-enhanced chemical vapour deposition (MWPE CVD) in hydrogen-methane plasma. However, NCD films grown by MWPE CVD consist of small grains with large amount of grain boundaries resulting in increased defect density. Thus, their properties differ in some aspects from those of perfect single crystalline diamond and polycrystalline CVD diamond thick layers.

In this study, photoluminescence (PL) and absorption spectroscopy have been used in order to investigate the electronic properties, defects, and impurity states in the energy gap. We were able to detect new defect states in the gap, which are characteristic for nanodiamond.

Nanodiamond films with thicknesses within the 200-1000 nm range were grown by MWPE CVD on silicon (100) substrates. After then, windows of 6x6 mm² were opened in the substrate by directional etching, leaving perfectly transparent, self-supporting nanodiamond membranes [1]. The structural properties of the films were visualized using scanning electron microscopy and atomic force microscopy. Typical nanograin sizes in the range 20-100 nm have been observed. The refractive index \( n \), the absorption coefficient \( \alpha \), and the thickness of the NCD thin films were calculated from the measured spectral dependence of their transmission and interference fringes using a procedure described in [2]. Photoluminescence emission and excitation spectra were studied within a wide temperature range (12 – 300 K) and the spectral (220 – 900 nm) region. PL emission spectra of NCD at 12 K consist of two main broad emission bands centred at 2.2 and 2.4 eV, two weak bands centered at 1.8 eV and 1.55 eV, and one sharp peak centred at 1.79 eV. Character of the observed bands and peak is partially related to the process conditions of NCD thin film growth. The origin of all the bands is discussed in detail and their connection with the unintentional incorporation of Si and N is shown. Finally, the experience with utilization of NCD films for construction of diamond-based DNA sensors (gene chips) from point of view of their PL will be reported too.

References

Transparent conducting non-doped and indium-doped zinc oxide (ZnO) thin films have been deposited by the spray pyrolysis method at 350°C substrate temperature. X-ray diffraction spectra of the films have shown that the films are polycrystalline and hexagonal wurtzite in structure. From these spectra, grain size and texture coefficient (TC) are calculated. The analytical method for calculating lattice constants is used to calculate a and c for the films. The results demonstrate that the non-doped ZnO thin film exhibits the preferential orientation of (002) plane, while In-doped ZnO thin films show high orientation of (101) plane [1, 2]. The scanning electron micrographs showed that the surface morphology is affected by the indium content. Depending on the increasing indium concentration, the surface morphologies of the films were deteriorated. These results are attractive to applications in solar cells.

The average optical transmittance of indium-doped ZnO thin films was over 84% in the visible range. The direct band gap value of the non-doped ZnO film was approximately 3.26eV. The $E_g$ value of the film was abruptly affected by indium incorporation. The widening of the $E_g$ attributed to the Burstein-Moss shift [3].

Electrical conductivity measurement of Ag-ZnO:In-Ag structures have been carried out using the two-probe method in dark, in the range of temperature from 10 to 320K. The conductivity of all the films increases with increase in temperature. The indium incorporation affects the conductivity of ZnO films. The 1 at.% In-doped film had a higher conductivity than other films and its value was 1337(ohm.cm)$^{-1}$ at 300K. These films present a high conductivity, as required for most contacts in optoelectronic applications [4]. In 225-320K, the activation energies $E_a$ values are estimated to be 16-22meV for the ZnO thin films. These values could be attributed to the donor levels formed by interstitial zinc atoms and ionization energies of oxygen vacancies stated. Furthermore, the activation energies increasing by indium incorporation have been considered to be closely related to the impurity band may be likely formed [5].

Consequently, the films obtained by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells and piezoelectric devices.

References

Nanosized materials are of particular interest for understanding the role of a dimensionality and surface states in optical, electrical, elastic properties and interparticle interactions. Surface states seem to be crucial in the application of GaN nanowires as building blocks for self-organizing nanostructures. In the present work an ab initio calculation of wurtzite-type GaN nanowires has been performed for different surface configurations. Generalized gradient approximation of density functional theory has been used for band structure calculations. Nanowires grown along $c$-axis have been considered as systems which are infinite and periodic in one dimension. The maximum diameter of calculated nanowires was 2 nm, which is smaller than obtained in experiments. Nevertheless, the main features have been reproduced at this size. It is stated that structural properties in the interior part of the considered nanowires are close to those obtained for the bulk material. The total energies per formula unit for different shapes of nanowires show that the most stable structures do not contain surface atoms with two dangling bonds. Therefore those nanowires that are containing surface elements similar to (100) and (110) surfaces of bulk GaN are energetically preferable. In order to show this similarity, which is not only topological, local properties of surfaces of nanowires and mentioned plane surfaces of the bulk material have been compared.
Composite materials on the base transparent insulators with metal nanoparticles have a high potential for optoelectronic application as a materials with enhanced nonlinear properties. The materials have a large third-order susceptibility especially around surface plasmon resonance in the visible light region. For optical device application non-linear optical materials with the following properties: picosecond or shorter response times, low-power switching threshold, high thermal stability, low two-photon absorption, wavelength tunability, and a high threshold for laser-induced damage are required. Alkali halide crystals with embedded metal nanoparticles still didn't consider as nonlinear materials. Among alkali halides crystals the LiF is most preferable because of its excellent physical and chemical properties. The crystals with colour centres have been used for wide band laser generation and it have been shown LiF thin films possibility as active waveguides [1]. Nanosize metallic particles in LiF crystal give chance new application of the crystal as an optical switching element with ultra fast response time and active waveguide based on the same host material.

The LiF crystal samples of 10 × 10 × 1 mm$^3$ sizes were used, which were bombarded by Cu$^{++}$ or Ag$^+$ ions. The ion fluencies were 5×10$^{16}$ and 1×10$^{17}$ ions per sq. cm and ion energy was about 100 keV. After ion bombarding an absorption $F$ band appears at 250 nm, which indicates the intrinsic lattice defects formation such as $F$-centres. The next stage was annealing of the ion bombarded crystals at near-melting temperature. When the annealing temperature rose to 650ºC, a weak absorption band appears at 570 nm in LiF implanted by Cu$^{++}$ ions. It should be note that so high annealing temperature leads to disappearing of all absorption bands in the irradiated crystals, due to disruption of the intrinsic defects and reconstruction of the regular lattice structure. On the other hand, the close band location has been observed earlier in amorphous silica glass and it is ascribed to surface plasmon resonance in nanosized copper particles. Hence, it is naturally to relate the absorption band appearance at 570 nm in our case with surface plasmon resonance of the copper nanoparticles. Taking into account that depth of the embedded ions layer is near 60 nm, one can estimates the peak of absorption coefficient as of the order of 5×10$^5$ cm$^{-1}$.

By means of the Transmission Electron Spectroscopy (TEM) it was shown that the copper particles distributed throughout the metal doped layer of the crystal have quasi spherical shape with 10–30 nm in diameter and average inter-particle distance of 50–80 nm. Hence, the present report shows possibility of manufacture of the nanosize copper particles in LiF crystals.
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ADSORPTION AND DESORPTION OF OXYGEN IN ZnO THIN FILMS DURING PHOTOCONDUCTION MEASUREMENTS

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The slow UV photoconduction response of ZnO thin films has been attributed to a surface related process where the chemisorbed oxygen ions on the surface of ZnO act as shallow traps that capture nonequilibrium holes, thereby releasing slowly electrons responsible for the conduction [1,2,3]. Adsorption and desorption of oxygen at the surface appears to influence strongly the photoconductivity [4]. In this work, we investigate this effect during the photoconduction of ZnO thin films by measurements of the photocurrent in an atmosphere of air and in an atmosphere of nitrogen at different temperatures. The photoconduction in air fades away after irradiation, whereas in nitrogen atmosphere, the conduction is more persistent (Fig. 1).

![Figure 1: Photocurrent curves of ZnO under UV light illumination in (a) air and (b) nitrogen atmosphere at 300 K](image)

We discuss an alternative mechanism for the photoconduction in ZnO thin films based on the creation of oxide vacancies and interstitials during the illumination with UV. A simple model is proposed that includes the formation and recombination of the oxygen vacancies and interstitials, and the adsorption and desorption of oxygen at the film surface.

References

The results of optical study of various type of diamond containing materials are presented in the work. We just dealt with three types of samples. First, these were oxide thin films created on the glass or quartz substrates, where nanoparticles of diamond had to amplify intensities of the radiations transitions in activator rare earth ions, especially, Yb$^{3+}$ ions. Really, efficiency of the Yb$^{3+}$ ions inner emission from $^2F_{5/2}$ level and charge transfer luminescence are determined by non radiation and radiation excitation energy transfer from charge transfer state to the mentioned above level of Yb$^{3+}$, by rate of direct inner excitation and transfer of excitation from electron-hole pairs created under high energy excitation, as well as by cooperative processes and formation of paired centres. These films were made by sol – gel method.

Second, there were modern electro technical composite materials (CM) those contain of diamond films and copper substrate (C-Cu). These CM allow solving the problem of the modern radiators for microchips design. These CM was made by CVD-method. The diamond layers were spread onto the copper foils with the following diffusive welding of bi-layers into a monolith. The thickness of copper (h) and diamond layers (H) was established it that why, that the thermal stress relaxation is realized in CM owing to the copper layers creep age. CMs where diamond layers are the compositions of micro layers were made too.

Natural mineral diamonds originated from various fields were third type of the samples. They had been used as patterns for comparative analysis.

Optical properties of mentioned materials were investigated. Main attention was paid to study behaviors of luminescent characteristics, as they make available to control the change of defect and impurity composition in its variety after thermal treatment and irradiation of diamond. Optical absorption, luminescence spectra, spectra of luminescence excitation, and kinetic of the luminescence decay were monitored in the wide range of the samples temperature (4.2 – 300 K) and wave lengths of light (20 – 1200 nm). These data are compared with some structure and electro physical characteristics of investigated samples.

Experiments with synchrotron radiation were performed at SUPERLUMI station at HASYLAB Laboratory, DESY synchrotron in Hamburg, Germany.
Thin films of bismuth sulfide \([\text{Bi}_2\text{S}_3]\) were prepared by chemical deposition method on glass substrate, using \(\text{Bi}^{3+}\) salt solution, triethanolamine, ammonia and thioacetamide as reacting agents. Thioacetamide has been found to be a useful sulfide ion releasing agent for deposition of \(\text{Bi}_2\text{S}_3\) thin films. The chemical deposition of \(\text{Bi}_2\text{S}_3\) film is sensitive to the pH, composition of the mixture, bath temperature and heat–treatment of the film after deposition. These factors affect the morphology of the deposited layers. The structure characteristics of the prepared samples were investigated by scanning electron microscopy [JSM-T20] and X-ray diffraction technique (Philips type PW 1390). It is found that the films are amorphous when grown below \(373\) K, crystalline when grown above \(373\) K [Fig 1]. The crystalline material had an orthorhombic structure and was highly oriented. The amorphous material that is photosensitive was tested in a photoelectrochemical cell to determine its efficiency in converting light to electrical energy. The electron micrographs show that the deposit was very uniform and free of cracks. The thermal stability of the films were analysed by using Shimadzu [DSC-50], which demonstrate two exothermic peak at \(231.2^\circ\text{C}\) and \(441^\circ\text{C}\).

Fig [1] XRD of \(\text{Bi}_2\text{S}_3\) thin films. (A): as deposited and (B): annealed at 623 K for 1 hour
INVESTIGATION OF LEAD-SULFIDE THIN FILMS DEPOSITED BY CHEMICAL METHOD

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Lead-sulfide (PbS) films have been deposited by chemical deposition method on glass substrate. The deposition of the PbS films was done at room temperature. The advantage of the low temperature used, that the growth process is little possibility of diffusion of constituents of the depositing film into the substrate. The composition of the films was determined by chemical analysis. The principle variations have involved changes in the concentrations of the lead nitrate and thiourea solutions used, the temperature of deposition, and the use of surface seeding nuclei as a means of improving the properties of the films. Microstructure characterization were carried out by X-ray diffraction and scanning electron microscopy in order to determine the crystallite size and study the surface morphologies of the as-deposited and heat-treated films. The grain size of the films as observed by SEM is found to increase with increase in thickness and clear change in the film formation due to annealing. It was established by X-ray analysis that PbS films prepared on glass substrates were polycrystalline and the [111] direction was the primary direction. The film is polycrystalline and the average crystallite sizes {15 nm}. Structural analysis for the powder and thin films were studied by X-ray powder diffraction with the help of very accurate instrument and a group of software programs. Atomic coordinates are (0, 0, 0) and (0, 1/2, 1/2) for Pb and (1/2, 1/2, 1/2) and (1, 1, 1/2) for S as shown in fig {1}. Distance between closest Pb atoms and closest S atoms are 0.42 nm. The differential scanning calorimeter (DSC) spectra shows two exothermic peaks, at {354.67 0C}, and {459.18 0C}.

X-ray diffraction pattern {Philips PW 1390}, scanning electron microscope {JOEL-JSM-T20}, and the thermal analysis {DSC-50} investigations were carried out in films prepared by chemical deposition of PbS.

Fig(1) Structure of PbS thin films.
A new approach through which the initial rise (IR) method can be used to estimate frequency factor ($s$), in addition to activation energy ($E$), is discussed in this paper. Up till now IR method is used to obtain only $E$ from a glow peak. The approach presented in this work requires that the phosphor be irradiated to a dose near or equal to the saturation dose of the glow peak to be analysed. By plotting $\ln(I)$ against $\frac{1}{T}$ for the TL glow peak, one obtains a straight line, which gradient is $-\frac{E}{k}$ and intercept is $\ln\left(\frac{n_0s}{\beta}\right)$. $I$ is intensity and $T$ is temperature. $s$ can therefore be determined from the intercept since $n_0$, which is the area under the glow peak, can be calculated. When the new approach was used to analyse two numerically generated glow peaks, the $E$ and $s$ values used to generate the glow peaks were reproduced within a reasonably good accuracy. Two experimental glow peaks were also analysed using the new IR method approach and peak shape method. There is a good agreement between the values of $E$ and $s$ obtained by the two methods.
Poster Session II
Impurity-vacancy complexes, dielectric relaxations, ionic diffusion
Mn centres in the model perovskite-type oxide SrTiO$_3$ (STO) have been a subject of a number of studies, starting from the early pioneering work by Mueller [1]. It was found that Mn ions occupy Ti site as cubic $Mn^{2+}_T$ centres. The reduction treatment is typically accompanied by the rapid decrease of the $Mn^{4+}_T$ centres and concomitantly produces cubic $Mn^{2+}_T$, axial tetragonal $Mn^{2+}_T - V_o^{-}$, and highly anisotropic $Mn^{2+}_T - V_o^{-}$ centres [2,3]. In addition, the presence of $Mn^{2+}_T$ in inhomogeneous distorted octahedral sites was reported for polycrystalline Mn-doped STO [4].

A new motivation for studying Mn doping effect in perovskite lattice has recently emerged because of: (i) attractive functional properties of Mn-doped STO electroceramics [5,6]; (ii) improvement of ferroelectric and pyroelectric properties in Mn-doped PbZrTiO$_3$ thin films [7]; (iii) unusual Debye-type relaxation and polar behaviour observed in STO:Mn ceramics [8,9]; (iv) promising properties of STO:Mn as diluted magnetic oxide for spintronic applications based on transparent materials [10].

In the present work, we will overview the results of Mn doping effect on the structural and dielectric properties of STO, especially focusing on the elucidation of the nature of dielectric relaxation. The data for Sr$_{1-x}$Mn$_x$TiO$_3$ and SrTi$_{1-x}$Mn$_x$O$_3$ ceramics and for SrTiO$_3$:Mn single crystals will be presented. In the latter case, the effect of the reduction treatment has been evaluated by means of different spectroscopic experiments (f-T low frequency dielectric permittivity, electron paramagnetic resonance, optical absorption, Raman spectroscopy) in order to identify the type of dominant Mn-related centres and to study their role in dielectric properties.

References

Li DOPING EFFECTS ON PROPERTIES AND PHASE TRANSFORMATIONS of KNbO$_3$.

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Properties of the materials containing randomly distributed dipole defects with orientation degree of freedom are an important topic in the physics of dielectrics. In this concern, attractive properties, dynamics and cooperative dipole ordering effects induced by Li admixtures in highly polarizable model quantum paraelectric perovskite-like oxide KTaO$_3$ (KTO) have been subject of extensive studies for a long period of time (see e.g. [1,2] and references therein). Li$^+$ ions substitute for K$^+$ taking six off-centre positions in the potential wells along the $<100>$ directions. This crucially modifies KTO properties, leads to appearance of a large relaxation polarization contribution to the dielectric permittivity and induces various low-temperature multi-scale dipole ordering effects, form polar glass to long range ordered polar states, depending on Li impurities concentration.

While the case of paraelectric cubic KTO have been investigated throughout enough, Li doping effect for related KNbO$_3$ (KNO) is not known at all. At the same time, potassium niobate is a well known ferroelectric, obeying three cubic-tetragonal-orthorhombic-rhombohedral ferroelectric phase transitions (PT) at 703 K, 493 K and 223 K respectively, keeping its orthorhombic symmetry from -50°C to 220°C. It has the largest effective nonlinear optical coefficient among the commonly used inorganic crystals, however, heating over 210°C and cooling below -40°C can easily destroy the crystal which limits its applicability for practice.

We report on the first synthesis and study of the Li doping effect on properties and phase transformations of potassium tantalate. Transparent colourless K$_{1-x}$L$_x$NbO$_3$ (KLN) single crystals with $x$ = 0.03 and 0.06 (in the batch) have been grown using a process similar to that described in [3]. Low frequency complex dielectric permittivity (100 Hz – 1 MHz) was measured within the 4.2 – 800 K temperature region. We believe that like in KTO, Li$^+$ ions substitute K$^+$ lattice sites in KNO and form strong $<100>$ off dipole centres. It was found that Li dipole impurities do not destroy dominant KNO lattice dynamics and all three characteristic PT remain the same in KLN. However, in contrast to KTO, low frequency dielectric dispersion related with Li$^+$ off centres reorientation did not reveal in KLN. Li$^+$ doping appreciably increases dielectric permittivity temperature maximum in the region of cubic-tetragonal PT. But the most important fact is that Li doping enlarges temperature region of the tetragonal phase stability, and cubic-tetragonal-rhombohedral PT points appears to be at 723 K and 458 K respectively for $x$ = 0.03.

Obtained data are supplemented by optical spectral and thermo-optical experimental results, and KNL ceramics investigations are discussed.

References

AN X-RAY ABSORPTION SPECTROSCOPY STUDY OF SOGGY SAND ELECTROLYTES

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‘Soggy sand electrolytes’ are new class of electrolytes consisting of liquid non-aqueous salt solutions (e.g. alcohols) and solid insulating particles (e.g. silica, alumina, titania, etc.) [1,2]. At high second phase content, the systems show strongly enhanced conductivities (when compared to the non-aqueous solution) and are a viscous grain ensemble wetted by the liquid. Unlike solid-liquid composites the effects are not simply additive but appear synergistic in that the overall conductivity is significantly higher (up to an order of magnitude) than the constituent phases. These new materials combine very high conductivity with the favourable properties of soft matter and have potential applications as battery electrolytes. The ALISTORE Network has undertaken detailed studies, both experimental and theoretical, of these materials.

The ionic conductivity of solutions salts in liquid alcohols is relatively low. This is because of the low dielectric constant of the alcohol and hence the presence of relatively few ‘free’ ions which can conduct; the bulk of the ions are bound in ion pairs. The conductivity enhancement on the addition of silica has been explained as due to the adsorption of one of the ions, most likely the anion, onto the surface of the silica and breaking up the ion pairs. It was sought to test this hypothesis with XAS studies.

A range of salts were studied where the ions were readily accessible to XAS, e.g. Rb and Br K-edges, in a number of solvents, e.g. THF and ethylene carbonate/dimethyl carbonate. Typical data for these systems are shown in Figure 1.

The EXAFS oscillations on the addition of silica were stronger and the peaks in the Fourier transform were enhanced. This is consistent with the model in which the Br⁻ ions are adsorbed at the silica surface, i.e. there is a more ordered structure around the Br⁻ ion than that found in the pure THF solution. These studies are now being extended to encompass polymer electrolytes (salts dissolved in polyethylene oxide) where the addition of silica has been reported as enhancing the ionic conductivity.

Figure 1. The FT of the Br K-edge EXAFS of 0.1M LiBr in THF at 273K. Solid line pure solution, dashed line with 10% silica.

References
ORIGIN OF 1/F NOISE AS A RUNAWAY PHENOMENON DUE TO THE ZERO-POINT FIELD (ZPF) OF QUANTUM ELECTRODYNAMICS (QED)

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The origin of electron transport noise whose power spectral density is inversely proportional to the frequency $f$ has been realized after 80 years of attempts. Here we give its conceptual explanation that has required a catena of five ideas and corresponding results: 1) The reduction of the nonlinear Boltzmann equation with electron-electron ($e-e$) interaction to a Fokker-Planck (denoted as $e-e$ FP) equation containing two electron collision frequencies $\nu_1(\nu)$ and $\nu_2(\nu)$; 2) The application of the $e-e$ FP to materials and its steady state solution that depends on $\nu_1(\nu)$, $\nu_2(\nu)$, and the square $a^2$ of the acceleration $a = eE/m$; 3) The steady-state solution of the $e-e$ FP equation becomes similar to the Fermi-Dirac distribution function if $a^2$ is considered as mainly due to the zero-point field (ZPF) of quantum electrodynamics (QED) or, realistically, of stochastic electrodynamics (SED); 4) In this $\delta \nu$ range the $e-e$ FP is similar to the usual FP solved by Stenflo when $\nu(\nu) \propto 1/\nu$. It is just because of $a^2_{ZPF}$ that for any conduction current there is always a small $\nu$ interval $\delta \nu$ for the electron speed $\nu$ where $\nu_1 \propto \nu_2 \propto 1/\nu$, condition that is at the threshold of runaways. The relevant time-dependent Green solution of the $e-e$ FP equation decreases as $\tau^{-\varepsilon}$ with $\varepsilon \leq 0.03$. The consequent power spectral density $S(f)$ turns out to be $\propto 1/f^{1-\varepsilon}$ in an indefinite medium. Our $S(f)$ also depends on the electrons concentration $N$ and excellently fits the experimental data; 5) In a finite sample the memory or a fluctuation is preserved beyond the electron transit time because the transmission of information is mainly due to $e-e$ interactions and to the diffusion coefficient $D_L$ that diverges at the threshold of runaways. A pimple (due to fluctuation) in the distribution function on the electron speeds is almost crystallized, decaying as $\tau^{-0.025}$ without any cut-off at the transit time.
In this work, we study the conduction mechanisms in RF-sputtered BaTiO₃ thin films deposited at low temperatures on copper electrodes. These films are amorphous and possess a dielectric constant close to 20, which make them interesting materials as high-k dielectrics for integrated capacitors. Cu/BaTiO₃/Cu capacitors were fabricated and the transient and steady-state conductivity were measured as a function of temperature and electric field to determine the defects which govern the leakage current.

Current-time measurements performed at constant electric field and at high temperatures reveal a Space Charge Limited Transient Currents (SCLTC) behaviour (Fig. 1 (a)). An experimental investigation, based on the voltage and temperature variations of the transient characteristics, was carried out to identify the transport process. The results show that measured current in the transient regime can be attributed to a low mobility process ascribed to the oxygen vacancies motion across the film. Calculated drift mobility of the oxygen vacancies was temperature dependent with an activation energy around 1 eV. This value is consistent with the activation energy for oxygen vacancies diffusion in bulk titanates.

Steady state currents were also measured as a function of the electric field. The J-E characteristics display a Space Charge Limited Current (SCLC) behaviour (Fig. 1 (b)). Based on the SCLC theory, we can predict the presence of shallow traps at 0.45 eV below the conduction band with an effective density around 4x10¹⁶ cm⁻³.

Figure 1: (a) Transient current response measured at 200°C for different values of DC bias and (b) variation of current density versus applied electric field for temperatures ranging from 50 to 175°C.
DEFECT STRUCTURE OF CADMIUM DOPED CsI-CsBr MIXED SINGLE CRYSTALS

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The CsBr$_x$I$_{1-x}$ solid solution (0.05≤x≤0.09) was proposed before as a new dielectric material for the storage targets of electron-beam memory devices [1]. According to [2], the dependence of the luminescence and scintillation characteristics of CsI-CsBr mixed crystals on bromide concentration testifies to direct influence of defect structure mixed crystals on the performance parameters of materials. The defect formation in CsI-CsBr mixed crystals has been studied before [3]. The results obtained evidence the increase of anion vacancy concentration and unchanged concentration of cation vacancies in CsI$_{0.93}$Br$_{0.07}$.

The present research aims at the investigation of the defect structure of cadmium doped CsI-CsBr mixed single crystals using the electroconductivity and ionic thermocurrent (ITC) methods. This finding reveals that the conductivity of cadmium doped CsI$_{0.93}$Br$_{0.07}$ crystal decreases as compared to that of undoped one which is caused by the decrease of anion vacancy concentration due to cadmium impurity adding. The contribution of cation vacancies (E$_a$=0.64 eV) in the conductivity of cadmium doped mixed crystals seems to be dominant. This assumption has been confirmed by the ITC method. There are two negligible low-temperature maxima at 185 K and 220 K and the intense maximum at 375 K on the ITC spectrum. The existence of maxima in low temperature region evidences the formation of (Cd$^+$-V$_c^-$) and (Cd$^{2+}$-V$_c^-$) dipoles in the crystals understudied. The calculated activation energies of corresponding relaxation processes are 0.12 eV and 0.16 eV, respectively.

References

DIELECTRIC SPECTRA OF ALKALI-METAL-DOPED AND RX-IRRADIATED CAF₂ CRYSTALS

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Information on impurity-defect aggregates in the alkaline-earth fluorides can be obtained from spectroscopic and dielectric relaxation techniques, the last being sensitive to aggregates with a dipole moment which can reorientate through migration of the anions. Temperature and frequency dependence of the complex dielectric constant give information about the relaxation processes and permits the determination of the activation energy and the reciprocal frequency factor of the relaxation time [1-5]. The dynamic techniques, such as ionic conductivity, ionic thermo current (ITC), dielectric relaxation, NMR relaxation, tend to measure the defect properties as diffusion constant and activation energy.

Pure and various concentration Lithium and Sodium-doped calcium fluoride crystals have been grown using the vertical Bridgman method [6]. Transparent single crystals have been grown in graphite crucible in vacuum (~10⁻¹ Pa); the addition of 4 wt% PbF₂ was used as scavenger of oxygen impurities. The 0.60mm thick disks, cut from the obtained single crystals have been irradiated with x rays at room temperature up to 4 hours. Room temperature optical absorption spectra were recorded by a Shimadzu 1650PC (190-1100nm) and FTIR (11000-400cm⁻¹) Nexus 470 spectrophotometers.

Capacitance $C$, conductance $G$, dielectric loss $D$ and $\theta$ measurements were performed on the samples using a RLC Meter type ZM2355, NF Corporation, Japan, over the temperature range 150–300 K, at five audio-frequencies. The real part of the dielectric constant $\varepsilon'$ at various temperature and frequency has been calculated from the measured capacitance $C$. The imaginary part of the dielectric constant, $\varepsilon''$ has been then calculated from: $D = \tan \theta = \varepsilon''/\varepsilon'$. Linear heating rates of 2 K/min were employed from liquid nitrogen to room temperature. The dielectric properties have been measured on the 10 mm diameter and 0.60mm thick disks, before and after RX irradiation.

The objectives of this study are: to analyze the effect of the alkali-metal ions and of the irradiation with x rays on the dielectric spectrum of CaF₂ crystals, to study the temperature and frequency dependence of the complex dielectric constant $\varepsilon^* = \varepsilon' + i\varepsilon''$, and to determine the activation energy and the reciprocal frequency factor in order to characterize the observed relaxations.

References

It is known, that lithium niobate crystals are used in quantum electronics as holographic materials. High temperature annealing of LiNbO₃ crystals has a great scientific interest because of its usage in hologram fixing.

Up to now the changes in optical absorption that take place in LiNbO₃ crystals under the influence of reducing/oxidizing (redox) thermal treatments have been studied at room temperature after a certain annealing procedure.

The present work is devoted to in-situ study of redox processes in pure LiNbO₃ crystals in the temperature range from 300 to 1300 K. This includes measuring of absorption spectra in the region of 300..3000 nm in-situ at high temperature in different atmospheres. The main feature of the experimental set-up used is the possibility of rapid (up to 3 min) replacement of a gas atmosphere in the furnace and the registration of the subsequent redox kinetics at a certain wavelength.

The wide absorption band with maximum at 10000 cm⁻¹ appears in LiNbO₃ crystals during heating from 300 to 1000 K in reducing atmosphere. The absorption growth in the band maximum depending on the temperature was obtained. The form of the dependence allows assumption of its activation character. Another wide absorption band with maximum at 16000 cm⁻¹ appears in LiNbO₃ crystals during the further heating from 1000 K to 1300 K in the reducing atmosphere. After the change of the annealing atmosphere from reducing to oxidizing the absorption bands disappear and the crystal became transparent. After cooling the sample in the reducing atmosphere from 1000 K the absorption band with maximum at 10000 cm⁻¹ decreases and the absorption band with maximum at 16000 cm⁻¹ remains stable up to room temperatures. Cooling the sample in the reducing atmosphere from 1300 K, when both absorption bands are present, does not change the spectra.

The redox kinetics have been analyzed in the framework of different diffusion models. The origin of the absorption changes caused by the redox thermal treatments is discussed in terms of transport and point defect structure of the studied crystals.

Assuming, that the main factor, which calls changes of optical properties in investigated crystals, is oxygen diffusion, one of the reasons of the absorption bands appearance in LiNbO₃ may be formation of bipolarons and polarons as the result of the Nb ions valence lowering during reducing annealing.
Commercially available soda-lime silicate (SLS) glass doped with copper ions has been investigated by using thermally stimulated polarization and depolarization current (TSPC and TSDC) measurements and the transmission electron microscopy (TEM) observations. The dopant ions were introduced into the matrix by immersing the specimens into molten bath of CuCl at temperatures between 723 (i.e. below the glass transition temperature, \(T_G \approx 833 \text{ K}\)) and 903 K (i.e. above \(T_G\)) for times between several minutes and 168 hours. Afterwards, the exchanged specimens have been annealed at 773 K for 5 h in a hydrogen atmosphere.

For all specimens, TSP1, TSP2 and TSD measurements were performed in a wide temperature range (100–450 K) as function of the polarizing parameters (temperature, time and voltage). TEM observations have been done for two types of replica (extraction and shadowed) taken from two exchanged glass-surfaces perpendicular to each other. Not exchanged specimens were also investigated.

It has been stated that TSDC-spectra of samples exchanged below \(T_G\) consist of two depolarization bands (the low (II) and high (III) temperature one) being similar to those recorded for the not exchanged specimens. With the increasing exchange temperature the location, amplitude and the number of bands was altered, and the TSDC spectra of samples exchanged at the highest temperature include only the band (II). The related processes have been explained in terms of interfacial Maxwell-Wagner polarization in heterogeneous dielectrics (band II) and the polarization conduction (band III). In the latter case, one has to consider the presence of some (rather short) conduction paths, which became destroyed in specimens exchanged at the highest temperature. The TSP2 data have been exploited for calculation of the dc conductivity and the related activation energy.

TEM observations have shown distinct changes of the glass morphology, confirming the above mentioned suppositions. It has been evidenced that these changes are consequences of a joint effect of the copper ions and the exchange temperature.
Defects at surfaces and interfaces
The oxide of the zirconium ZrO₂ is one of most widely used in technique. Last time the special attention is spared to the nanosize powders ZrO₂ as the most respective material for an electronic technique (piezoceramic materials on the basis of zirconate-titanate of lead, fuel sells and etc). The electrophysical parameters of these materials are depended on the size of particles, composition and concentration of intrinsic and impurities defects.

By the ESR and NMR methods the influence of annealing on the charge state of nanosize particles defects of zirconium oxide is investigated. The following samples are studied: ZrO₂ – 3% Y₂O₃ – 0,5% Cr₂O₃ (D1) and ZrO₂ – 0,5% Cr₂O₃ (D2).

NMR signal from the hydroxyl groups OH⁻ localized in the crystalline structure ZrO₂ for sample with a yttrium (D1) in 1,5 times more intensive, than for a sample without a yttrium (D2). Annealing of samples at T ≤ 1500°C leads to strong decrease of intensity of the signal NMR OH⁻. After annealing at T ≈ 4500°C hydroxyl groups in the samples D1 and D2 practically disappear.

The loss of hydroxyl groups in D1, D2 samples is accompanied by the change of the charge state of ions of chrome and appearance of the ESR signal, which relate with the ions Cr⁵⁺. The ESR signal in D1, D2 intensive increase after annealing in the interval of the temperatures 120°C – 450°C. The processes of the thermogeneration signal ESR Cr and deleting of the OH- groups are connected. At T > 450°C intensity of the signal I(Cr) reduces.

The nanoparticles ZrO₂ have the maximal concentration of the Cr⁵⁺ ions when the hydroxyl groups (OH) disappear and the specific surface of particles is yet high. Reduction of the ions Cr⁵⁺ concentration at T > 4500°C is related to healing of the defects formed at deleting of the OH-groups from the crystalline lattice and with reduction of specific surface of nanoparticles.

Determined, that the ions of yttrium substantially influence on a width, form and value of the g-factor ESR signals of Cr.

The effect of termogeneration local tensions in the structure ZrO₂ is detected.
THE INFLUENCE OF EXCIPLEX FORMATION AT ORGANIC/ORGANIC INTERFACE ON CAPACITANCE-VOLTAGE DATA

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It has been shown recently [1] that the room temperature capacitance – voltage data of monolayer metal/organic/metal structures provide various information like the bias dependent, at the cathode/organic interface, induced net charge density, the organic charged traps density and their electric field within the organic layer, the exponent of the space charge limited current within such a structure, etc. All such information subsequently lead to the parabolic LUMO and HOMO transport band shape predictions [1], the fact that has been in part independently verified already [2]. The C – U data of the bilayer metal/organic/organic/metal structures [3] are, in addition to the above, characterized also by the excess charge and electric dipole densities that occur in the neighbourhood of the organic/organic interface [4].

In this work the room temperature capacitance – voltage data of Ca/Alq₃(30 nm)/NPB(60 nm)/ITO and Ca/Alq₃(60 nm)/NPB(30 nm)/ITO structures are analyzed /3/. It will be shown that the Alq₃/NPB interfaces significantly differ in the electric dipole densities, Dₚ, equal to 30 x 10⁻¹¹ Asm/m², and the electric fields, E_{int}^{traps}, of the charged trap densities equal to 0.05 x 10⁸ V/m for the former, and 4 x 10⁻¹¹ Asm/m² and 2 x 10⁸ V/m for the latter structure, respectively. In both cases the trap densities, N, as obtained in the fitting, are N_{Alq₃} = 5.2 x 10²³ m⁻³ and N_{NPB} = - 4.8 x 10²³ m⁻³. In addition, although the charge densities occurring at the organic/organic interface are similar in magnitude and positive, i.e. 3 x 10⁻² As/m² for the former and 3.3 x 10⁻² As/m² for the latter structure, the (positive) net charge densities induced at Ca/Alq₃ interfaces at zero external bias, also differ for about the factor of 2 in the above two cases. The relationship between these findings and the exciplex formation will be addressed and the effect of non-radiative relaxation of excitons at the Alq₃/NPB interface on the room temperature C-U measurements will be discussed.

References

INVESTIGATION OF SURFACE TOPOLOGY OF CRYSTALS BY SEM AND AFM PROCESSING WITH MULTIFRACTAL ANALYSIS

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We investigate potassium sulphate crystals, grown up from a solution by a method of slow evaporation at constant temperature. The structure of crystal surfaces was investigated by means of Scanning Electron Microscope (SEM) and Atomic-Force Microscope (AFM). The brought up crystals irradiated with X-ray beams and scanned a surface of this objects. Determining defect formation on a superficial layer, distinctly is shown a branching of growing paths. The set of structural hills, at which steps there is a basic growth of a crystal is found on the crystals surface. The obtained structures are analyzed by a multifractal analysis method.

As objects to study we used crystals of potassium sulfate $\text{K}_2\text{SO}_4$ and crystals of potassium sulfate activated by thallium $\text{K}_2\text{SO}_4: \text{Tl}$. Crystals have been brought up from a solution by a method of slow evaporation at constant temperature. Studying relief of the surface of crystal $\text{K}_2\text{SO}_4: \text{Tl}$, we have found out bow-shaped lines on all surfaces (figure 1). The structure of paths and a branching of growing edges surface of impurity crystal substantially differ from a surface of crystal $\text{K}_2\text{SO}_4$. Here a little bit other structure of a surface is already seen. On the surface of the crystal $\text{K}_2\text{SO}_4$, each line is distinctly visible (figure 2). The paths are straight lines contrary to the previous case.

For the description of systems with the non-uniform, statistically ordered structure it is convenient to use methods of the fractal analysis. Such fractal structures are multifractals and they are characterized by an infinite set of measures. The approach used for studying of these structures allows, besides the geometry of an analyzed sample, to establish connection of their physical and chemical properties with the parameters of multifractal spectrum as the so-called multifractals measures. [1]

Reference

There is a vast scope for technological exploitation of the phenomenon of p to n transition observed in such chalcogenide glasses in preparing a new class of p-n junctions.

\( \text{Pb}_{20}\text{Ge}_y\text{Se}_{80-y} \) \((y = 10 – 25)\) were prepared by melt-quenching process and characterized using X-Ray Diffraction and Energy Dispersive Analysis of X-Ray. Glass Transition Temperature \((T_g)\) and Glass Stability were calculated for all concentrations. Charge transport in chalcogenide glasses is occurred through participation of charged defects "dangling bonds".

Chalcogenides are characterized by the presence of charged defect pairs of the type \( (C^+ \) and \( (C^-) \) where \( C \) is for the chalcogen atom; the subscript and the superscript are referred to the coordination and the charge of defect state respectively. The change of the resistivity as functions of temperature were investigated and as a function of germanium concentration. The mobility of holes and electrons were calculated. A structure model based on the chemical nature of the constituents has been proposed to account for the observed properties of these glasses. The model can be extended to account for Carrier Type Reversal. Effect of Ge incorporation on local structure and qualitative consequences on the energy band structure of \( \text{Pb}_{20}\text{Ge}_2\text{Se}_{80-y} \) glasses has been considered.
Surfaces lead to modification of crystal properties in near surface layer. For example, the presence of developed surface in alkali halide nanocrystals determines the distinctive features of colour centres (CC) formation in them on exposure to ionizing radiation [1]. High radiation sensitivity of crystal surfaces and effects of contacting medium influence greatly on defect formation.

In this paper we will focus ourselves on the study of the spectral properties of $\gamma$-irradiated LiF crystals inside bulk or on a surface. The aim is to investigate the point defect concentrations in the subsurface layer of LiF single crystals and in the bulk. Ratios of the luminescence intensities of $F_2$ and $F_3^+$ CC were measured under excitation in the subsurface layer or in the bulk. For comparison reasons the measurements were performed also after cleaving the irradiated LiF single crystals.

We have found specific features of the intensity ratio between luminescence of $F_2$ and $F_3^+$ CC in the subsurface layer and in the bulk. In crystals irradiated at room temperature (RT) the ratio of the $F_2$ maximum luminescence intensity to the $F_3^+$ one ($F_2/F_3^+$) was more in the bulk in comparison with subsurface layer. The opposite situation was observed in the case of irradiation at temperatures less than temperature of vacancy mobility. The ratio ($F_3^+/F_2$) was more in the bulk than on the surface.

Possible explanations of the measured effects are discussed in the report. The type of irradiation (electrons, ions, $\gamma$ radiation) determines features of radiation damage of subsurface layers, which are caused by specificity of energy state of a surface. A surface is characterized by parameters of a lattice distinguished from bulk, high speeds of diffusion processes and movement of charge carriers. On a surface the bandgap may be substantially different from the bulk. Besides intrinsic surface states on a real surface the centres of localization of charge carriers are created by numerous impurities and adsorbents. For example, OH- ions during irradiation break up to atoms of the hydrogen, being electronic traps, and singly charged oxygen ions O'. In crystals with oxygen content formation of positively charged aggregated centres is suppressed, because oxygen remove electronic traps from a crystal.

The surface and bulk have mutual effect on formation of radiative defects. During irradiation diffusion of ions from volume to a surface takes place, the element composition of a subsurface layer and its charge state change. A surface represents itself as a trap of ions, dislodged in bulk, what increases stability of bulk anionic vacancies.

In case of local heating of a crystal in the region of irradiation (electron irradiation as an example) there should be phenomena of ionic transfer. For crystals with NaCl structure in the region of irradiation ions of metal will accumulate (in subsurface layer), while for crystals with CsCl structure the inverse ratio takes place - accumulation of halogen atoms on a surface.

References

The structure and the dynamical behaviour of oxide surfaces play an important role in phenomena like sintering, grain growth, oxidation, surface roughening, which are related to many technologically important applications [1]. Uranium dioxide is a technologically interesting materials since is used in the fabrication of commercial nuclear fuel [2].

We present a study of the vibrational properties of UO$_2$ (110) surface. Using a rigid ion potential adapted for UO$_2$ [3] we performed molecular dynamics simulations and we calculated the phonon local density of states (LDOS). The phonon LDOS was obtained for both the anionic and cationic sublattices as a function of the distance of the atomic planes from the surface. The observed behaviour along the principal crystallographic directions as a function of the distance from the surface is discussed and related to the topological properties of the surface.

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References

Metal oxide nanocrystallites, such as MgO, CeO$_2$ and ZrO$_2$, are of current interest for their numerous applications for catalysis and nanoelectronics. They can be fabricated in a number of ways, using chemical vapour deposition for example, and can be subsequently annealed to obtain nanocrystallites with a well defined size distribution (typically $d$<10nm) [1]. Although the structures of very small clusters have been well studied [2], relatively little is known about the detailed atomic structure at the surface of real nanocrystallites which may contain upwards of 1000 atoms. Recent transmission electron microscopy (TEM) studies have demonstrated the complex structure of such surfaces [3], although it is difficult to extract anything but qualitative information as TEM reveals a projection through the nanocrystallites. The quantitative details of the surface structure, such as the number of step, kink, corner and perhaps less coordinated sites, determines many important spectroscopic and catalytic properties and yet is presently not well understood.

In order to investigate this fundamental and technologically important problem we have performed novel Monte Carlo (MC) calculations to investigate the equilibrium structures of metal oxide nanocrystallites and to extract the density of microstates. A number of modifications to the standard MC method were made in order to ensure ergodicity and a good sampling of the potential energy surface in a computationally achievable time. We have considered MgO and CaO as model systems as they are well described by a shell model potential, however the methodology we have developed is general. We have analysed the structures generated and drawn connections between their relative energies, degeneracies and structural properties. Accurate quantum mechanical calculations of surface defects using an embedded cluster method [4] have also been performed to validate this approach.

These results are important as they provide realistic structural models of nanocrystallites that can be used in conjunction with quantum mechanical calculations of defects, and can also allow direct quantitative interpretation of spectroscopic data which depends on structural features, such as the relative numbers of 3 and 4 coordinated anion sites for example [5].

References

NANOSTRUCTURED ME/OXIDES COATINGS

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Metal/oxide interfaces play a crucial role in many important present-day technological applications such as optoelectronic and microelectronic systems, heterogeneous catalysis, oxide dispersion-strengthened alloys, powder materials, solid state joint devices, anticorrosion and thermal insulation coating industry, etc.; moreover, they have found important applications in medicine [1]. Strong interfaces between dissimilar materials, such as metal and metal oxide, are also critical for future nanotechnology development. These problems are especially actual for metal/oxide coatings.

In this work Al and Cu coatings on glass and MgO substrates were obtained by the microtribological method of a rotating wire brush at room temperature. As the procedure is performed in air, it involves intensive oxidation of transferred metal particles. Dynamic behaviour of coating formation and particle interaction in conditions of severe shear deformation show similarity to the microscopic act of friction or tribology scheme. The results of SIMS show the presence of metal oxygen compounds practically throughout the coating. The AFM, SEM, EDX and XRD studies of coatings showed that transferred metals have a non-homogeneous, thermally stable composite nanostructure with a grain size from 30 to 200nm. The microhardness values of the obtained coatings were by a factor of 8-13 higher than that for the source metals. Such properties are determined by the nanostructured state of metal based composite coatings, stabilized by the presence of oxide interlayers. The metal-oxide composite coatings show a high adhesion and a good wear resistance. From SIMS and microhardness data it was possible to estimate the mutual diffusion coefficient ($D$) of oxygen in nanostructured Al or Al in glass in the interfacial reaction zone. Assuming, that reaction zone ($\approx 2 \mu m$), $D$ was equal to about $7 \cdot 10^{10}$ cm$^2$/s. This result can be explained with the high density of point defects in the surface layers of oxide and formation of nanostructure in metal during plastic flow [2].

![AFM image of Al coating on glass (a); Microhardness dependence on the indentation depth for Al coatings on Al glass substrates and a depth profile of the intensity of SIMS-signal of Al$^+$ in the Al coating on glass (b).](image)

References

POINT DEFECTS AND INTERACTION BETWEEN DISLOCATION LINES IN GaAs THIN FILMS

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Thin films of GaAs single crystal doped with Cr and, O grown as epitaxial growth has been studied using transmission and, electron diffraction technique. Point defects and dislocation lines have been observed. The contrast and the Burger vectors resulted at (GaAs,Cr) indicate the presence of different types of dislocation lines such as pure edge or mixed dislocation. Two beam - bright field condition beside stereoscopic technique examination were used to throw more light on the formation and configuration of the dislocation; furthermore; Lomer dislocation was also observed and attributed to interaction between two dislocation lines; one has Berger vector of (1/2)a(10\bar{1}) and the other of (1/2)a(0\bar{1}1). Point defects and clusters which have white – black contrast were observed in (GaAs,O). These defects were created as a result of electron beam damaging effect. The population of the defects was found to increase with increasing the exposure to the electron beam. The presence of the clusters attributed to the presence of vacancies and interstitials which were produced from displacing crystal atoms from their lattice sites as a result of the electron beam energy.
INFLUENCE OF IMPURITIES AND OPERATING REGIME ON FORMING DENDRITE STRUCTURES OF KNO₃ CRYSTALS DURING SPONTANEOUS CRYSTALLIZATION

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The process of forming of dendrite structure of KNO₃ crystals from water solution on the dielectric bases (glass, stone, ceramics, wood) during of spontaneous crystallization have been investigated. It was found that due to some impurities it was possible to develop radiate type structure. At Fig. 1a the radiate dendrite structures is presented in comparison with natural dendrites structure, Fig. 1b (both like frost patterns on windows). It was shown that (using process of spontaneous crystallization KNO₃ from water solution with impurity management, using operating regime with chisel) it was possible to create the crystal pictures [1, 2]. Some of such crystal pictures on glass and wood bases are presented at Fig. 2–4. All results are discussed.

References

Quantum Mechanics / Molecular Mechanics (QM/MM) approaches are currently used to describe several properties of silica-based systems, which are local in nature and require a quantum description of only a small number of atoms around the site of interest, e.g. local chemical reactivity or spectroscopic properties of point defects.

We present a QM/MM scheme for silica suitable to be implemented in the general QM/MM framework recently developed for large scale molecular dynamics simulations, within the Quickstep approach to the description of the quantum region. Our scheme has been validated by computing the structural and dynamical properties of an oxygen vacancy in $\alpha$-quartz, a prototypical defect in silica. We have found that good convergence in the Si-Si bond length and formation energy is achieved by using a quantum cluster as small as eight atoms in size. We check the suitability of the method for molecular dynamics and evaluate the Si-Si bond frequency from the velocity-velocity correlation function.

We have further applied this scheme to the study of the properties of organic molecules on two-membered silica rings at the surface of amorphous silica [1]. In particular, we have compared the reactivity of two-membered rings and residual silanols (Si-OH bonds) for the grafting of a TEOS molecule which has the same functional group (ethoxy) of the organosilanes most used in the coatings of optical fibres.

References

Modeling and computational methods
Lithium niobate, LiNbO$_3$, at room temperature is a ferroelectric material with many important technological applications due to its diverse physical properties, which lead to its use in elastic, elasto-optic, opto-electronic, non-linear optic and photorefractive devices. Computer modelling can help understanding the physics and chemistry of the material.

Recently a new set of pair wise potentials were fitted to both the ferroelectric and the paraelectric phases of LiNbO$_3$ [1]. In the present work this new potential set is used to model the important intrinsic defects (Schottky, Frenkel and anti-site disorder), as well as the extrinsic defects induced by incorporation of divalent and trivalent substitutional dopants in LiNbO$_3$ in both ferroelectric and paraelectric phases at 0 K and room temperature.

The substitution of the doping cations was considered at both cationic sites, Li and Nb, and a range of possible charge compensation schemes were considered. When divalent or trivalent metallic ions substitute at the Li site the following charge compensation schemes were considered: Li$^+$ vacancies, Nb$^{5+}$ vacancies, and Li$^+$ substitution at the Nb$^{5+}$ site. On the other hand, when the dopant ion substitutes at the Nb site, the following charge compensation mechanisms were considered: O$^{2-}$ vacancies, Nb$^{5+}$ at the Li$^+$ site and O$^{2-}$ vacancies plus Li$^+$ vacancies. The possibility of incorporation of the dopants via partial substitution at the Nb$^{5+}$ and Li$^+$ sites were also modelled, where the relative concentration of the partial substitution at both cationic sites was set to preserve the charge neutrality. For all the above mechanisms, solid-state reactions were devised and the appropriate solution energies were taken into account to predict the most probable mechanism.

As LiNbO$_3$ shows important optical properties when rare earth trivalent ions are dissolved in the crystalline matrix, the possible mechanism of incorporation of such dopants were also studied. In this case, the relaxed symmetry of the most stable (least energetic) defect configuration was used to calculate the crystal field parameters ($B^k_{4q}$). These parameters were then used to predict the splitting of the 4f energy levels of the rare-earth trivalent ions leading us to predict the location of the main 4f-4f optical transitions. The results were compared to available experimental results.

References

Elpasolites (M$_2$ALX$_6$, with M and A monovalent cations, L a trivalent cation, especially rare earth ions, and X = Br, Cl or F) are a wide class of crystals that have been under investigation due to their optical properties. There is a particular interest in knowing the spectra of these materials, because in the cubic form, each L$^{3+}$ is surrounded by a perfect octahedron of six X$^{-}$ ions in its first coordination sphere meaning that electric dipole 4f–4f transitions of L$^{3+}$ ions are forbidden.

The methodology employed in this work uses a combination of atomistic modelling, in which interactions between ions are described by effective potentials with defects being modelled by Mott–Littleton methodology, and a modified form of crystal field calculations, which takes into account the symmetry of the dopant ion and its surrounding lattice. In the present work the following systems were modelled: Cs$_2$NaLF$_6$, Rb$_2$NaLF$_6$, Cs$_2$NaLCl$_6$, Cs$_2$NaLBr$_6$ (L = Ln$^{3+}$, Y$^{3+}$ and Al$^{3+}$). The potential parameters were fitted to their crystalline structure and agreement between the experimental and calculated values is better than 0.5%. Intrinsis (Schottky, Frenkel and anti-site) and extrinsic defects have also been calculated.

The results obtained from the preceding step are then used to calculate the set of crystal field parameters ($B_k^{\infty}$) that enable predictions to be made about the optical behaviour of the doped materials. The $B_k^{\infty}$ were used to calculate the 4f energy levels of the rare-earth dopant ions in the M$_2$ALX$_6$ matrix, following the same methodology described in previous work [1, 2].

Applications of the method are presented for rare earth doping in the cubic Cs$_2$NaYF$_6$ and Cs$_2$NaAlF$_6$, where energy level comparisons are made with recent experimental results [3], and also in the perovskite system Ln$^{3+}$:Cs$_2$NaAlF$_6$.

References

We present results on an ab-initio study of paramagnetic centres in yttria-stabilized cubic zirconia (YSZ). The doping of ZrO$_2$ with substitutional yttrium introduces oxygen vacancies for charge compensation which make YSZ a fast ion conductor used as electrolyte in solid oxide fuel cells and sensors. At low temperature the oxygen vacancies interact giving rise to complexes such as vacancy pairs assigned to prominent signals in EPR and optical spectra of reduced samples. However, a compelling experimental evidence of the existence of di-vacancy complexes is still lacking. In fact, other extrinsic defects (such as Ti) have also been claimed responsible for the spectroscopic signals. In this work we have studied the electronic properties of paramagnetic di-vacancy complexes by computing the EPR g-tensor from density functional perturbation theory [1]. These first principles calculations allow to discard the experimental assignment of the $T$-centre to an extrinsic Ti$^{3+}$ ion nearest neighbour to a single vacancy [3]. Instead, the calculated EPR g-tensors of both a Zr$^{3+}$ or a Ti$^{3+}$ ion at the centre of a di-vacancy aligned along the $\langle 111 \rangle$ directions are compatible with the experimental EPR signal. However, since the EPR signal of the $T$-centre is correlated experimentally with an optical absorption band at 370 nm, calculated optical excitations in the B3LYP scheme allow us to decide in favour of the Ti$^{3+}$ di-vacancy complex.

References

Atomic scale simulation techniques have been employed to study the intrinsic defect processes of a range of bixbyite compounds using a transferable set of potentials. The efficacy of the approach is demonstrated through comparison of the predictions to previous experimental and theoretical (DFT) results. The aim is to provide data that can be used as a basis for future structural optimizations targeting the use of mixed bixbyite sesquioxides as buffer layers for the fabrication of epitaxially coated high-temperature superconductors on different substrates.

The internal energies for the three possible intrinsic defect reactions (Schottky, cation Frenkel and oxygen Frenkel) have been calculated (Figure 1). From this plot it is evident that the lowest energy intrinsic process is the oxygen Frenkel for all the bixbyite sesquioxides considered. Surprisingly, the oxygen Frenkel energy does not depend greatly on the host cation radius. The implication of this result is that the lowest energy intrinsic defect occurs on the oxygen sublattice and therefore will be most likely to serve as electron and hole traps. These traps are important for the scintillating properties of bixbyite sesquioxides as they act as non-radiative centres that reduce the efficiency of scintillator materials.
The geometry of O-vacancies and Ti-interstitials in defected TiO$_2$ rutile has been investigated using periodic density functional calculations. Both “traditional” point defects (a missing O-ion or an added Ti-ion) and the “reconstructed” models, where a Ti-ion neighbouring the defect is displaced to an interstitial position were considered. The computed energy of the “reconstructed” vacancy was found to be 0.004 eV per formula unit lower than that of the traditional model. By placing the Ti-ion along the pathway the barrier associated with such displacement is estimated to 0.16 eV. Similar reconstruction upon introduction of additional interstitial Ti-ion was found to be thermodynamically unfavourable. Furthermore, thermodynamics of various ordering patterns of defects was examined including that in the shear planes. Comparison of the defect energies revealed that in highly non-stoichiometric rutile Ti-interstitials are more stable than O-vacancies. However, the energy difference decreases rapidly as rutile becomes more stoichiometric, indicating that at very low departures from stoichiometry O-vacancies may become more stable.
For many applications, for example X-ray detectors, laser windows and photorefractive devices, it is necessary to have semiinsulated material with very low conductivity up to $10^{-9}$-$10^{-10}$ (Ohm·cm)$^{-1}$. The doping by shallow donors is often used to grow such high resistive CdTe with desirable properties. Usually as dopants chlorine, indium and aluminium are used due to the self-compensation phenomenon. But gallium, bromine and iodine also can be suitable for these purposes. Since the semiconductor properties depends on point defect (PD) structure and the latter forms at high temperature, the goal of this work was to study PD structure of CdTe, doped by different donors, at high temperature equilibrium and to model it in the dependency on temperature, Cd pressure and dopant activity.

The crystals were grown by Bridgman method. Dopant concentration in the melt was $\sim 5 \times 10^{18}$ at/cm$^3$. High temperature Hall effect measurements were carried out under well defined $P_{Cd}$ pressure up to 900°C. Samples were placed in sealed quartz ampoules and 6 clamped graphite or welded tungsten contacts were used. Using experimental Hall data and Kröger’s quasichemical reaction theory the PD concentrations in CdTe, doped by different donor content, were calculated. In low doped CdTe (Fig.1) the electron content $[e^-]$ didn’t depend on temperature up to 700°C. At higher temperature it is determined by Cd interstitials. For heavily doped material (up to $\sim 10^{20}$ at/cm$^3$) $[e^-]$ was independent both of temperature and Cd vapour pressure. It was sufficiently higher than in undoped CdTe, but does not exceed $2 \times 10^{18}$ at/cm$^3$. Due to strong self-compensation an electron concentration can be expressed by the next equation:

$$[e^-] = [In^{+}Cd] - [In^{+}Cd - 2CdV^-]$$

The self-compensation can be estimated as more than 99.99%.
COIN METAL ADSORPTION ON PERFECT AND DEFECTIVE MgO(001) SURFACES: THE ELECTRONIC STRUCTURE CALCULATIONS AND THERMODYNAMICS OF THIN FILM GROWTH

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Periodic slab simulations have been performed for copper and silver adsorption over uniformly distributed point defects on the non-polar MgO(001) surface (\(F_s\) and \(V_s\) centres caused by \(O^{2-}\) and \(Mg^{2+}\) vacancies, respectively). Defective interfaces have been calculated by means of the CRYSTAL-03 code, which implements Gaussian-type basis set (BS) representation of atomic wave functions. Both \(F_s\) and \(V_s\) centres were modelled by retaining in the vacancy the BS of the missing \(O^{2-}\) and \(Mg^{2+}\) ions.

According to DFT-B3PW calculations, regular surface \(O^{2-}\) ions have been found to be more preferable for metal atom adsorption on a perfect substrate rather than atop \(Mg^{2+}\) ions. On a defective substrate, metal adatom bonding is by a factor of 4-5 larger above the \(F_s\) centres as compared to regular \(O^{2-}\) sites. It is accompanied with a substantial charge transfer towards each adatom (0.3-0.4 \(e\)). When approaching the \(V_s\) centre, metal adatom donates 1.0-1.1 \(e\) towards the nearest surface \(O^{2-}\) ion and its binding energy is much larger than that over the \(F_s\) centre. These results were used as a basis for the thermodynamic analysis of thin metal film growth mode on perfect and defective surfaces. We considered all possible superstructures that may be formed in 2D “adatom-empty site” solid solution above the defective MgO(001) surface with \(F_s\) centres as suggested by us previously [1,2]. It was found that all these structures are energetically unfavourable as compared with heterophase mixture at \(T=0\).

When solving a set of equations for the mixing energies for these phases, we obtained a positive value for the key energy parameter \(V(0)\). This is the Fourier transform of the mixing potential at \(k=0\), which defines the mixing energy in the solid solution:

\[
\Delta E = -\frac{1}{2} V(0)c(1-c).
\]

In the presence of 5% surface \(F_s\) centres \(V(0) = 2.1*10^{-2} eV\) for the case of Cu adsorption. The negative sign of the mixing energy means the disordered distribution of adatoms. Thus, the presence of defects at the surface allows us to predict formation of more or less homogeneous monolayer at the initial stages of the thin metal film growth. In contrast, for the perfect MgO(001) the mixing energy turns out to be positive, and the spinodal decomposition occurs. This means that well separated metal clusters grow on the substrate.

References

Dielectric oxide crystals of tungstates AWO₄ (A = Zn, Cd, Pb) are widely used as scintillation materials in various scientific and technical applications. Despite intensive investigations of their experimental properties carried out in the last decade, there is no a commonly assumed view on the origin of luminescence processes in these crystals. However, it is generally believed that the point defects like vacancies and impurities are the centres of luminescence of the crystal samples obtained in mass production and such defects in great measure determine their scintillation and optical properties. Effective examination of the optical properties of tungstate crystals with defects can be obtained via theoretical calculations of the electronic structure.

Calculations of the electronic structure of AWO₄ (A = Zn, Cd) crystals with defects were done in cluster approach. A small part of each crystal was treated ab-initio in the calculations. Such parts usually contained two closest tungstate groups WO₄ and two A cations. Both the crystals with regular structure and with point defects (oxygen VO and cation VA vacancies, molybdenum and some rare-earth impurities) are modelled in the ab-initio regions. According to the most of the present conceptions, such a part of the crystal should contain the centre of luminescence emission. Energies and oscillator strengths of electronic transitions of the ab-initio regions are obtained in Graphical Unitary Group Approach (GUGA) based Configuration Interaction (CI) computation using GAMESS program [1]. The initial molecular orbitals (MOs) for the CI GUGA calculations were obtained in the specially constructed larger clusters. In such clusters the ab-initio regions were surrounded by about few hundreds of atoms treated in calculations as effective electrostatic potentials (dipoles and monopoles).

Dependence of the energies of the ground and several excited electronic states of the ab-initio region on some vibration coordinates was computed. The different participation of cations and tungstate groups in formation of vibronic spectra of the crystal fragments represented by the ab-initio regions is qualitatively analyzed comparing the CI states with different character of excitations (in which the excitations of cationic or tungstate MOs clearly dominate).

Results of calculations obtained in cluster approach are compared with experimental data on luminescence, excitation and absorption of corresponding tungstate crystals and with the electronic structure results obtained by another method of calculations.

References

AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF E\textsuperscript{-} CENTERS IN AMORPHOUS SILICA: STRUCTURAL AND OPTICAL PROPERTIES

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The study of point defects in silica-based materials is essential in order to understand and to predict the damage-response of electronic and optical devices in nuclear environments. Among the defect structures shown in silica [1], the E\textsuperscript{-} centres have been extensively studied since their discovery in 1956 by R. A. Weeks [2]. At the microscopic level, it is now well established that these defects exist within two metastable structural configurations [3]. These two structures, as well as the reaction paths between them, have been studied using cluster type calculations and condensed matter computations. But up to now, the optical absorption bands associated with each configuration have only been calculated using the cluster approach.

Recently, we have investigated [4] the structural and optical properties of neutral oxygen-deficient centres in pure and Ge-doped silica supercells using the density functional theory with plane waves basis sets associated to the Kubo-Greenwood formalism to compute the optical conductivity. Our results qualitatively agree with experimental ones. And we show that the optical properties of each defect strongly depend on its short-ranged neighbours. It is then important to be able to reproduce the amorphous character of such materials.

Using our condensed matter approach, we will present structural and optical properties of E\textsuperscript{-} centres. The discussion will include the differences of optical behaviours between each expected metastable defect structure and the influence of their environment on their properties.

References
DENSITY OF DEFECT STATES IN CADMIUM IODIDE: THERMALLY STIMULATED DEPOLARIZATION CURRENT STUDIES

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The study of the localized states density in the band gap is considered to be one of the main problems in the solid state physics. This problem can be solved experimentally by using thermostimulated techniques. This work utilizes a novel approach used for the study of localized density of states which is based upon the solution of incorrect integral equations.

Thermally stimulated depolarization current $I(T)$ can be expressed as

$$I(T) = \int g(E) \exp \left(-\frac{E}{kT} - \frac{\omega}{\beta} \int_0^T \exp \left(-\frac{E}{kT}\right) dT' \right) dE$$

where $\omega$ – is the frequency factor, $\beta$ – denotes the heat rate and $E$ is an activation energy of defect.

The latter equation is considered as incorrect integral equation in case $I(T)$ function is known. The solution allows to obtain $g(E)$ i.e. the density of defect states.

Mentioned approach is used for the study of defect states density change in the nominally pure CdI$_2$ crystals and in CdI$_2$ crystals with controlled deviation from stoichiometry. Preliminary data show that excess stoichiometric Cd atom are localized in the van der Waals voids and are chemically bonded with anions from neighbour layers. Thus, the formation of [CdI$_6$]$^-$-centers is manifested in electronic emission and absorption spectra.

It was established, that in nominally pure CdI$_2$ the wide spectrum of defect states with maxima at 0.17 eV, 0.28 eV, 0.44 eV and 0.56 eV is observed. Introducing of excess-stoichiometric cadmium leads to the significant decrease of defect states with energies 0.17 eV and 0.28 eV and, on the other hand to the increase of defect states with the energy of 0.56 eV. At higher concentrations (more than 0.1 molar percents) all defects except those with the energy of 0.56 eV disappear.

Obtained results are explained in frames of a model which suggest interactions between non-stoichiometric interstitial atoms. Such interactions are the reason of the decrease of local centres concentration and formation of metallic clusters by the coagulation of non-stoichiometric cadmium atoms.
Silica glasses containing SnO₂ nanocrystals and erbium (with and without fluorine as codopant) have been found to display narrow transitions in the high-resolution optical absorption spectra; the corresponding peaks become sharper at lower temperatures [1], as expected for rare-earth ions embedded in an ordered environment. In the course of this study, several reference compounds were characterized to investigate the possible inclusion of Er³⁺ in crystalline nano-phasess. The present work deals with polycrystalline Er₂O₃ and ErF₃. Absorption spectra were measured on pellets of both compounds; the obtained energy levels, together with available literature data, were then analyzed by means of crystal-field theory and Newman’s superposition model [2]. The resulting parameters for Er-O and Er-F pairs were favourably compared with those published for other compounds [3]; they will be used to calculate the predicted energy levels for erbium in different crystalline environments and unravel the complex spectra of erbium in nanostructured glassceramics.

References

A noticeable interest to investigation of manganites La\(_{1-x}\)M\(_{x}\)MnO\(_3\) (M=Ca, Sr, Ba) properties is caused by discovery of colossal magnetoresistance effect in these compounds. The researches have shown the complicated character of the ground state of manganites, which is caused by strong correlation between spin, electron, and lattice degrees of freedom. The striking example of this correlation is a forming at different doping rate x of charge ordered (CO) phases with specific pattern of Mn\(^{3+}/\)Mn\(^{4+}\) ions ordering. The CO mechanisms are not enough studied and are under discussion at once. For La\(_{0.333}\)Ca\(_{0.667}\)MnO\(_3\), the model of Wigner crystal and bistripe model are discussed [1,2]. In the paper [1], the experimental data are in a good agreement with the first model.

In the current work, the possible types of CO in La\(_{0.333}\)Ca\(_{0.667}\)MnO\(_3\) are investigated. The model of a crystal takes into account the Coulomb interaction between holes, Jahn-Teller ordering of orbitals on Mn\(^{3+}\)ions, and compression of oxygen octahedral surrounding Mn\(^{4+}\) ions. The charge-orbital order is obtained using Monte-Carlo methods. It is shown, that more stable is “Wigner crystal” ordering. The CO temperature is in a good agreement with the experimental one \(T_{CO}=260\) K [1].

The orbital structure of CO phase of La\(_{0.333}\)Ca\(_{0.667}\)MnO\(_3\) causes the magnetic ordering. The exchange parameters are estimated using the approach of orbitally-dependent superexchange interaction [3]. The Neel temperature \(T_N=170\) K is in an agreement with experiments: \(T_N=140\) K [1] and \(T_N=170\) K [2]. The magnetic structure is found to be strongly dependent upon orbital structure. The slight change of orbital structure change the wave vector of magnetic structure from \(k=(0,0,0)\) to \(k=(0,0,\frac{1}{2})\). The last wave vector coincides with experiments [1,2]. The ordered magnetic moments form ferromagnetic trimers in the chain Mn\(^{4+}\)–Mn\(^{3+}\)–Mn\(^{4+}\). These trimers are antiferromagnetic within a stripe and approximately perpendicular in the neighbour stripe. The directions of magnetic moments of trimers nearly coincide with pseudocubic axes.

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References

OPTICAL PROPERTIES AND ELECTRONIC STRUCTURE OF NaTiP$_2$O$_7$ CRYSTALS

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The crystals of sodium titanium diphosphate NaTiP$_2$O$_7$ belong to the family of the complex phosphates of the alkaline and polyvalent metals. NaTiP$_2$O$_7$ can be considered as the base for development of new crystallophosphors, since it is characterized by stable, chemical and thermally inert crystal lattice. New luminophors can also be designed by making the solid state solutions on the base of sodium titanium diphosphate matrixes.

Both experimental and theoretical investigations of NaTiP$_2$O$_7$ optical properties are carried out. Luminescence spectra are measured in 350 – 1200 nm spectral region in temperature range 4.2 – 300 K. Several bands of luminescence in blue-green and orange-red region were found in the spectra.

The electronic structure of NaTiP$_2$O$_7$ is calculated by full potential Linear Augmented Plane Wave (FLAPW) method implemented in WIEN2k program code [1]. The perfect crystals, the crystals with sodium impurities and oxygen vacancies are considered. The structures of the electronic bands, the energy dependencies of the components of dielectric tensor, reflection and absorption spectra are obtained. Results of the calculations of perfect and defective sodium titanium diphosphate crystals are compared with each other and with experimental data on reflection and luminescence excitation in wide energy region obtained using synchrotron radiation at SUPERLUMI station (HASYLAB, Hamburg, Germany).

The role of defects in formation of the spectroscopic properties of sodium titanium diphosphate crystals is elucidated. The origin of the NaTiP$_2$O$_7$ luminescence bands is discussed.

References

Amorphous silicon dioxide is a key component in many technological domains, from microelectronics to nuclear waste storage. In all these domains, presence of point defects affects the performance of silica by changing its electrical, optical or mechanical properties. In this paper, we present an extensive ab initio study of self-defects, neutral and charged ones and try to give a general view of the equilibrium defects which control the diffusion at low oxygen partial pressure and in the homogeneous regime.

A 108 atoms (36 silicon atoms + 72 oxygen atoms) glass model is used to perform first principles calculations in the frame of the Density Functional Theory (DFT) in the Local Density Approximation (LDA) using plane wave-pseudopotentials. We calculate the formation energies, structures and electronic properties of neutral and charged self-defects for all possible sites in the cell. Starting from these results, we estimate the diffusion barriers of some defects. An example of a calculated barrier is given in figure 1.

The calculated diffusion barriers allow us to describe diffusion mechanisms. These mechanisms will be discussed and compared to previous theoretical [1,2] and experimental results [3].

References

AB INITIO INVESTIGATION OF MONO-ATOMIC CHALCOGEN DEFECTS IN ALKALI HALIDES

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The study of chalcogen doped alkali halide lattices is motivated by the discovery of superfluorescence for di-atomic XY⁻ (X, Y = O, S, Se) molecular ions in these lattices. In spite of their apparent simplicity, relatively little is known about the precise defect model of the mono-atomic X⁻ centres ions in alkali halide lattices.

Using Electron Paramagnetic Resonance (EPR), X⁻ centres with tetragonal, orthorhombic and monoclinic g tensor symmetry have been observed. Because interpretation of experimental EPR results in terms of the geometry and the defect structure is not a simple task, the location and nearest environment of the X⁻ ion could not be yet convincingly established for any of these three classes. The systems under study are challenging for computational methods, since some of the proposed defect structures may be quite extended, involving vacancies. Various schemes, comprising cluster in vacuo, embedded cluster and periodic models, have been applied and tested to their validity in reproducing the observed EPR parameters.

The final assignment of a defect structure to a particular class of X⁻ ions is based on the qualitative and quantitative reproduction of experimental g and hyperfine values. A model involving a next nearest neighbour and nearest neighbour halide vacancy found to be valid for the X⁻ ions with tetragonal and orthorhombic-I g tensor symmetry respectively [1]. For the mono-atomic ions with monoclinic-I g tensor symmetry, a perturbed interstitial defect model is suggested [2].

References

Excitons, impurities, and defects II
STUDY OF Mn$^{2+}$ LUMINESCENCE IN Zn (PO$_3$)$_2$ GLASSES USING DIFFERENT CONCENTRATIONS


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Zn (PO$_3$)$_2$ glasses with different concentrations of Mn$^{2+}$ were studied by the luminescence technique, at 14K, 77K and 300 K. The excitation of Mn$^{2+}$ in Zn (PO$_3$)$_2$ produces an emission spectrum between 580 to 630 nm depending on the manganese concentration. The position of the maxima also depends on the excitation wavelength. The results clearly show that the manganese can be located in this material with different environments that produce a green or red luminescence. This implies that the Mn$^{2+}$ ions can be located with different oxygen coordination. This is also consistent with the lifetime measurements, which although they are in the milliseconds range present significant differences.
EXCITATION PROCESSES OF THE BLUE LUMINESCENCE IN CRYSTALLINE SiO$_2$ PROBED BY SINCHROTRON RADIATION MEASUREMENTS

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The photoluminescence (PL) properties of crystalline SiO$_2$ under excitation around the energy gap (~9 eV) are influenced by different kinds of emission channels that are distinguished in terms of the nature of the electronic transition producing them. In this work we present experimental results evidencing two excitation pathways, both giving rise to isoenergetic luminescence bands centred at 2.7 eV. Time-resolved luminescence were carried out by synchrotron radiation excitation in the vacuum-ultraviolet range, temperature ranging from 10 K to 300 K, in as grown and irradiated α-quartz. Figure 1 shows the different features of the excitation profiles associated with fast and slow decay of the 2.7 eV emission. The first decay follows the excitation at 7.6 eV that takes place in defects induced in quartz by γ- and β-radiation [1], the second is excited by band-to-band transition and is related to the radiative recombination of self-trapped excitons [2]. Moreover, on increasing the temperature both bands decrease their intensity in agreement with the enhancement of non-radiative processes occurring in the excitation pathway.

Figure 1: Time-resolved excitation profiles of the 2.7 eV PL detected at different delays from the excitation pulses in irradiated quartz at 10 K;

References

FEATURES OF LUMINESCENCE LIFETIMES IN QUARTZ ANNEALED CLOSE TO ITS PHASE INVERSION TEMPERATURE

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The sensitivity of optically stimulated luminescence from quartz is known to undergo significant changes close to the quartz phase-inversion temperatures of 573 and 867°C (Botter-Jensen et al., 1995; Galloway, 2002). In view of this, time-resolved optical stimulation of luminescence has been used to investigate the temperature dependence of luminescence lifetimes in quartz annealed at 600 and 800°C, that is, close to the said phase transformation temperatures. Time-resolved luminescence spectra were measured between 30 and 200°C at 470 nm either immediately after irradiation or after storage. The influence of bleaching at 470 and 525 nm, irradiation, storage, and pulse-width on both the principal and secondary luminescence lifetimes were examined. The results are discussed in terms of the temperature dependence of the density of recombination centres as well as charge transfer between several types of luminescence centres in quartz.

References


PTh39

LOW TEMPERATURE PHOTOLUMINESCENCE OF PURE AND DOPED PARATELLURITE (TeO$_2$) CRYSTALS

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Photoluminescence measurements aimed at defining the precise nature of scintillation reported [1] in paratellurite (TeO$_2$) crystals are presented. Measurement results are discussed for TeO$_2$ crystal samples (pure and Mg, Mn, Nb, Zr doped) studied for their photoluminescence properties in the 10-300 K temperature range. The nature of scintillation peaks reported [2] on these samples is explained.

Conclusions are drawn concerning the possibility to improve the scintillation yield of TeO$_2$ crystals to be used as cryogenic bolometers operated at 10mK in experiments studying the $\beta\beta$ decays of $^{130}$Te [3].

References

ENERGY TRANSFER FROM THE HOST EXCITATIONS TO IMPURITY IONS IN DOPED YTTRIUM AND SCANDIUM BORATES AND PHOSPHATES

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Efficient optical excitation of high-lying excited states of impurity ions in insulating crystalline matrices is important for the operation of VUV-excited phosphor materials. Often, however, the absorption responsible for the direct excitation of the excited states of impurity ions is weak. Thus alternative schemes of excitation, including nonradiative energy transfer, are required. These schemes may include absorption by the impurity centres or by the host lattice itself, followed by nonradiative transfer to acceptor ions. The excitation of Gd3+ ions to high-lying states is especially important in connection with the problem of so-called “quantum splitting”, a processes in which the absorption of a single photon results in the emission of two or more photons (quantum yield >1).

Studies of materials in which the absorption of light by the crystalline host is followed by efficient transfer of energy to impurity ions are presented. The main feature that distinguishes these kinds of materials is intense fluorescence from the intrinsic excitations in the undoped materials. This emission is usually ascribed to self-trapped excitons (STE). The spectral overlap of the host emission with the acceptor ion absorption is the necessary condition of the nonradiative energy transfer. Yttrium and scandium borates and phosphates (YBO3, ScBO3, YPO4, ScPO4) are interesting materials for sensitizing impurity ions because these host materials exhibit short-wavelength UV fluorescence that is efficiently excited with VUV radiation. The measurements reported include fluorescence and excitation spectra and time-resolved fluorescence.

The demonstration of energy transfer from the host excitations to the impurity ions was performed in ScPO4 doped with Ce3+ which have a short excited state radiative lifetime (~20 ns); thus Ce3+ emission intensity allows the observation of Ce3+ excited state dynamics with high temporal resolution.

Energy transfer from the host excitations (STE) to Gd3+ ions was also observed in yttrium and scandium borates and phosphates. The most important results were obtained with ScPO4:1%Gd3+ in which efficient energy transfer from the host results in the excitation of 6G state of Gd3+. This excitation is followed by the 6G → 4P → 8S cascade emission of photons which may be considered as a case of quantum splitting in which one visible and one UV photon are emitted. Though this material cannot be considered as a practical phosphor, it was demonstrated that Gd3+ ions may be efficiently excited via the energy transfer from the host excitations. The addition of a second activator, which can receive energy from the 9P state of Gd3+, could convert the UV photon into visible emission producing a practical phosphor.
A series of experiments on visible reflectance bands and on the thermally and optically stimulated luminescence signals from glass matrix of blue-green ancient and modern mosaic tesserae have been carried out. We have already shown that the use of both Thermally Stimulated Luminescence (TSL) and reflectance measurements to investigate the properties of glasses gave successful results in the identification of the metal ions responsible for the blue coloration [1].

Starting from SEM-EDS measurements performed to obtain information on the elemental composition of the materials, we have obtained some possible links between the reflectance spectra and the colorant concentration.

Moreover TSL (both conventional and wavelength resolved) and Optically Stimulated Luminescence (OSL) allowed to get information about traps and luminescence centres. The observed thermoluminescence characteristics (heating rate 1°C/s) were close to that of quartz, showing the presence of an “easy to bleach” trap (300°C, 1.95 eV) and of a “hard to bleach” trap (350°C, 2.20 eV); charge transfer phenomena, involving the low temperature peaks have been observed. There is a strong indication that the easy to bleach traps are responsible for both OSL and TSL emission at 300°C.

References

EFFECT OF MATRIX DEFECTS ON THE RADIATIONS PROCESSES IN DOUBLE PHOSPHATES DOPED WITH d-ELEMENTS

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The luminescence properties of MAlP2O7 (M = Na, K, Cs) and Zn2P2O7 double phosphates compounds doped with chromium and manganese ions associated with the d-elements internal transitions are investigated by us earlier [1 - 2]. All the same time process of the energy excitation transfer from matrix and matrix defects to these impurity ions are insufficiently studied. So, the purpose of the work is to investigate own and impurity luminescence of mentioned systems.

Polycrystalline samples of the MAlP2O7 (M = Na, K, Cs) crystals were synthesized from a melt of the mixture of the M2O-Al2O3-P2O5 oxides those chemical qualifications were “Chemically pure”. Impure chromium ions were incorporated into the sample composition by adding of the Cr2O3 oxide in the mentioned above mixture. The solid solutions of the hydrated double phosphate of certain compositions were obtained by combined precipitation of suitable cations by double phosphate – ion from water solutions of a mixture of their sulphates. Water solutions of the MIISO4 (MII = Zn, Mn) and K4P2O7 sulphates were used as initial reagents.

Photoluminescence spectra (PL), reflection spectra and luminescence spectra at the high-energy excitation by synchrotron radiation were obtained for the investigation systems. Luminescence properties all of presented compounds were investigated in the spectral region 100 – 1050 nm in temperature interval 4.2 – 300 K.

Formation of different defect types and their influence on the transfer energy processes are discussed. The structure of self-trapped excitons is considered.

References

Recently some radioluminescent properties of tetravanadates \( M_2Sr(VO_3)_4 \), where \( M=Na,K,Rb,Cs \), have been described [1]. In this report the new family of non-activated and \( \text{Eu}^{3+},\text{Ce}^{3+} \) activated cyclic tetravanadates \( M^{(I)}_2M^{(II)}(VO_3)_4 \), where \( M^{(I)}=Cs,K,Ag, M^{(II)}=Ca,Sr,Ba \) (which were successfully prepared by solid state route) will be described. The structure of these compounds is tetragonal. It is isostructural to \( M^{(I)}_2M^{(II)}(PO_3)_4 \) [2].

The \( M^{(I)}_2M^{(II)}(VO_3)_4 \) and \( M^{(I)}_2M^{(II)}(VO_3)_4:Eu,\text{Ce} \) radioluminescence spectra under X-ray and electron beam excitations have been measured and compared with their photoluminescence spectra. The exciton luminescence spectra have main maxima at 540-560 nm for \( M^{(I)}=Cs,K \) and at 640-720 nm for \( M^{(I)}=Ag \). The \( \text{Ce}^{3+} \) activated compounds have wide 540-560 nm band. For \( \text{Eu}^{3+} \) there are 7 peaks in spectrum. The main peak at 619 nm has intensity comparable with intensity of radioluminescence for \( \text{YVO}_4:\text{Eu} \). The examples of spectra are presented at Fig.1. The role of disorder transformation of crystal structure and conditions giving rise to intense luminescence \( M^{(I)}_2M^{(II)}(VO_3)_4 \) and role of \( \text{Ag} \) ions giving rise to red-shift of spectrum are discussed.

![Figure 1: Pulse cathode luminescence spectra for \( Ag_2Sr(VO_3)_4 \) (a) and \( Cs_2Sr(VO_3)_4:Ce \) (b) crystals.](image-url)
Aluminium nitride, the widest direct band gap III-V semiconductor, through the years attracts attention of researchers due to the outstanding combination of mechanical, thermal, electrical and optical properties [1,2]. Recently, significant efforts have been put into synthesis and further investigation of various AlN nanostructures such as nanotubes, nanocoils, nanorings etc [3,4] which are considered to be prospective for future technological applications.

In present report we will focus on distinctions in luminescence from commercially available aluminium nitride powder and nanostructured AlN, particularly nanoparticles and nanotubes, which were synthesized by using a highly nonequilibrium dc-arc plasma method and characterized by different techniques [5]. Here we will discuss our results on cathodoluminescence (CL) of AlN samples containing 95 % of spherical nanoparticles and samples consisting mostly of AlN nanotubes (85 % nanotubes and the rest nanoparticles). Low temperature CL spectra of these nanostructures exhibit features in 2.2–3.8 eV photon energy range which are not revealed in the spectrum of microcrystalline commercial powder. Significant difference was observed also between electron beam excited emission from nanoparticles and nanotubes.

References

SPECTROSCOPIC STUDIES OF CdWO₄:Tb³⁺ CRYSTALS

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Cadmium tungstate (CdWO₄) is well known as a scintillator in computed X-ray tomography. Tungstates are classified as so named “self-activated” crystallophosphors. It was established that the own blue luminescence of such crystals could be regarded with emission of WO₆ (or WO₄) groups of lattice. Luminescence properties and performance of scintillator materials are affected easily by doping with different impurities and annealing in proper atmosphere. Physical mechanism of impurities effect on the crystal properties is still under discussion.

This contribution presents investigations of the optical absorption, excitation and luminescence spectra of Tb-doped CdWO₄ single crystals in a wide spectral range (1.5 – 25 eV) using photo excitation and synchrotron radiation. The measurements were carried out in the temperature region 10 – 300 K. For a comparison the luminescence measurements were also performed on the CdWO₄ activated both Tb and Li, Ca ions. The crystals were grown by Czochralski method.

Besides intrinsic emission the emission related to activator of Tb³⁺ ions (broad band centred at about 2.25 eV) are observed in CdWO₄ crystals under excitation with energies hν>5eV. Both lattice emission (2.5 eV) and predominantly green Tb³⁺ emission due to ⁵D₄ – ⁷F_j transitions (bands at about 490, 550, 590, 630, and 660 nm) are present under excitation with energy hν=4.1eV at 10K and the 2.5 eV lattice emission was reduced with respect to activator luminescence.

Excitation spectra of the main 2.5 eV emission of CdWO₄ reveal the intensive sharp peak at about 4.1 eV and several overlapped weak bands at hν>10 eV. Dominant peak 4.1 eV is observed at energy lower than the energy of interband transitions (hν>5 eV). This is in a good agreement with data presented in [1]. The excitation spectrum of the activator emission is mainly similar to those of intrinsic emission. The influence of additional doping by Li and Ca impurities on photoluminescence spectra is also investigated.

The luminescence properties of Tb-doped CdWO₄ and Tb-doped PbWO₄ recently investigated in [2] are compared. The models of activator centres and possible mechanism of energy transfer between defects of the host matrix and activator centres have been discussed.

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References

Development of efficient and durable luminescence materials has been widely explored in recent years due to the rapid development of new applications like plasma displays, LED emitters, solid state lasers and various scintillators. The wide band-gap, high refractive index, good transparency in visible spectral region and low phonon energies make titanium, zirconium, and hafnium increasingly popular hosts for doping by rare earth (RE) ions. Although success has been reported in doping of these matrices with several RE ions, the excitation mechanism of the ions is still not clarified. The aim of this work was to study the excitation processes taking place in RE-doped TiO$_2$, ZrO$_2$ and HfO$_2$ thin films.

The samples have been prepared by using atomic layer deposition (ALD) method followed by ion-implantation with Sm$^+$, Eu$^+$, or Er$^+$ ions and a sequence of annealing cycles to restore the structure of the film. Photoluminescence (PL) of the samples was excited using 355 or 193 nm laser radiation whereby the PL excitation spectra were measured using synchrotron radiation in the photon energy range of 4–20 eV. The annealing of the samples led to an increasingly strong emission characteristic to the implanted RE ions in trivalent state. The PL spectra and the decay kinetics of RE ion luminescence were measured after each step of annealing. From the PL spectra of Eu$^{3+}$ ions, it was possible to determine the site symmetry of the emitting ions.

The behaviour of decay kinetics of RE$^{3+}$ emission revealed different time domains of the decay starting with a fast stretched exponential part (<10 µs), followed by an approximately single exponential decay and a long-lasting tail governed by a power law (>10 ms). These ranges are attributed to various excitation and de-excitation processes dominating in the different time scales.

Using excitation spectra recorded and the theoretical approach developed in [1], the relative positions of RE$^{3+}$ energy levels within the energy gap of the host matrix will be estimated. A particular attention will be paid to the vicinity of the interband absorption edge of the host material, where the charge transfer absorption is expected. Route of electronic excitations of RE ions will be discussed.

References

STUDIES OF THE NaCl:Mn$^{2+}$ SINGLE CRYSTALS BY PHOTOACOUSTIC AND OPTICAL SPECTROSCOPY

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The Mn-precipitate inside the alkali halide host can take a nanostructure shape well-known so-called Suzuki phase (SF). The first studies of optic spectroscopy and photoacoustic of NaCl:Mn$^{2+}$ are presented and compared.

Samples with dissolved and precipitated Mn$^{2+}$ impurities inside of NaCl matrix were used in this study. Quenched samples have emission peaks around 610 nm. The growth of another emission band peaking at 505 nm, is observed in annealing samples, at room temperature or at temperatures below 100 °C, which is related to the presence of Suzuki-type precipitates (Fig. 1).

To understanding the phononic behaviour of NaCl:Mn$^{2+}$ samples in SF we carry out a photoacoustic study (PA). The first results indicate that applying the FFT to the PA signal can be identifying acoustic frequencies associated to the precipitate states, and this, to correlate it with the optic spectroscopy results (grown bands). See Fig. 2.

References

**LUMINESCEENCE CHARACTERISTICS OF THE LPE-GROWN UNDOPE, IN- AND Ge-DOPED ZnO THIN FILMS**

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ZnO single crystals, thin films, nanostructures and powders are intensively studied due to an extended range of expected applications in the field of the UV-blue light emitters, field-effect transistors, sensors and piezoelectric devices. A possibility to exploit very fast, subnanosecond excitonic emission of ZnO for superfast scintillators was recently discussed in the literature as well [1]. Due to small Stokes shift of Wannier exciton emission in the direct-gap ZnO structure a severe re-absorption may occur, which prevents an efficient collection of such emission from bulky scintillation elements. A way to overcome such problem consists in the manipulation of the excitonic emission by exciton localization at suitable defects, which could shift the excitonic band to lower energies. In the case of double donor-acceptor doping also radiative recombination within the donor-acceptor pairs can be considered to obtain low-energy shifted emission. A crucial aspect is, however, if such modified luminescence centres in ZnO structure will keep the superfast character of the decay kinetics.

As the doping of hydrothermal-grown bulk ZnO [2] appears rather difficult, we have used the liquid phase epitaxy (LPE) growth process to obtain high quality single crystal films of several micrometer thickness [3], where the doping by various elements can be accomplished much more easily and also the time scale and economy of the experiments get much more favourable. Another advantage of LPE method is that the sample surface is not mechanically treated, which appears as a possible source of problems in the case of polished bulk crystals as the penetration depth of the UV excitation in the region of ZnO intrinsic absorption is less than 100 nm.

Photo- and radioluminescence spectra were measured at the undoped, In and Ge-doped ZnO thin films using a steady-state UV and X-ray excitation sources, respectively. The decay kinetics of the exciton-based and donor-acceptor radiative recombination was studied using a femtosecond laser excitation. The results of these experiments will be demonstrated and discussed in the light of possible application of ZnO-based materials in superfast scintillation detectors.

References

Thermoluminescent measurements at room temperature of “beta” irradiated divalent Europium doped binary mixed alkali halides are shown, the crystals has KCl and KBr components at several concentrations x in molar fraction.

The experiments have been carried out to identify the effect of composition on glow peaks.

A typical glow peak has been distinguished for each x. This is associated with the size change of ions Cl and Br. Besides is given the behaviour of the mixed binary crystals with components KCl and RbCl, doped with divalent Europium.
ORIENTATION DEPENDENCE OF THE UV-BLUE ION BEAM AND CATHODOLUMINESCENCE OF ALBITE

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Ion beam induced luminescence and cathodoluminescence of albite produce unexpected differences between (010) and (001) aligned samples. The emission spectra are modified by temperature and different components change in their relative intensity as a result of excitation by different ion beams of H⁺, H₂⁺ and ⁴He⁺. A consideration of processes which can induce the orientation dependence and the role of excitation density that influences the component features are both discussed.
INVESTIGATION OF IMPURITY DEFECTS IN ZNO


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Wide-band II-VI compound are characterized by the deviation of stoichiometry towards the metal component, which is caused by the excess of donor defects, which in its turn causes n-type conductivity in them. ZnO is very interesting material among the II-VI wide gap semiconductors. It is well known ZnO is naturally characterized by n-type conductivity. Obtaining of conductivity type inversion in ZnO is especially problematic due to the native strong tendency to self-compensation [1].

For obtaining impurity p-type conductivity in ZnO we carried out the following experiment: n-type ZnO (wurtzite structure produced by Cermet, Inc.) was implanted by $N^+$ ions at the $E=110$ keV energy and at the dose of implantation $D=10^{16}$ cm$^{-2}$. The current density was $j=15$ $\mu$A/cm$^2$. Healing of the created radiation defects in the implanted ZnO crystals was implemented by RBQE method in the atmosphere of activated oxygen radicals ($T=400^\circ$C, $t=4$ hours, $n_o=10^{14}$-$5\times10^{15}$cm$^{-3}$) [2]. In this way we obtained p-type ZnO layers.

We have investigated electrical and optical properties of ZnO. Van Der Pauw method was used to measure Hall Effect. According to the measurements of Hall-Effect the resistivity was $\rho=10^2$ $\Omega$cm, the hole mobility $\mu_p=230$cm/ vs and the hole concentration was $N_p=5\times10^{18}$cm$^{-3}$. We measured I-V characterization, after them we obtained p-n junction.

We have studied Photoluminescence (PL) spectra of ZnO layers. PL measurements were made at 70 K and 300K. The centres observed in PL spectra were identified. In the ultraviolet part of the PL spectra of ZnO we observed intense peaks and the visible part were reduced. Observation of exciton in ZnO layers obtained by RBQE are characterized by high purity and perfection structure and significantly reduced number of point defect, which is one of the most important problems. For structural characterization of ZnO layers were checked with a Siemens D5000 XRD (X-Ray diffraction) spectrometer (CuK$_\alpha$ line, step size 0.02$^\circ$).

References

Optical devices, 
photorefractive materials, lasers
HIGH-RESOLUTION SPECTROSCOPIC PROPERTIES AND EMISSION DECAY OF RARE-EARTH DOPED TRANSPARENT LASER CERAMICS

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Transparent ceramics activated with laser active ions are currently investigated as possible substitutes for the crystalline materials. These ceramics consist of randomly oriented crystalline grains and the degree of transparency is determined by the density of pores between grains and by the extent of grain boundaries. The density of pores becomes very small when the grain sizes are of the order of tens of microns. Besides obvious technological advantages and lower cost, the ceramic materials offer some functional advantages such as homogeneous distribution of doping over the whole body of ceramic, higher compositional versatility and the possibility to incorporate higher concentrations of doping ions than the crystals. Nevertheless, important problems, such as the variety, structure and spectroscopic properties of centres formed by the doping ions, the distribution of the doping ions at the available sites and in the volume of the ceramic grains as well as the effects of granular structure on the ion-ion interactions that govern the energy transfer or on the electron-phonon interactions remain of concern and the data from literature are still contradictory.

This paper presents new high-resolution spectroscopic and emission decay data on Nd-doped garnet (YAG) or sesquioxide (Y₂O₃, Sc₂O₃) ceramics produced by solid-state mixing of oxides [1] in comparison with single crystals. In the transparent ceramics the sizes of grains are of several tens of microns; several translucent ceramics with smaller grains are also investigated for comparison. The maximum Nd concentration in ceramics was much larger than achievable in single crystals. The main conclusions of this investigation are: (i) the doping ions could occupy in these ceramics sites similar to those from the corresponding single crystals as well as defective sites at/or near the surface of grains, the ratio between these sites being determined by the size of grains: in transparent ceramics the normal sites dominate completely the optical spectra; (ii) the structures of spectral satellites indicate that the distribution of the doping ions and that of some specific lattice defects (such as the excess Y³⁺ ions in the garnets) in these ceramics is random; (iii) the spectroscopic properties (positions of lines, intensities and cross-sections, emission decay) of the Nd-doped garnet and sesquioxide ceramics are similar to those of the single crystals; in this respect our data diverge from those given for wet-synthesis-based Nd:YAG ceramics, where very large differences between the cross-sections in ceramics and crystals are reported [2]; (iv) increased compositional versatility of ceramics enables tailoring of new laser materials These data indicate that from the spectroscopic point of view the Nd-doped garnet and sesquioxide ceramics produced by solid-state mixing of oxides are similar to the single crystals and show potential for substitution of the crystals in construction of lasers and for development of new laser materials.

References

New laser materials that have fluorescence with strong oscillator strength and wide bandwidth have been pursued for ultrafast optical devices working in the visible and infrared regions. Ti and Mn-doped MgAl$_2$O$_4$ spinel have been successfully grown [1] and spectroscopically investigated in view of the potential use as a short-wavelength solid-state laser. On the other hand, octahedrally coordinated Ni-doped MgAl$_2$O$_4$ seems to be a potential candidate for new cw tunable solid-state laser between 1 and 1.5 µm.

Strong blue emission is observed from Ti-doped MgAl$_2$O$_4$ and green emission from a Mn-doped one. The optimum condition to obtain the strongest emission was studied by changing the doping concentration. These two broad luminescence bands around 455 nm and 518 nm were obtained by photo-excitation in the absorption band edge in UV region (Fig. 1.a). It is important to reveal the optical process and their decay times.

Ni$^{2+}$-doped crystals exhibit a broad emission band in the near infrared with long emission lifetime and high quantum yield and their broad absorption around 980 nm is very suitable for InGaAs laser diode pumping (Fig. 1.b).

Figure 1: (a) RT emission spectra of Mg(Al$_{0.7}$Ti$_{0.3}$)$_2$O$_4$ and (Mg$_{0.95}$Mn$_{0.05}$)Al$_2$O$_4$ under the forth harmonic pulsed Nd:YAG laser excitation at 266 nm, (b) RT absorption and emission spectra of (Mg$_{0.99}$Ni$_{0.01}$)Al$_2$O$_4$ under excitation at 980 nm.
Strontium lanthanum hexaaluminate \( \text{SrAl}_{12}\text{O}_{19} \) crystals doped with trivalent rare earth ions (RE\(^{3+}\)) are currently investigated as laser materials or phosphors. This crystal has hexagonal magnetoplumbite structure and offers for substitution with RE\(^{3+}\) an unique \( \text{Sr}^{2+} \) site (2d) of \( D_{3h} \) symmetry and with 12 \( \text{O}^{2-} \) coordination. This grants low nephelauxetic effect, which determines high barycentres of the energy manifolds, and moderate crystal field effects. These properties could be used for design of new laser materials or phosphors. The charge compensation for substitution of \( \text{Sr}^{2+} \) by RE\(^{3+}\) can be accomplished by co-doping with Mg\(^{2+}\) that substitutes \( \text{Al}^{3+} \). Due to growth conditions and emission concentration quenching, diluted with La\(^{3+}\) crystals \( \text{Sr}_{1-x}\text{La}_{x-y}\text{RE}_y\text{Mg}_x\text{Al}_{12-x}\text{O}_{19} \) (ASL: RE) have been also studied.

The paper presents a comparative investigation of the disorder effects in ASL, in a large compositional range up to \( x=1 \), on the spectral properties of Nd\(^{3+}\) (interesting for 900 nm laser emission) \([1]\) and Pr\(^{3+}\) (for visible laser emission and for UV-VIS quantum cutting) \([2,3]\). The presence of two compositional centres \( C_1 \) and \( C_2 \) at low \( x \) (<0.3) is reported for the first time for Pr\(^{3+}\) ion, \( C_2 \) is prevailing at very low \( x \), and \( C_1 \) is dominant at higher \( x \) (≥0.3), as observed also for Nd: ASL \([1]\). Additional satellite lines are detected for Pr\(^{3+}\), as reported in \([2]\). From the composition dependence of the spectral data and crystal structure it is inferred that for the two main Pr\(^{3+}\) centres at low \( x \), as in the case of Nd\(^{3+}\), the Pr\(^{3+}\) ion resides at a (2d) site, for \( C_2 \)-centre the first (2d) cationic coordination sphere contains only \( \text{Sr}^{2+} \) ions, while for \( C_1 \) centres one up to all six sites of this sphere could be occupied at random by Ln\(^{3+}\) (La, Pr) ions and perturb the crystal field at the Pr\(^{3+}\) site mostly by electric charge, but also by ionic size difference. This model is consistent with the polarisation spectra and with the selective inhomogeneous broadening of the lines, and indicates a selective manifestation of the energy transfer processes with effects on the emission decay and quantum efficiency.

The Nd\(^{3+}\) spectra for \( x=1 \) (LMA) reveal three main centres as remarked before \([4]\), two of them with similar spectral behaviour and one with quite different spectral and polarization characteristics. Arguments that the first two Nd\(^{3+}\) centres have the same ionic environment, but differ by cationic composition (La\(^{3+}\) and Nd\(^{3+}\)) of near neighbours sites – size effects- are given. For the third centre a model implying lower n.n. anionic coordination number is assumed. The paper discusses the spectral data and the implication of these compositional effects on laser and quantum cutting properties of Nd\(^{3+}\) and Pr\(^{3+}\): ASL crystals.

References

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LASER ACTIVE CENTRES WITH YELLOW-ORANGE EMISSION IN LiF CRYSTALS

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Most of researchers [1,2] believe that the laser active centres with yellow-orange emission ($\lambda=600$ and 620 nm) in LiF crystals represent $F_3^+$ perturbed centres. This conclusion is based on the fact that the quantum efficiency, optical gain and photo- and thermostability of these new centres were much the same as those of $F_3^+$ centers. Having made a lot of observations we found that it is necessary to take impure composition and method of creation laser active centres into account. The lasing medium is LiF crystal grown by the Stockbarger technique in vacuum of coloured $\gamma$-irradiation on special technologies. The emission spectrum excited of the second harmonic of YAG-Nd laser ($\lambda=532$ nm) at 78 K shows peak at 600 nm or 620 nm at RT in LiF crystals grown by the Stockbarger technique in vacuum; at 600 nm at RT in LiF crystals grown by the Kyropoulos method in air and enriched with oxygen. Spectroscopic analysis indicates that the absorption bands corresponding to 600 and 620 nm peaks locate at M absorption region in LiF. The shift of maximum emission can be stipulated by a different encirclement of defects. However, the yellow-orange emission is extinguished in LiF-Me, O, OH crystals at 78 K unlike samples grown by the Stockbarger technique in vacuum. Consequently luminescence belongs to different centres in two type crystals. The charge state of the 600 nm centres in LiF crystals grown by the Stockbarger technique in vacuum was determined using optical bleaching in F band at 78 K under the action of the fourth harmonic (266 nm) of YAG-Nd laser. The concentration of broken F centres reached 2.5x10$^{17}$ cm$^{-3}$. At the same time the destruction of $F_3^+$ centres and manifestation of 420 nm and 600 nm bands in excitement and emission spectrums are observed. These results indicate that the 600 nm centres possess a neutral charge and do not interact with electron of the F centres. It explains the high optical stability of the laser active centres. The photo- transformation of $(F_2^-Vc^-)...Me^{2+}$ centres ($\lambda_{ex}=580$, $\lambda_{em}=840$ nm) into $(F_2^-Vc^-)...Me^{2+}$ centres ($\lambda_{ex}=420$, $\lambda_{em}=600$ nm) was realized under the action of xenon tube integral light. Therefore, laser active centres with yellow-orange emission are $(F_2^-Vc^-)...Me^{2+}$ in LiF crystals grown by the Stockbarger technique in vacuum. $Me^{2+}$ does not enter in structure of centre. Otherwise shift of maximum of band emission would be observed in more long wave region of spectrum for radiation $F_2$ centre (650 nm).

References

Holmium doping provides the yttrium aluminum borate (YAB), a good non-linear optical laser host, with an attractive 2 µm emission, well suitable for eye-safe laser applications. High resolution FTIR spectroscopy has been applied to investigate a YAB:Ho\(^{3+}\) single crystal in the wave number range 2000-25000cm\(^{-1}\) and in the temperature range 9-300K. The single crystal was grown by the top-seeded flux method from K\(_2\)O/MoO\(_3\)/B\(_2\)O\(_3\) flux and the Ho\(^{3+}\) concentration was 1 mol\%. The complex Ho\(^{3+}\) (4\(f^{10}\)) non-Kramers ion transitions from the ground 5I\(_8\) to the excited 5I7, 5I6, 5I5, 5I4, 5F5, 5S2+5F4, 5F3, 5F2, 3K8, 5F1+5G6, and 5G5 manifolds are analysed (see e.g. Fig.1). In addition the low-temperature high resolution spectra of the investigated manifolds show for many electronic transitions hyperfine structures related to the Ho\(^{3+}\) nuclear magnetic moment.

The experimental data are fitted by a single ion Hamiltonian and the crystal field parameters are obtained [1]. The results are critically compared with those previously published for other dopants in the same matrix [2].

![Figure 1: Optical absorption spectrum measured at 9K in the region of the 7I\(_6\)\(\rightarrow\)1\(_1\) transition](image)

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References


HOLOGRAPHIC PROPERTIES OF AZOBENZENE OLIGOMERS WITH DIFFERENTLY BONDED CHROMOPHORE GROUPS

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Holographic properties of the two types (I and II) of azobenzene oligomers (ABO) have been experimentally studied. In the case of type I ABO the chromophore groups (paranitrophenylazobenzene, 4-nitronaphthylazobenzene, 9,10-antraquinone-α-azobenzene, β-chlore-9,10-antraquinone-α-azobenzene) were covalently bonded to either tolyle or hexamethylene matrix. In the case of type II ABO the dialkylaminoazobenzene chromophore groups were dispersed in polystyrene matrix, and their concentration was changed from 0.005 to 0.200 mol/l.

In both cases the diffraction efficiency exposure time dependences were measured for the holographic grating period of 2 µm at 633 nm. The maximal diffraction efficiency and the corresponding recording energy were determined. The diffraction efficiency of more than 2% and the specific recording energy of less than 260 J/(cm²%) were achieved in both cases. In the case of type I ABO the best results were achieved with 4-nitronaphthylazobenzene chromophore groups in hexamethylene matrix. The chromophore concentration threshold within 0.01 – 0.04 mol/l range and the holographic efficiency growth with chromophore concentration were found in the case of type II ABO.

For both types of explored ABO films we have found that recording was mainly based on the photoinduced refractive index change due to the photoorientation of chromophore groups perpendicularly to the electric vector of the polarized 633 nm recording light. The main conclusion is that the holographic efficiency of the samples with dispersed chromophore groups can be comparable with that of covalently bonded groups. This is important for practical applications since the holographic properties of ABO films with dispersed chromophore groups are more predictable.
NEW ASPECTS OF LIGHT-INDUCED CHARGE TRANSPORT PROCESSES IN POTASSIUM TANTALATE CRYSTALS DOPED BY COPPER AND IRON.

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In photorefractive crystals a light pattern may be transposed into a refractive index pattern. Illumination excites charge carriers into conducting or valence band, which are trapped on the defects after migration. A detailed understanding of the microscopic processes is required for optimization of the crystals by, as for instance, doping and thermal annealing, and for improvements of experimental procedures. The main results of the process in many materials were reviewed in [1].

The light-induced charge transport process in $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ single crystals with copper impurity and $KTaO_3$ with iron impurity were studied by electron paramagnetic resonance (EPR). EPR method allows to careful determination of charge trap centres in the crystal. “As grown” single crystalline specimens and specimens thermally treated in oxygen atmosphere were investigated. EPR spectra of Cu$^{2+}$ centres [2] in the “as grown” crystals disappear when the crystals are illuminated by UV light (365 nm). Contrary to this it was found a sizeable increasing of EPR signal of Cu$^{2+}$ centres (except signal from exchange coupled pair centres) under UV illumination in the crystals after thermal treatment in oxygen atmosphere. Thus, the charge exchange between Cu$^+$ and Cu$^{2+}$ was estimated. The temperature dependence of the EPR signal under light illumination potassium tantalate crystal containing copper ions was measurement. In the $KTaO_3$:Fe crystal the charge exchange between Fe$^{3+}$ and Fe$^{2+}$ was observed. The reducing of Fe$^{3+}$ (axial) centre [3] EPR signal is observed in oxygen atmosphere thermally treated $KTaO_3$:Fe crystal under UV light illumination. In “as grown” crystal this effect was not observed. The important roles of oxygen vacancies, which compensate extra charge in crystal, were estimated in both the crystals. The mechanisms which include the stabilization of Jahn-Teller distortion by oxygen vacancies are discussed.

References

Lithium niobate (LN) crystals doped with Hafnium exhibit a significant suppression of the photorefractive effect and represent a promising material for wavelength conversion devices (substrate for wavelength converter devices). In this work we present a systematic investigation of their structural and optical properties.

In this work we present the systematic characterization of the structural and electro-optical properties of a set of Hf:LN samples with increasing concentration of HfO₂ (from 2mol % to 11 mol%), that have been grown as described in [1].

By taking advantage of the fact that some features of the Raman spectrum are very sensitive to the crystal composition, or to the amount of intrinsic defects related to the non-stoichiometry [2], we evaluated homogeneity, structural properties and stoichiometry of the Hf-doped samples by monitoring the changes in Raman spectra with respect to that pertinent for congruent undoped crystals. The changes in peak position, linewidth and intensity of some Raman modes observable using different scattering geometries allowed to obtain information about the role of Hf ion as structural modifier when inserted in the ferroelectric chain.

The effective EO coefficient $r_c = r_{33} - (n_e/n_o)^3 \cdot r_{13}$ was determined through a polarimetric method. The results at variance with Hf doping were correlated to the Raman data.

The detailed structural and optical characterization is a fundamental requirement to better understand the photorefractive behaviour, characterized by a strong reduction of photorefractivity and higher photoconductivity for Hf doping above 4% [1,2]

References

Optical fibres are, along with mirrors and windows, passive optical components of great interest for use in the future International Thermonuclear Experimental Reactor (ITER) as they will be included in: plasma diagnostics systems (i.e. light-guides), remote handling assembles, distributed sensors and optical data communication links. Optical light-guides (fibrescopes) are needed to pick-up the optical signal from plasma and to carry it to the diagnostics instrumentation remotely located, through a noisy electromagnetic environment, under high temperature, high gamma-ray total dose/dose rate and high neutron fluences. In irradiated optical components two phenomena can be present depending on the irradiation conditions (dose rate, total dose, operating temperature, etc.) and the material ingredients and defects: the radiation-induced absorption (RIA) and the radiation-induced luminescence (RIL) or radioluminescence. Until now, ONLY silica optical fibres were extensively investigated under various irradiation conditions, the measurements being carried out over the optical spectrum from 200 nm to 1.7 µm. In the case of RIA, colour centres are linked to radiation induced defects.

According to our knowledge, the present paper is the first report on irradiated sapphire optical fibre. The sapphire optical fibres have over their silica counterparts two advantages: they exhibit a good spectral transmission far into the IR (i.e. 5 µm), and they can be used at very high temperature (i.e. 2000 °C).

The purpose of this study is to assess the degradation of the optical transmission for sapphire optical fibres subjected to gamma irradiation (⁶⁰Co source with a total irradiation dose of 536 kGy, at a dose rate of 0.33 kGy/h) and 5.2 MeV energy neutron (Cyclotron deuterons impinging on a Be target with a fluences up to 3.15 x 10¹⁵ n.cm⁻²). All the investigations were carried off-line; after each irradiation session the optical fibres were measured in the Laboratory. We performed also some off-line measurements for electron beam irradiated sapphire optical fibres (total irradiation dose 25 kGy, at a dose rate of 2 kGy/min). In order to evaluate the radiation induced luminescence we done some on-line measurements under proton irradiation (energy of 10 MeV, total irradiation dose of 6.27 MGy, at a dose rate of 200 kGy/s). The measurements were done over the 200 nm – 1000 nm interval with a multi-channel optical fibre spectrometer, while in the 700 nm – 1700 nm range we used an optical spectrum analyzer. We noticed a variation of the attenuation characteristics in the 280-450 nm range from sample to sample. No significant degradation of the optical transmission was identified from 400 nm to 1700 nm, except a slight decrease in the 380-460 nm and 1410-1600 nm spectral ranges. The major radiation induced effect we observed refers to three radioluminescence emission bands, one wider between 380 nm and 520 nm, and two narrower at 605 nm and 695 nm. Further in situ investigations are planned in order to monitor the dynamics of both attenuation and emission spectra.
Phonons, electron-phonon interactions
A RAMAN STUDY OF THE SUPERIONIC BEHAVIOUR OF CaF₂
CRYSTALS CONTAINING TRIVALENT LANTHANIDE IONS

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Pure fluorite crystals are known to exhibit superionic behaviour at temperatures in excess of 1000 K [1,2]. Lanthanides readily enter the fluorite lattice in the trivalent form which necessitates the introduction of interstitial fluorine ions for charge compensation and, relatively high dopant concentrations can be accommodated. Lanthanide doping has the effect of lowering the temperature at which superionic behaviour commences in fluorite crystals [2-4].

In this work, results from Raman scattering studies of the T 2g mode in an undoped CaF₂ crystal and in CaF₂ crystals separately doped with 10% of Tb³⁺, Tm³⁺ and Nd³⁺ ions as well as 10% to 20% of La³⁺ ions in the temperature range 300 K – 1350 K are presented.

The linewidth (FWHM) of the T 2g peak is found to increase almost linearly with temperature, up to the transition temperature of 1025 K for the undoped and of between 875 K and 975 K for the 10% doped crystals. Thereafter the linewidth increases are steeper in all cases, with the rate of increase becoming almost double that of the initial stage. The 15% and 20% La³⁺- doped samples show the same behaviour as for 10% except for a slightly lower transition temperature. Further, for the La³⁺- doped samples, the rate of increase of the linewidth with temperature decreases from ~1050 K onwards, indicating saturation of the effects responsible for the broadening. The results show that the temperature at which superionic behaviour commences in doped fluorites is influenced by the relative size of the dopant to the host cation.

In the doped samples, the T 2g peak is shifted to lower energies by up to 8 cm⁻¹ compared to pure CaF₂. Further, as the temperature of each sample is raised, the peak gradually drifts to lower energies until the transition temperature is reached. Above the transition temperature, the energy position of the peak increases slightly before decreasing much more rapidly. This is consistent with the high mobility of extrinsic interstitial fluorine ions above the transition temperature.

References

HYDROXYL IONS IN SCHEELITE TYPE MOLYBDATES AND TUNGSTATES

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Tungstates and molybdates with the tetragonal scheelite structure (space group I4₁/a) are good candidates for efficient nonlinear solid state materials for stimulated Raman scattering [1]. The crystals are often doped with rare earth elements, but their defect structures are rarely studied. Oxide crystals grown in air in the ~1000-1500 °C temperature range usually contain hydroxyl ion impurities which may influence the physical properties of the crystals utilized in the applications [2]. In the present work the incorporation of OH⁻ ions in some scheelite type molybdates (CaMoO₄, SrMoO₄, PbMoO₄) and tungstates (BaWO₄ and SrWO₄) has been investigated via their stretching vibration detected by high resolution FTIR absorption spectroscopy.

The crystals were grown from melt either by the modified Stepanov technique or the Czochralski method. Oriented samples were cut parallel and perpendicular to the tetragonal c-axis. Absorption bands related to hydroxyl ions have not been observed in the room temperature spectra of the crystals. At 9 K, however, very weak bands appeared in the 3200-3500 cm⁻¹ wavenumber range for CaMoO₄, SrMoO₄, and SrWO₄. In both PbMoO₄ and BaWO₄ crystals a number of OH⁻ bands with different frequencies, halfwidths and intensities were detected due to the different O-O bond lengths and cation environments (see e.g. Fig. 1). The vibrational properties (e.g. anharmonicity, phonon coupling etc.) of the hydroxyl ions and their possible defect sites will be discussed.

Figure 1: Absorption bands related to hydroxyl ion vibrations in BaWO₄ crystal at 9 K

References

THE EFFECT OF Mg DOPING ON THE RAMAN SPECTRA OF LiNbO₃ CRYSTALS

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LiNbO₃ is a well-known non-linear optical material, but its application is often limited by the photorefractive effect. The optical damage resistance can be improved by doping the crystal with MgO above a threshold concentration [1]. Many physical properties depend on MgO addition and change at the threshold value, e.g. OH-vibration [2], UV absorption edge [3], Raman spectrum [4] etc. In previous Raman experiments the Mg incorporation was investigated only in congruent crystals [4,5]. In the present work LiNbO₃:Mg crystals grown from congruent, stoichiometric and intermediate compositions were systematically studied by the Raman spectroscopic method.

The E(TO₃-TO₉) and A₁(TO₁-TO₄) phonon modes were investigated on y-cut samples in the y(zx)y and y(zz)y backscattering geometries, respectively. The position of the E(TO₇) band slightly shifted towards higher and that of the A₁(TO₂) and A₁(TO₃) bands towards lower wavenumbers, while the frequency of the remaining bands essentially did not change with increasing Mg content. The halfwidth of every Raman mode showed the threshold effect depending on the Li/Nb ratio and Mg content, while it increased linearly as a function of Mg concentration for the above-threshold samples, similarly to the behaviour of the UV cut-off wavelength [6]. There is a strong Mg dependence of the position and halfwidth of the 2-phonon band seen in y(zz)y geometry at about 688-704 cm⁻¹.

The A₁(LO₄) phonon mode, measured on z-cuts, showed at the high frequency side a small side-band disappearing in undoped stoichiometric crystals. With growing Mg concentration above the threshold the halfwidth of the main band increased linearly (with constant position at 873 cm⁻¹) in both the congruent and stoichiometric crystal series. The ratio of the areas of the main and side bands showed again the well-known threshold effect. The Raman band at about 740 cm⁻¹, attributed earlier to antisite NbLi [7], vanished at the threshold but reappeared again for further increasing Mg content.

A non-destructive method for the determination of the Mg concentration in above-threshold LiNbO₃:Mg samples was demonstrated. The results of Raman measurements confirmed the models of Mg incorporation in LiNbO₃ crystals with various Li/Nb ratios.

References
EPR- AND OPTICAL SPECTROSCOPY OF MnO$_4^{2-}$ DOPED PROPER FERROELASTIC K$_3$Na(CrO$_4$)$_2$: LOCAL TRANSITION AND JAHN-TELLER EFFECT.

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The investigation of two types of local instabilities, local transition and Jahn-Teller (JT) effects, interacting with each other in soft matrices is important topic for physics of defects. Molecular impurity ions attract special attention in this context.

High optical quality single crystals of K$_3$Na(CrO$_4$)$_2$ proper ferroelastic doped with MnO$_4^{2-}$ molecular complexes were grown from aqueous solution saturated with K$_2$CrO$_4$ and Na$_2$CrO$_4$ in a molar ratio 3:1 and containing KMnO$_4$ corresponding to 0.3% of MnO$_4^{2-}$ ions in respect to CrO$_4^{2-}$ ions.

The first near-infrared luminescence (NIRL), luminescence excitation (LE) and the optical absorption spectra of these crystals are reported. The broadband luminescence spectra were studied in the region 8500-11500 cm$^{-1}$ under Kr$^+$- laser and Xe-lamp excitation in resonance with the MnO$_4^{2-}$ charge-transfer (CT) absorption band. A good correspondence of the LE-profile to the CT-absorption band shape allows ascribe the NIRL to MnO$_4^{2-}$ impurity ions substituting the CrO$_4^{2-}$ ions in the host lattice. The NIRL spectrum has been assigned to d-d ($^2T_2$ – $^2E$) transition of the MnO$_4^{2-}$ in accord with [1 2].

The detailed study of the polarized luminescence spectra of K$_3$Na(CrO$_4$)$_2$ :MnO$_4^{2-}$ in the interval 300 – 8K showed up a well-resolved vibronic structure at low temperatures. At 8K two main vibrational progressions originated from two zero-phonon lines at 10605 cm$^{-1}$ and 10461 cm$^{-1}$ were observed and attributed to the strong vibronic interaction between electron and bending (e) local mode of the MnO$_4^{2-}$ centre. The conclusion was drawn about splitting of the $^2E$ ground electronic state of MnO$_4^{2-}$ caused by removing of its orbital degeneracy in the monoclinic crystal field of the host lattice. The single crystals of K$_3$Na(CrO$_4$)$_2$ with the MnO$_4$ molecular impurity ions substituted for CrO$_4$ have been studied for the first time also by EPR spectroscopy methods. At 3.5K the EPR spectrum consists of the set of narrow hyperfine lines due to Mn$^{6+}$ embodied in the MnO$_4^{2-}$ ion. Sharp decreasing of these lines intensity in rather narrow temperature range (from 10 to 20K) and simultaneous increasing of another part of EPR-spectrum could be related to local transition of the first order. The appropriate conditions for JT- or pseudo-JT- effects formation are appearing due to local transition effect. Spectrum dynamic averaging with respect to different JT-configurations could explain detected transformation with temperature of the EPR-spectrum.

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References

Emission and absorption of phonons play a key role in the non-radiative relaxation processes between electronic states of rare earths embedded in laser crystal matrices. The study of vibronic transitions by absorption spectroscopy may provide information about the interaction between the optical active ions and the host lattice [1]. High resolution FTIR spectroscopy has been applied to monitor the electron-phonon interaction in YAl$_3$(BO$_3$)$_4$ (YAB) single crystals grown by the top-seeded flux method and doped with Dy$^{3+}$ and Er$^{3+}$. In a previous work the related low temperature (9K) sharp zero-phonon (ZP) line spectra, due to the intraconfigurational 4f$^n$ transitions have already been measured and interpreted [2].

In the present work the weak vibronic lines, monitored on the high energy side of the ZP ones, have been analyzed in detail. The energy separation between vibronic and the ZP lines are compared both with IR-active modes (see Fig 1) and with Raman-active modes measured on YAB crystals. Boron isotopic effects are also put into evidence. In Er doped YAB the ZP line temperature-dependent broadening and shift are discussed in the framework of a two phonon Raman relaxation model [3].

![Figure 1: Infrared vibrational spectrum of YAB measured at 9K.](image)

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References

Cadmium iodide (CdI$_2$) single crystals possess with layered structure formed by identical I–Cd–I sandwiches. Within I–Cd–I layers atoms are held together with strong ionic–covalent bonds while interactions between adjacent layers are due to weak van der Waals forces. Such anisotropy of chemical bonds makes CdI$_2$ suitable for different microelectronic applications [1].

Phonons in CdI$_2$ have been studied earlier by Raman spectroscopy [2]. For the 4H polytype interlayer vibration mode at nearly 16 cm$^{-1}$ and intralayer modes, related to atoms vibrations at higher wavenumbers were observed. Herewith we report the results of our far-infrared and mid-infrared transmission studies on pure and doped with different impurities (In, Sb, Sn, Te and excess Cd) CdI$_2$ crystals. Measurements were made for wavenumbers range of 30 to 8000 cm$^{-1}$ at different temperatures from 10 K up to 300 K.

In the low-temperature far IR transmission spectra of 4H-CdI$_2$ bands corresponding to lattice vibration modes are observed at 105 cm$^{-1}$, 90 cm$^{-1}$, 64 cm$^{-1}$ and 35 cm$^{-1}$. The absorption band at 64 cm$^{-1}$ is not revealed at \( T > 150 \)K due to the broadening of the 90 cm$^{-1}$ band. The band at 90 cm$^{-1}$ shifts to 82 cm$^{-1}$ upon heating to RT and its intensity show specific non-linear dependence on temperature. The activation of crystals by diffusion during/after growth does not have any significant effect on their far IR spectra.

Mid-infrared transmission spectra of all investigated samples reveal several features in 800–1100 cm$^{-1}$ wavenumbers region. Relative intensity of these peaks varies depending on the impurity. This result is in good agreement with our preliminary SEM analysis and optical data which confirmed the formation of microsized metallic clusters within CdI$_2$ crystals.

References

The mercurous halides $\text{Hg}_2\text{Hal}_2$ ($\text{Hal} = \text{Cl, Br, I}$) are isomorphic at room temperature and have the specific crystal structure consisting of parallel chains of linear Hal-Hg-Hg-Hal molecules, weakly bound to one another and forming a body-centred tetragonal lattice $D_{4h}^{17}$ with two molecules per unit cell. The chain-like structure of these crystals gives rise to a very strong anisotropy of their physical properties, in particular, to a strong elastic anisotropy. For example, $\text{Hg}_2\text{I}_2$ crystals exhibit a transverse (TA) sound velocity $V_{\text{TA}} = 254\text{m/s}$, a record-low characteristic among solids, a record-high birefringence $\Delta n = +1.5$ and a very high acousto-optical coupling ($M_2 = 4284 \times 10^{-18} \text{s}^3/\text{g}$ for the TA wave).

At the cooling, these crystals undergo improper real and incipient ferroelastic phase transitions from the tetragonal to orthorhombic structure ($D_{4h}^{17} \rightarrow D_{16}^{17}$), at $T_c = 144 \text{K}$ ($\text{Hg}_2\text{Br}_2$) and $T_c \approx -20 \text{K}$ ($\text{Hg}_2\text{I}_2$, incipient ferroelastic). Phase transition in $\text{Hg}_2\text{I}_2$ crystals was observed only under a high hydrostatic pressure ($P_c = 9\text{Kbar}$ at $T = 293\text{K}$). These transitions are induced by condensation of the slowest (TA) branch at the Brillouin zone-edge (X-point) of the tetragonal paraphase and are accompanied at $T \leq T_c$ by a doubling of the unit cell, $X \rightarrow \Gamma$ zone folding, onset of spontaneous strain and nucleation of ferroelastic domains.

In the present work the Raman spectra of mixed crystals $\text{Hg}_2(\text{Br,I})_2$ were studied in a wide temperature range in various polarizations. The Raman spectra revealed multimode behaviour of vibrations, which is bound with existence in these crystals of molecules of three types, namely, $\text{Hg}_2\text{Br}_2$, $\text{Hg}_2\text{I}_2$ and $\text{Hg}_2\text{BrI}$. In low-frequency spectra the overtone of the TA-soft branch from X-point of the Brillouin zone-edge (at $T > T_c$) and the fundamental tone (at $T < T_c$) of the same branch at the centre of Brillouin zone ($\Gamma$-point) were observed. The temperature behaviour of the soft modes in these mixed $\text{Hg}_2(\text{Br,I})_2$ crystals of a series of compositions was studied. The values of critical exponents, describing the temperature dependencies of the soft mode frequencies as in paraphase and in ferroelastic phase of these mixed crystals were received.

The influence of disorder of an anionic sublattice on violation of translational symmetry and infringement of the momentum selection rules was studied. As a result of these infringements the density of one-phonon states of the soft TA-branch was observed in spectra. In case of medium compositions the strong diffusion of all effects of phase transitions was discovered. At low temperature ($T = 10\text{K}$) in the range of frequencies of stretching vibrations Hg-Hg in spectra the quasilocal (as a triplet) and resonant stretching vibrations, bound with existence of ferro- and antiferroelectric nanoclusters and induced by mixed dipole molecules Br-Hg-Hg-I and their proximate environment, were observed. The nature of the found out effects in these model mixed crystals was discussed.

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ANOMALOUS OPTICAL SPECTRA OF THE CENTRES WITH SOFT DYNAMICS IN THE FINAL STATE

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Optical transitions in the centres having a soft or weakly unstable vibrational dynamics in the final electronic state are considered. This type of dynamics takes place if there exists a configurational coordinate which has only a little influence on the energy of the system. Examples can be found in the electronic transitions of the centres with the pseudo-Jahn-Teller effect, in photodissociation transitions with emission of a weakly bonded particle, and in the hot luminescence of excimer-type self-trapped excitons.

The shape of the optical spectra of the impurity centres in crystals is determined by the interaction of the optical electrons of the centre with phonons. In the case of electronic transitions between the states with hard and soft dynamics the electron-phonon interaction includes a strong quadratic term, which is responsible for the change of the elastic force constants, causing the softening of the local dynamics. This change of elastic force constants leads to a strong mixing of the normal coordinates during the transition (a rotation in the space of normal modes). In crystals this is the mixing of about an Avogadro number of phonon modes. To take this mixing into account we apply the operator transform method. We also proposed an algorithm allowing the exact consideration of the arbitrary quadratic vibronic coupling based on the Stratonovich identity and the path-integral-type calculations.

One of the essential characteristics of the case under consideration is a strong enhancement of the effect of low-frequency phonons, resulting in a drastic increase of the low-frequency part of the phonon sideband of the spectrum. The spectrum gets a shape resembling an asymmetric lambda. This type of spectra has actually been recorded experimentally [1]: instead of a zero-phonon line one observes almost a jump–like shape of the spectral intensity of the type $\Theta(\omega - \omega_0)F(\omega)$, where $\omega_0$ is the resonant frequency, $\Theta(\omega)$ is the Heaviside step function and $F(\omega)$ smoothly decreases with $\omega$. In some cases the lambda-like spectrum may be modulated, the modulation originating from the Airy oscillations characteristic for almost free (weakly accelerating) motion of a quantum particle. The spectra with a modulated lambda-shape have been observed in the hot luminescence of self-trapped excitons in solid Xe [2]. This type of spectrum was also observed for the electronic transitions of single molecules in superfluid $^4$He droplets [3]. The quantum motion in this case corresponds to one-particle ($^4$He atom) excitations in the superfluid droplet.

References

Radiation effects II
Cordierite, of chemical formula \((\text{Mg,Fe})(\text{Al}_4\text{Si}_5\text{O}_{18})\text{n}(\text{H}_2\text{O},\text{CO}_2)\) is found in Minas Gerais State, Brazil as natural mineral of silicate. \(\text{SiO}_2\) (47.77 mol%), \(\text{Al}_2\text{O}_3\) (31.7 mol%), \(\text{MgO}\) (7.52 mol%) and \(\text{F}_2\text{O}_3\) (8.31 mol%) are basic components of the crystal. As foreign molecules \(\text{MnO}\) (0.287 mol%), \(\text{CaO}\) (0.46 mol%), \(\text{Na}_2\text{O}\) (0.84 mol%) and \(\text{K}_2\text{O}\) (0.3 mol%), are also found. Other elements are present in much smaller concentration. Its glow curve is composed of one broad TL peak extending from 50 to 250°C. The peak positron seems to be around 140-150°C. The TL intensity grows superlinearly as function of the radiation dose up to 1000 Gy. Beyond that the TL intensity becomes sublinear. Samples pre-annealed at 500°C, 600°C, 750°C and 950°C for one hour and then irradiated to 500 Gy present following behaviour. The 145°C peak in 600°C pre-annealed sample presents about 5 times enhanced TL reading. The 750°C pre-annealed sample also presented a sensibilized 145°C TL peak, however, the peak positron shifts by 25°C to higher temperature region. In the 900°C pre-annealed sample a shift of 50°C to higher temperature was observed.

The method of two heating rates for TL reading and the method of initial rise were used to find \(E\) and \(s\) values. The isochronous decay curves show that 4 to 5 peaks must be present in that broad TL glow curve mentioned above. The Glow curve deconvolution calculation confirms this result.

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PHOTOTRANSFER EFFECTS ON $\beta$- AND UV-IRRADIATED RbBr:Eu$^{2+}$ AND KBr:Eu$^{2+}$ CRYSTALS

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As is well known, defects induced by ionizing radiation on KCl:Eu$^{2+}$ and KBr:Eu$^{2+}$ crystals at room temperature (RT) were found to be mainly F centres. While in KCl:Eu$^{2+}$ almost all the F centres recombine around 200 °C [1], in KBr:Eu$^{2+}$ they recombine around 100 °C [2] showing a shift in the glow peak temperature during thermoluminescence (TL) read out. On the other hand, photostimulation (PS) with F light at RT in partial thermal bleached KCl:Eu$^{2+}$ [1] and RbCl:Eu$^{2+}$ [3] samples produce a phototransfer in the TL glow curve (PTTL) recovering some glow peaks around 150 °C due to the F to F$_Z$ conversion. Considering that these effects could be common to the europium doped alkali halides, in this work the PS effects on the TL of $\beta$ and UV irradiated RbBr:Eu$^{2+}$ and KBr:Eu$^{2+}$ crystals have been studied in the 180-375 K temperature range. The TL glow curve of RbBr:Eu$^{2+}$ irradiated with UV at 200 K show four main glow peaks located at 234, 272, 316, and 363 K, while in KBr:Eu$^{2+}$ the glow curve consists of four glow peaks at 264, 275, 319, and 373 K. Thermoluminescence after phototransfer shows that the 234 and 272 K glow peaks in RbBr:Eu$^{2+}$ and the 275 and 319 K glow peaks in KBr:Eu$^{2+}$ are recovered with PS under F light after being thermally bleached. A similar PTTL effect occurred after PS at 200 K of RT $\beta$-irradiated RbBr:Eu$^{2+}$ and KBr:Eu$^{2+}$ crystals. These results indicate that these crystals behave as KCl:Eu$^{2+}$ and RbCl:Eu$^{2+}$ crystals but in a different temperature range.

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References

THE PECULIARITIES OF HYDROXYL IMPURITY BEHAVIOR IN CRYSTALLINE MgO AND LiF MATRICES UNDER THE ACTION OF RADIATION

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It is well-known that the hydroxyl $OH^-$ impurity plays an important role in formation of radiation-induced defects in alkali halides [1]. In other ionic compounds (e.g. MgO) which represent the different class of ionic systems, the hydroxyl is not fully studied, though the molecular $OH^-$ has no alternative for formation of hole defects [2,3]. The existence of this impurity in crystals is usually revealed by means of stretching vibrations of $O-H$ in 3750-3500 cm$^{-1}$ region [4,5].

In the given work the irradiated MgO and LiF single crystals were investigated. Before irradiation the maximum concentration of $OH^-$ was equal to $\sim10^{18}$ cm$^3$. Among the MgO samples there were those which were free of $OH^-$ impurity.

The irradiation of MgO was carried out by mixed ($\gamma, n$)-radiation in the channels of Dubna (Russia) and Tashkent (Uzbekistan) reactors. LiF crystals were irradiated earlier in the channels of Tbilisi reactor. Maximum doses of neutron radiation in all cases were more than $\sim10^{17}$ n/cm$^2$. The irradiation was also carried out by gamma-sources of different intensities. Maximum gamma-irradiation doses were $\sim10^8$ rad. Besides, MgO crystals were irradiated at neutron generator.

IR-absorption spectra were registered at room temperature using the spectrophotometer “Specord-75IR” (Karl Ceiss, Iena).

The results, for MgO samples were compared with the results obtained in LiF. The analysis of these results allowed us to establish the following:

- In LiF after the action of radiation a decrease of intensity of $OH^-$-bands takes place with the increase of irradiation dose and the bands about 2000 cm$^{-1}$ (U$_1$-band) and 1000 cm$^{-1}$ (U-band) appear [6,7].

- In contrast to LiF, in MgO which was free of $OH^-$ ions, there appear the bands, due to the presence of hydroxyl (3290 and 3370 cm$^{-1}$). Moreover, there was observed the band at 1600 cm$^{-1}$, early not known so far. This can be explained by the presence of hydroxyl ion as well [8].

- Independent of irradiation dose and sources of radiation (reactors, gamma-sources, etc.) for MgO crystals of different origin a linear interdependence was observed for IR-bands caused by hole centers ($OH^- - [Mg^{2+}] - O^{2-}$ and $OH^- - [Mg^{2+}] - OH^-$).

- In MgO containing $OH^-$ before the irradiation a nonmonotonous dependence on dose was observed.

The work was partially supported by ISTC grant G-646.

References
OPTICAL STUDIES OF RADIATION EFFECTS IN UNDOPED AND II-VI NANOCRYSTAL-DOPED ALKALI ZINC BOROSILICATE GLASS


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Highly transparent in visible range alkali zinc borosilicate glasses are often used as host matrices for semiconductor nanocrystals embedded by solid-state precipitation. Both undoped and semiconductor-doped glasses of such type are popular optical materials extensively used under a variety of external factors including ionizing radiation. Hence, optical studies of radiation effects in these materials seem quite significant.

Here we report on optical spectroscopic studies of SiO$_2$–B$_2$O$_3$–ZnO–K$_2$O–Na$_2$O glass, both undoped and doped with II-VI semiconductor nanocrystals, exposed to irradiation with X-rays (40 keV, from 100 to 2500 Gy, Cu K$_\alpha$ radiation) and electrons (7 MeV, $10^{14}$ cm$^{-2}$, M-30 accelerator) at room temperature. For the semiconductor-doped samples the average radius of the nanocrystals was estimated from the optical absorption spectra while their chemical composition was determined by Raman spectroscopy as Cd$_{0.68}$Zn$_{0.32}$S$_{0.32}$Se$_{0.68}$ [1].

Similarly to zinc-free alkali borosilicate glass [2], both X-ray and high-energy electron irradiation of undoped alkali zinc borosilicate glass at 293 K result in the same changes of the optical absorption spectrum. In our case in the spectral range under study they can be well approximated by a superimposition of three absorption bands centered at 1.9, 3.1, and 4.6 eV with halfwidths 0.4, 1.1, and 1.2 eV, respectively. Note that the irradiation-induced absorption band energy positions are somewhat higher than those for zinc-free alkali borosilicate glass (2.0, 2.7, and 4.0 eV) [2] where they are attributed to H$_3^+$, H$_2^+$, H$_4^+$ radiation colour centres, respectively.

For the nanocrystal-doped glass the absorption spectrum is characterized by a typical absorption edge and size-dependent confinement-related maxima. Under irradiation with both X-rays and high-energy electrons the absorption edge blue shift (up to 0.12 eV) and smearing of the confinement-related features are observed, both effects increasing with the irradiation dose. The observed behaviour is related to the nanocrystal ionization due to charge transfer between them and radiation colour centres formed in the glass.

References


Primary and aggregate point defects in lithium fluoride (LiF) have attracted renewed attention due to the exciting results obtained in the realization of miniaturized optical devices. The increasing demand for low-dimensionality photonic devices imposes the use of advanced irradiation methods for producing luminescent structures with high spatial resolution [1], such as extreme ultra-violet lithography (EUVL) [2]. Recently, the idea of using LiF as a film-like image detector for soft X-ray microscopy, based on optically-stimulated luminescence from colour centres, was proposed [3], tested [4], and it is still under further development [5].

We will discuss about the formation efficiency of F and F₂ centres in LiF crystals by using EUV and soft X-ray radiation generated by an intense laser-plasma source. Optical absorption and photoluminescence measurements were performed at room temperature (RT) and at high doses. High concentrations of stable primary and aggregate electronic defects were obtained at the surface of the LiF irradiated crystals, in a very thin layer, whose depth was estimated around 50 nm [6].

From the optical absorption spectra, an F formation efficiency of 2–4 centres/keV is inferred, a value comparable with the ones found in the literature for low-energy electrons with similar penetration depth in LiF [7]. The F₂-center formation behaviour follows the F-centre one. At such high concentrations, no quenching of the F₂ luminescence intensity was observed at RT in very thin coloured-LiF layers.

References

In our precedent works [1,2] we have reported that two distinguishable electron paramagnetic resonance (EPR) line shapes of the E’γ centre can be distinguished in γ-ray irradiated a-SiO2. One of these line shapes, L1, is typically observed for irradiation doses <10 kGy, whereas the other one, L2, is observed for doses >10^3 kGy. For intermediate doses the EPR line shape results from a combination of L1 and L2. Furthermore, isochronal thermal treatment experiments have pointed out that for temperature higher than ~400 K the L2 line shape converts to L1. To explain these features we have supposed the existence of two distinct typologies of E’γ centres in a-SiO2, characterized by slightly different microscopic structure [1,2] and, probably, originating by irradiation from different precursors sites [2].

In order to further characterize these two typologies of E’γ centres and to gain more information on their microscopic structures, here we report a study of the hyperfine doublet of the E’γ centre, split by ~42 mT and originating from the hyperfine interaction of the unpaired electron with a 29Si nucleus (nuclear spin I=1/2, natural abundance 4.7%). To achieve the sensitivity necessary for this study the hyperfine doublet has been acquired in the high-power second-harmonic detection scheme. Our results show that, similarly to what observed for the main resonance of the E’γ centre, two different 42 mT hyperfine doublets can also be distinguished (Figure 1). These two hyperfine doublets have a nearly equal main split of ~42 mT, but differ in the width of the right and of the left components. The structural implications of the observed differences in the hyperfine structure line shapes are discussed.

References

Dosimetric evaluation is important specially at high dose levels. For this purpose, many devices have been developed and applied in various work areas. Glass dosimeters are important for the various high-dose levels e.g. in medical, industrial and food irradiation applications. Glass dosimeters are used in several high-level exposure applications, employing mainly spectrophotometric or densitometric analysis of colour-centre formation [1,2]. The profusion of electron-hole and recombination processes in glasses exposed to ionizing radiations is rich of interesting phenomena that involve charge and energy transfer processes which occur among populations of specific impurity and defects [3]. Since the discovery of bioglass, several research projects have focused on glasses and glass-based material as biomedical materials, which can repair damaged living tissues and organs by interacting with biological systems. In this work, a different application for this material is proposed with bioglass (50% P₂O₅, 30-40% CaO, 20-10% Na₂O) as a thermoluminescent dosimeter (TLD). The glass samples were powdered, and grains were obtained with diameter between 0.074 and 0.177mm. This grains were prepared in the proportion of 2(Teflon):1(glass), pressed, sinterized and transformed in pellets of 50mg and 2mm of thickness, and 6mm of diameter. For reutilization and to avoid residual TL, the pellets were thermally treated at 300°C/1h. The pellets were irradiated with ⁶⁰Co with absorbed doses between 0.5Gy and 20kGy. The TL glow curves were obtained using a Harshaw TL reader of Nuclear Instruments Systems, model 2000 A/B, and the data acquisition was performed using a virtual instrument (ADC-212 Pico Technology Ltd.) and a personal microcomputer. The glow curves present two peaks at 110°C and 275°C. The TL response repeatability presented a maximum coefficient of variation smaller than 10%. The calibration curve is linear between 0.5kGy and 20kGy. Results about energy dependence and minimum detection limits will also be presented. The efficiency of electron and hole-centre generation depends on the basic bioglass composition, and it is almost independent of the ionizing radiation type. The gamma radiation dose response and the thermal stability were studied to establish the suitability of bioglass as a TL dosimeter.

References

Radiation defects generated by $\gamma$-irradiation in single NaCl crystals with 0.04% and 0.08% concentrations of Cu$^+$ impurity were analyzed by optical absorption and thermoluminescence methods. The crystals were exposed to gamma rays from a $^{60}$Co source (0.954 to 30 kGy). The radiation-induced defects were mainly F, Cu$^-$ and Cu$^+$ centres, with absorption bands located at 464, 256.7 and 236 nm, respectively. The absorption bands were found to be independent of the Cu impurity concentration. As the gamma dose irradiation increased, the absorption band at 256.7 nm decreased while the band at 236.3 nm increased highly along with the 256.7 nm band.

The F-centres produced at high gamma radiation dose while thermally bleached showed an increase of the Cu$^+$ optical absorption bands with a simultaneous decrease of Cu$^-$ absorption band. The bleaching with F-light showed the participation of the F centre generated by gamma radiation on the ion valence changes of the doping impurity as well as on the TL phenomenon. The TL measurements in NaCl:Cu crystals with both impurity concentrations demonstrated that the Cu$^+$ concentration has a strong influence on the intensity and shape on the glow peaks.
PTh77

EPR HYPERFINE STRUCTURE OF F-TYPE CENTRES IN PURE LiBaF₃ CRYSTAL

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LiBaF₃ crystals are materials considered for various applications including scintillators [1]. F – type centres in LiBaF₃ crystals were recently studied by optical [2] and magneto optical (MCD-EPR) methods [3] as well as EPR methods in Fe - doped crystal [4]; however their structure has not been completely clarified. The MCD-EPR measurements performed in [3] did not resolve hyperfine (hf) structure of the F-type centres, but in Fe activated crystal the contribution of the activator could not be excluded and spectrum overlapped with some additional unidentified lines [4].

We studied EPR spectra of pure LiBaF₃ sample of high quality. For EPR measurements LiBaF₃ sample was X-irradiated at room temperature, however spectra could be observed at low temperatures - at 77K. We could well resolve all hyperfine structure lines of F-type centre. Qualitative analysis with g-tensor parameters derived from magneto-optical measurements showed that the F-type centre observed earlier by MCD-EPR techniques is the same F-type centre we observe with the EPR. In this work we will analyse origin of the hyperfine structure of the EPR spectra and their angular dependencies and discuss the structure of F-type centres in the LiBaF₃ crystal.

References

OPTICAL ABSORPTION STUDY OF Fe$^{2+}$ AND Fe$^{3+}$ SPECTRA IN AQUEOUS SOLUTIONS AND HYDRATED CRYSTALS

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After a short review and comment of literature data on the crystal field spectra of compounds containing Fe$^{2+}$ and Fe$^{3+}$, new absorption spectra of aqueous solutions and hydrated crystals are shown up to 50000 cm$^{-1}$, in order to examine also the interval in which charge transfer transition occur. Several details on the Fe$^{2+}$ spin-forbidden transitions which up to now have received little attention, are put in evidence: as a consequence we have proposed for the lower energy transitions different attributions respect to the commonly accepted ones. The diagnostic features of the Fe$^{3+}$ spectrum have been confirmed. The charge transfer transitions have been observed in both cases.

![Absorption spectra of Fe$^{2+}$ and Fe$^{3+}$](image.png)

Figure 1: Absorption spectra of: Fe(BF$_4$)$_2$ aqueous solution (dashed line); FeSO$_4$ single crystal (full line); FeCl$_2$ single crystal (dotted line).

References

EFFECTS OF UV-LIGHT IRRADIATION IN SrTiO₃, KTaO₃ AND KTa₁₋ₓNbO₃ STUDIED BY DIELECTRIC AND RAMAN SPECTROSCOPIES

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In recent years, low-temperature giant photo-induced dielectric permittivity and relaxation have been reported in the perovskite oxides SrTiO₃ [1] and KTaO₃ [2]. Two models were proposed. One ascribes the effect to fluctuating dipoles originating from carriers induced by interband excitation and localized as small polarons. The other is a Maxwell-Wagner model in which it is assumed that photo-excitation induces metallic clusters separated by thin non-conducting layers. Other authors [3] observe effects similar to those reported in [1,2], but emerge only if a dc electric field is applied together with interband light irradiation. Therefore, it is apparent that further investigation is needed to clarify important features of the reported effects and the microscopic nature of the observed phenomena.

In the present work, we present results of temperature-frequency dielectric permittivity measurements in the incipient ferroelectrics SrTiO₃ and KTaO₃, and in ferroelectric KTa₁₋ₓNbₓO₃. The experiments have been performed in different illumination conditions, in the presence and in the absence of a dc field. We also report Raman scattering spectra as obtained in the presence and in the absence of interband excitation, which help to clarify whether polar structural modifications can be induced by illumination. We compare our results with the existing literature and discuss the plausibility of different models, including those already proposed by other authors.

References

Spatially separated stable charge centres – trapped electrons and self-trapped holes (STH) were generated in Ar matrix doped with Xe and N\textsubscript{2} under irradiation by an electron beam. Energy stored by the sample during electron bombardment can be released thermally or optically. The study presented concerns photon-stimulated processes. Generation of centres and following relaxation were monitored by combination of the cathodoluminescence with photon-stimulated luminescence (PSL) and exoelectron emission (PSEE). Photons promote the trapped electrons into the conduction band (CB), and these can be extracted and detected as exoelectrons or recombine with the positively charged STH and dopants to yield VUV luminescence:

\[
\text{STH}^+ + e^{-} \rightarrow \text{STE}^* \rightarrow \text{Rg} + \text{Rg} + h\nu_1, \quad \text{Rg}_2^+ + e^{-} \rightarrow \text{Rg}_2^* \rightarrow \text{Rg} + \text{Rg} + h\nu_2
\]

The concentration of detrapped electrons in the CB can be expressed as:

\[
N_c = N_0 \tau_c \exp(-gt), \quad (1)
\]

where \(g\) is the product of photon density and the effective cross section of their interaction with trapped electrons. \(\tau_c\) is the effective lifetime of the electrons in the CB. \(N_0\) – the initial concentration of electrons in the traps. Intensity of VUV recombination luminescence as well as PSEE depends on the concentration of electrons in the CB and decays exponentially. Spectrally resolved VUV luminescence induced by He-Ne laser and PSEE from Ar samples have been discussed in [1] and [2,3] respectively.

In the N\textsubscript{2}-containing matrix the electron irradiation produces efficiently metastable N atoms, which radiatively return into the ground state (the well-known \(^2\text{D} \rightarrow ^4\text{S}\) transition with the lifetime of about 20s in Ar matrix). This green emission provides an “internal” source of visible photons. In this case \(g(t)\) will decay exponentially with the characteristic lifetime of \(^2\text{D} \rightarrow ^4\text{S}\) transition. The simultaneously registered PSEE and luminescence of the N line showed exponential decay with the 20 s lifetime. We measured also VUV intrinsic and extrinsic recombination luminescence from pre-irradiated samples. Lifetime, extracted from all decay curves, situated within the limits of measurement errors, is of about 20s in Ar matrix. The similar lifetime for the N line decay, PSEE yield and intensities of the VUV recombination luminescence give us a direct proof that the emission of exoelectrons and VUV recombination luminescence are stimulated by the radiative transition of metastable N atoms – some kind of “internal photoeffect” followed by conversion of visible light into VUV photons. New results on photo-stability of charge centres at low temperature were obtained.

References

Thermal Transformation of Color Centers in LiF Crystals with Given Content of O<sub>2</sub> and Metal Ions

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Processes of radiation creation and annealing of Frenkel defects as well as their transformation processes have been studied in RT gamma-irradiated LiF single crystals containing various impurities, by means of highly sensitive methods of measurements of thermal stimulated changes in absorption and luminescence spectra.

Novel important information about the density of colour centres in LiF crystals which depends on irradiation doses, cation impurities and temperatures [1-5], have been obtained for various contents of oxygen, hydroxyl and metal ions as reported in Fig.1.

Figure 1: Examples of optical spectra of LiF crystals containing different metal impurities, samples C and D, and annealed at different temperatures in air.

A preliminary comparison of annealing parameters of various LiF crystals [6] subjected to different doses of irradiation, but to the same thermal procedure, has been performed and will be discussed critically.

References

INFLUENCE OF HIGH ENERGY ELECTRON BEAM ON OPTICAL PROPERTIES OF LiF:Sc SINGLE CRYSTALS

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Investigation of optical absorption is one of the base methods for defects in material research. The goal of present work is investigation of modification of optical absorption of LiF:Sc single crystals under high energy electron beams for different depth of penetration of radiation. The LiF:Sc single crystals was choose as subject of investigation because them effective atomic number is closely related to effective atomic number of tissue. It allows to use LiF:Sc material for creation of tissue-equivalent dosimeters. Also it gets some advantage for LiF:Sc crystals over another materials.

The LiF:Sc single crystals was growth by modified Kiropoulos method in platinum crucible on air. It was made at Institute of physics of National Academy of Science of Kyrgyzstan. The packet of LiF:Sc single crystals was prepared for irradiation. The packet was containing from 10 separated crystals (with thickness 1.5 mm of each) packed closely together on common base (Fig. 1).

Irradiation of the packet was made by electron beam (energy 10 MeV) on air. Electron beam was obtained by means of microtron (Russia, Ekaterinburg, USTU-UPI) and had current about 8 µA. During 2 minutes of irradiation the face side of the packet got dose 28-32 kGy, the back side of the packet got dose – 21-30 kGy. Values of dose was determined by special CO PD(F)R-5/50 film dosimeters on the base of polymer with phenazine colorant. The optical absorption spectra of LiF:Sc crystals was measured by Helios Alfa spectrophotometer.

The spectra of optical absorption of crystals from packet are presented on Fig. 2. These spectra show that F (240–250 nm) and F2 (440–450 nm) colour centres is appeared under electron beam irradiation. Experimental determined depth distribution of absorbed dose verify theoretical conception, in frame of which dose on surface of samples is lower than dose into samples. Using experimental results (intensity of absorption bands) we can estimate depth on which maximal effect of radiation modification is observed. In our case it is depth 4-6 mm.

![Figure 1: Packet of LiF:Sc crystal plates](image1)

![Figure 2: Absorption spectra of LiF:Sc crystals (a – area of absorption of F-centers; b – area of absorption F2-centers). The crystals was situated under surface on depth, mm: 1 – 0; 2 – 3.0; 3 – 4.5; 4 – 7.5; 5 – 13.5](image2)
COLOUR CENTRES
IN THIN INORGANIC-ORGANIC FILMS ON GLASS

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Inorganic-organic hybrids are a new kind of multi-functional amorphous materials which often characterize uncial properties and application (1). These hybrids can be compatible matrix for organic compounds of luminescence, laser and colour properties (2-3). Two kinds of inorganic-organic hybrids were produced by applying the sol-gel method. The gels were got from the following compounds:

A class: TEOS $\text{Si(OC}_2\text{H}_5\text{)}_4 + (R_x)_n\text{Si(OR)}_{4-n} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$; ($R_x$: vinyl (CH=CH$_2$), phenyl (C$_6$H$_5$) and methyl (CH$_3$) groups)-

B class: PhTES – phenyltriethoxysilane [(OC$_3$H$_5$)$_3$Si(C$_6$H$_5$)] + GPTMS – 3-glycidoksypropyltrimethoxysilane [(OCH$_3$)$_3$Si(CH$_2$)$_3$OCH$_2$CHOCH$_2$] + TBA – aluminium tri-sec-butylate [Al(OCH[CH$_3$]C$_2$H$_5$)$_3$]

Hybrid materials were coloured using ORASOL dyes. The structure of obtained hybrid materials were examined by spectroscopic methods FTIR and $^{29}$Si MAS NMR. It has been found that in the case of A class hybrids copolymers between units of TEOS (Q) and organic modifiers (D) are formed. In the case of B class hybrids the connected inorganic - organic network occurs. Thin coatings on glass slides were obtained using these hybrid materials. The coatings characterised intensive blue, orange and red colours. Chemical resistance of coatings as well as stability of colour at higher temperatures (up to 200°C) were determined. Moreover the optical characteristic of coatings by the measurement of selective transmission in the range of visual wavelength (UV-VIS spectrophotometer) were made. Intensity of colour and its stability were dependent on the kind of hybrid matrix. Best results were obtained for TEOS + PhTMS matrix (A class), as well as for B class matrix. On this base discussion about the character of colour centres in hybrid materials was carried out.

References

CORRELATION BETWEEN THE EPR CENTER (SiO$_4^{5-}$) AND TL PEAKS IN ZIRCON

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In the present work was investigated a zircon sample from Minas Gerais State, Brazil. The single phase of zircon was verified by XRD and the lattice parameter and density using Rietveld Method was calculated. Also, EPR and TL measurement was realized for this sample. The EPR measurement was performed using oriented monocrystal foil (5mm x 4mm x 1mm) parallel to b axis. The angular variations of EPR spectral showed an isotropic signal SiO$_4^{5-}$ in $g = 2.000$ [1]. Was observed TL peaks to 140$^\circ$C, 215$^\circ$C and 270$^\circ$C due Dy$^{3+}$ impurity corroborated with ICP-MS measurement.

The UV bleaching experiments of irradiated samples were carried with a 30W mercury lamp. TL peaks decay in approximately 60 minutes, same behaviour is observed in EPR centre (SiO$_4^{5-}$). This correlation between TL and EPR suggest that during irradiation Dy$^{3+}$ release electrons (Dy$^{4+}$) and part of these electrons are trapped by SiO$_4^{5-}$ centre (SiO$_4^{5-}$) and process inverse occurs during UV light exposition.

References

Time-resolved pulse spectrometry methods were used to study the influence of spin multiplicity on direction of the charge radiation-induced evolution of F$_2$ centres in LiF crystals.

Radioluminescence (PL) and temporal variation of optical absorption (OA) of F$_2^+$-, F$_2^-$ and F$_2^-^-$ colour centres induced by nanosecond electron pulse have been investigated in temperature range 60…300K and in time range $10^{-8}$…$10^{-1}$s after electron pulse effect on crystals. (Electron energy is 0.2MeV, energy density per pulse is 0.1J/cm$^2$). As time and energy characteristics as temperature dependences of the creation/destruction processes of these centres have been investigated.

Following processes occur under electron pulse exposure.

Trapping of a band electron by F$_2^+$-center results in formation of the F$_2^-$centre in a radiative singlet state (S$1$) or in long-lived triplet state (T) by (1), (2). The lifetime of the F$_2^-$ centre in S$1$ state is 17ns, whereas lifetime of the F$_2^-$centre in triplet state is $10^{-3}$s at 300K.

$$F_2^+ + e \rightarrow F_2(S_1) \rightarrow F_2(S_0) + \nu(F_2),$$

$$F_2(T) \rightarrow F_2(S_0).$$

The subsequent transitions into singlet ground state (So) result in increase of the F$_2^-$ centres number measured in nano- and millisecond time intervals with respect to the end of electron pulse action respectively.

It has been established that efficiency of electron capture by a F$_2^+$ centre is independent of the temperature but in temperature interval 80…200K there are a quenching of singlet (S$1$-S$0$) RL (emission is at 670nm) of F$_2^-$ centres by (1) and increasing of F$_2^-(T)$-centres yield by (2). Since photoluminescence of the F$_2$ centres does not depend on temperature in the same temperature interval [1] it is obvious that a reason of quenching of F$_2^-$ centres RL is S-T conversion and that transition to the triplet state occurs from a higher than S$1$ radiative singlet state.

The subsequent charge radiation-induced evolution of a F$_2^-$ centre formed by (1), (2) is determined by its spin multiplicity. Electron capture occurs on the F$_2$-center being in the triplet state (T), while there is a hole localization nearby to a F$_2^-$ centre being in the singlet ground state (S$0$) [2]. The former process causes flip effect and formation of the F$_2^-^-$ centre in a ground state by (3), whereas the latter causes formation of the F$_2^+$-centre in radiative state by (4) (emission is at 910nm)

$$F_2(T) + e \rightarrow F_2^-, \quad (3)$$

$$F_2(S_0) + p \rightarrow F_2^+ + e^0 \rightarrow (F_2^+)^* \rightarrow F_2^+ + \nu(F_2^+), \quad (4)$$

where e and p are an electron and a hole respectively; e$^0$ is a near – defect exciton.

It has been established that RL intensity of F$_2^+$ centres by (4) does not depend on concentration of these centres presented in the crystal prior to electron pulse exposure but it is determined by the concentration of the F$_2$(S$0$) centres preliminary created.

Thermally activated formation of F$_2$(T) – centres by (2) at a range 60…200K is a reason of increasing of F$_2^-$ – centres yield by (3) ) under electron pulse exposure at the same temperature range and with the same meaning of activation energy (0.06eV).

References


Change of optical and electrical properties of SiO₂ glass is a very important task for solid state physics and applications in optoelectronics and microelectronics, for example, decrease of dielectric permittivity (K) – low-K [1]. Low-K dielectrics reduce the parasitic capacitance in integrated circuits (ICs). One of the ways to reduce K is transition to porous low-k dielectrics [2,3], but materials with micrometric size of pores become brittle, and can be absorbed by photosist contaminating it. Another way is possible to use Fluorinated Silicate Glass [4] instead Silicon Dioxide. It is known that if absorption factor ($\alpha$) is changed, reflection factor (n) simultaneously is changed too, but $n = \sqrt{\varepsilon}$, where K is low frequency part of $\varepsilon$. We can conclude: K is possible to change by both formation of pores or new defects generation. Of course, change of defects concentration leads to gradual change of optical parameters of material.

In the present study we report experimental results of investigation of LR interaction with the SiO₂/Si structure. P and n-type Si with SiO₂ top layer were grown by oxidation method used in our experiments. YAG:Nd laser second harmonic (wavelength $\lambda = 530$ nm, pulse duration $\tau = 10$ ns) was used as a source of light. The experiments were carried out at room temperature and atmospheric pressure. The SiO₂ layer is transparent for this laser radiation, but Si is strongly absorbed. The SiO₂ layer with thickness 0.21 µm had red colour in reflecting light due to the interference. After irradiation by the laser with intensity $I = 20$ MW/cm² the SiO₂ layer has changed red colour to yellow. We explain such change of optical properties by change of optical pass. Measurement of SiO₂ layer capacity C by capacity – voltage (CV) characteristics method is shown decrease of C to more than 20%. It is possible if dielectric permittivity (K) decreases or thickness of the SiO₂ layer increases. Atomic force microscope measurements did not show any change of the SiO₂ layer thickness. It means that after irradiation of the SiO₂ layer decrease of K - low-K dielectrics [1] takes place. We suppose that such change of K-factor occurs due to the formation of nanopores in SiO₂ or generation of new defect at the interface of Si-SiO₂ takes place. Particularly this is in agreement with measurements of microhardness, using a precision microhardness tester at small test loadings. After irradiation both microhardness and brittleness of SiO₂ decreases, that could be connected with the relaxation of internal stresses due to the nanopores. At the same time near the interface microhardness increases, that could be explained with the formation of defects at the Si-SiO₂ interface after irradiation. A measurement of n from ellipsometry is in agreement with our hypothesis.

Reference

Most of the diamonds contain nitrogen atoms for main impurity and a diamond is classified into a type according to its aggregation form: II (no nitrogen), Ib (single nitrogen atoms), IaA (nitrogen pairs: A-aggregates) and IaB (B-aggregates). The negatively charged nitrogen-vacancy pair (the (NV)⁻ centre [1]) is one of the most popular and important complex defect in radiation damaged diamond, because it is a starting unit for the formation of the nitrogen aggregates or nitrogen contained larger defects by annealing. It must be studied in depth. However obtained information is not sufficient in spite of a lot of previous works. We performed a laser illumination on diamonds contained the (NV)⁻ centres and the absorption measurement of zero-phonon line (ZPL) of this defect was carried out after the laser turned off. In low temperature, it was observed that the width of the ZPL peak becomes more than two times persistently by the illumination (Figure 1). So far as we know, such an extreme and persistent ZPL broadening induced by illumination has not reported previously in any other defects. The relations between the broadening and the excitation photon energy, illumination time, sample temperature and defect concentration were studied. Based on these results an interpretation is proposed.

![Figure 1](image.png)

**Figure 1:** (a) the ZPL absorption of the (NV)⁻ center before (dashed line) and after (solid line) illumination. The width becomes more than two times. (b) their difference spectrum.

References

Experimental investigation of early stages of exciton creation became possible when femtosecond spectroscopy of these crystals was available. According to the model proposed in [1], after irradiation of crystal the weekly bounded electron-hole pairs then relax (for approximately 5 ps) into STE in off-centre configuration. The nature of intermediate state of electron-hole pair during relaxation is not clear. K. Tanimura proposed it can be on-centre (symmetric) configuration of exciton. This on-centre exciton is the $V_K$-centre and electron localised in some its vicinity. The state of electron may be quite diffuse and radius of such exciton can be several lattice constants. In this work we present a theoretical investigation of self-trapped and impurity trapped excitons in CaF$_2$ and SrF$_2$ crystals containing Ce$^{2+}$ and La$^{3+}$ by means of ab initio Hartree-Fock and DFT calculations performed in embedded cluster approach. Our main purpose is to clarify the early stage of exciton creation.

The equilibrium configurations of STE and STH were calculated with Hartree-Fock method and B3LYP functional in embedded cluster approach. The results of STH simulation show that Hartree-Fock method fails to describe the structure of $V_K$-centre correctly, leading to spurious localisation of the hole on one lattice fluorine. This can be fixed, however, by artificial freezing of the positions of all atoms except few nearest neighbours of $V_K$-centre. The B3LYP functional shows, on the other hand, delocalisation of hole which is clear from comparison of calculated and experimental hyperfine parameters. Modifications of B3LYP functional containing 40-50% of Hartree-Fock exchange provide most adequate description of self-trapped hole.

Correct description of the F-centre ground and excited states requires electronic correlation to be taken into account. The best description so far is obtained with modified B3LYP functional in relatively large cluster with all-electron basis set on ions comprising 1st to 4th spheres of F-centre neighbours. Hartree-Fock method and MP2 correlation provide much worse description in the same cluster. To represent the right coulomb and exchange-correlation potentials of the cluster environment we constructed ab initio nonlocal pseudopotentials for the ions surrounding the cluster. This approach is somewhat similar to model potentials of the work [1]. The results on excited states calculation with such potentials are discussed.

Concerning the STE creation mechanism we may suggest that the intermediate state of relaxing electron-hole pair, which ends up with STE creation, is the on-centre exciton in one of its higher excited states. It exists for few picoseconds and than, after non-radiative transition to $\sigma_g$-state immediately relaxes into off-centre configuration, since $\sigma_g$ is a transition state rather than a local minimum of exciton's total energy.

References

PTh89

OPTICAL PROPERTIES AND THERMOLUMINISCENT RESPONSE OF NaCl DOUBLE DOPED CRYSTALS UNDER GAMMA IRRADIATION

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The defects produced on solids under irradiation can be understood by the study of interaction between ionizing radiation and matter. There are a great number of phenomena during interaction. However, transfer and energy storage are key effects. This research concerns the study of the defects produced by gamma irradiation on NaCl double doped crystals with different concentrations.

The effect of dose and rate dose was studied, using luminescence stimulated by heat and optic absorption, glow and coloration curves were obtained.

Glow curves obtained were proportional to the density of occupied traps and centres formed by irradiation. These curves are characteristic and unique for each crystal[1], and the area under the curve is proportional to the quantity of defects produced and were obtained at a rate 0.66 Gy/min.

Coloration curves were obtained at different doses rates (0.563, 2.405, 4.153 kGy/h). They provide an indication of the rate of defect production (in particular F-centres) and the evolution of the colour curve. Irradiated crystalline solids present a maximum absorption peak around 460 nm which is characteristic of colour centres. The presence and quantity of activators in crystal modifies the response in both curves.

Correlation of both, optical and thermoluminescent properties helps us to elucidate the association of F-centres with the glow curve and contributes with the identification of the principal irradiation pair-defect produced. These defects are associated with the appearance of the main peak of the glow curve (dosimetric peak)[2].

References

Yttrium orthovanadate (YVO$_4$) crystals are used in optical devices and solid state lasers (for example, YVO$_4$:Nd). The point defects and trapping states are responsible for coloration problem and material quality. The transient absorption induced by pulsed electron beam excitation (270 keV, 8 ns) was studied in a set of samples with different absorption level in near-edge absorption spectral region 3.2-3.5 eV.

It is known that hole was trapped at oxygen ions (regular or bound on some defects or impurities). Different type of V$^{4+}$ centres was known as the trapped electron centres according to EPR studies [1].

Transient absorption spectra shows at least three broad overlapping bands (~1.3 eV, ~2.0 eV and ~3.0 eV, it will be point out the spectral range from ~1.25 eV up to 2.7 eV is covered by strong transient absorption. The last one peak position is close to the near-edge absorption band and correlation between transient absorption band and absorption due to stable colour centres was studied.

The process of near-edge absorption annealing in air of was studied up to 1500C. Though the near edge absorption drops significantly the yellow coloration survives. Two stages of annealing process with activation energies 0.16 eV and 0.38 eV was obtained. The role of oxygen vacancies on observed effects was discussed.

It is suggested that absorption bands at ~1.3 eV and ~2.0 eV are due to electron and hole polarons, correspondingly. The effect is well known in other oxide materials. We do not found notable dependence of optical density of these bands on near-edge absorption. The transient absorption level is lower in YVO$_4$:Nd crystals in comparison with undoped crystals. The laser pumping photon energy (~1.5 eV) is in the range of transient absorption bands observed. The role of transient absorption is very important since the laser higher harmonics (532 nm or 266 nm) may generate electron-hole pairs.

References

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In the 1970’s investigators have established that zircon mineral (ZrSiO₄) can in principle be used for thermoluminescence (TL) geochronometry (see e.g. [1]). Zircon has the advantage over other minerals, which are used for luminescence dating (quartz and feldspars), because they contain radioactive U and Th impurities, which radiate the mineral internally at dose rates much higher than those from external environmental sources. In this way the major source of variability observed in quartz-based luminescence dating, which is due the heterogeneity of the external irradiation field, is eliminated. However it was recognized at the same time that serious problems associated with anomalous fading and the inhomogeneity of zircon (due to e.g. zoning and metamictization) exist, which are responsible for intra-grain variations of the luminescence properties. Recently, these problems have been overcome and successful TL dating of young sediments using zircon have been performed [2], which leads the question whether zircon can be used for optically stimulated luminescence (OSL) dating.

Mineral zircon grains (75-100 µm) of high optical quality have been extracted from dune sand from the Dutch barrier island Ameland using special procedures [2]. The glow curves recorded for gamma-irradiated mineral zircon show a peak at about 150 °C, which is due to Dy³⁺ related shallow traps, and a broad peak ranging from 300 to 450 °C, which is due to Tb³⁺ related traps [3]. The shallow traps, responsible for short-term fading, have been removed successfully by a short preheat at 150 °C.

IR stimulation with wavelengths >700 nm gives rise to OSL at 550nm (i.e. the ⁷D₃ → ⁷F₅, Tb³⁺ line transition) and luminescence in the UV around 380-390nm, which is attributed to de-excitation of [SiO₄]³⁻ groups [4]. The dependence of the OSL signal on the bleaching temperature (after preheats at subsequently higher temperatures) show that the OSL associated with the UV band is bleached thermally at 400°C, while the 550nm OSL is stable up to 520 °C. After optical bleaching of the OSL signal, the two broad TL peaks at 320-340 °C and the one at about 420°C decrease to respectively ≈20% and ≈60% of the original intensity. The experimental results indicate that high temperature TL originates from at least two types of trapped charge populations, which are responsible for the TL peaks at 320-340 °C and ≈420 °C. However only the deep traps associated with the 420°C TL peak contribute directly to the Tb³⁺ related OSL. The deep traps associated with the 320-340 °C TL peak contribute to OSL associated with de-excitations of [SiO₄]³⁻ groups.

References
PTh92

RADIATION-INDUCED DEFECTS IN CHALCOGENIDE GLASSES CHARACTERIZED BY COMBINED OPTICAL SPECTROSCOPY, XPS AND PALS METHODS

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It is known that radiation-induced optical effects in chalcogenide glasses (ChG) are associated with covalent bond switching accompanied by formation of pairs of specific negatively and positively charged topological, under- and over-coordinated atomic defects, respectively. A nanostructural model was successfully developed for γ-induced optical effects in sulfur-containing ChG, using special topological-mathematical modelling procedure and IR Fourier spectroscopy data [1]. Upon γ-irradiation, the appearance of free volume around under-coordinated defects, and densification of glass-like network in the vicinity of over-coordinated defects are expected in the glass structure. Because of strong electron-phonon coupling in ChG such atomic rearrangement should correspond to the changes in electronic sub-system of γ-irradiated ChG. The first type of processes can be observed with positron annihilation lifetime spectroscopy (PALS) [2], while the other processes can be detected with high-resolution X-ray photoelectron spectroscopy (XPS) as in the case of band gap light-induced transformations [3].

In this work, the γ-induced changes in Ge-Sb-S glasses are studied for the first time by combining optical spectroscopy, PALS and XPS methods. It is shown that high-energy γ-irradiation (Co60 sources, ~2 MGy dose) causes a shift of the fundamental optical absorption edge to lower energy (i.e. darkening) in the investigated samples. This shift is recovered on annealing the sample at sub-Tg temperatures. The XPS results show a decrease in the concentration of lone-pair electrons at the top of valence band upon γ-irradiation. This observation supports the formation of over-coordinated positively-charged sulfur-atom defects via covalent bond redistribution. In parallel, the distinct changes are found in the long-lived lifetime component of PALS spectra, which indicate additional free volume and support the formation of negatively-charged under-coordinated defects.

References

Recently commercial glasses[1], sand[2], topaz[3] and jade[4] have been studied using the termoluminescent technique, and the results showed potential applications for high-dose dosimetry. In this work, the thermoluminescent properties of pellets containing powdered Wollastonite embedded in Teflon were studied. Wollastonite is a silicate of calcium: Ca(SiO₃) of the family of the pyroxen that occurs as mineral metamorphic, and it can accept considerable amounts of Fe and Mn replacing Ca. The studied sample was found at Itaoca, São Paulo, Brazil. The sample was received in the form of rude mineral; it was broken with a geological hammer, powdered, and grains were obtained with diameter between 0.074 and 0.177mm. A Frantz Isodynamic (model-L1) was utilized to remove the ferromagnetic grains. Pellets of Wollastonite-Teflon (50mg) were prepared in the proportion of 2(Teflon):1(Wollastonite). The preliminary results using gamma rays from a $^{60}$Co source showed linearity at the calibration curve between 0.5Gy and 10Gy. The main TL peaks are located at 125, 200 and 245°C (Figure 1). The repeatability of TL response presented a maximum coefficient of variation of 6.3%. The material can be used in successive irradiation-reading-annealing cycles without an appreciable change in its sensitivity. The calibration curve with source ($^{60}$Co) up to 20kGy and the minimum detection limits will also be presented. The results show that these Wollastonite-Teflon pellets present possibilities for use as TL dosimeters.

![Figure 1 - TL glow curves of Wollastonite-Teflon composites.](image)

References

OPTICAL IN-SITU STUDY OF REDUCTION/OXIDATION PROCESSES IN YAlO$_3$ AND YAlO$_3$:Mn CRYSTALS

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It is known, that yttrium orthoaluminate single crystals (YAlO$_3$) of high structural and optical quality can be obtained by the Czochralski method from slightly non-stoichiometric charges enriched with the yttrium oxide ($R$=Y$_2$O$_3$/Al$_2$O$_3$≥1). This non-stoichiometry is considered responsible for the characteristic red-brown coloration of as-grown crystals. The crystal coloration leads to both passive and active losses in YAlO$_3$-based laser elements. The crystal coloration can be essentially lowered by annealing the crystals in a reducing atmosphere or in vacuum. On the other hand, annealing in air or oxygen intensifies the crystal coloration.

Up to now the changes in optical absorption that take place in YAlO$_3$ crystals under the influence of reducing/oxidizing (redox) thermal treatments have been studied at room temperature after a certain annealing procedure.

The present work is devoted to in-situ study of redox processes in pure YAlO$_3$ and Mn-doped YAlO$_3$ crystals in the temperature range from 600 to 1000 K. This includes measuring of absorption spectra in UV-Vis-NIR region in-situ at high temperature in different atmospheres. The main feature of the experimental set-up used is the possibility of rapid (up to 3 min) replacement of a gas atmosphere in the furnace and the registration of the subsequent redox kinetics at a certain wavelength.

The increase of the absorption bands at 22000 and 40000 cm$^{-1}$, which are caused by intrinsic color centers, during the annealing in oxidizing atmosphere as well as their bleaching during reduction have been studied in YAlO$_3$ crystals. In the case of YAlO$_3$:Mn crystals the redox processes can be observed via the Mn$^{4+}\leftrightarrow$Mn$^{5+}$ recharging process. In particular the increase/bleaching of the absorption band at 15000 cm$^{-1}$ caused by Mn$^{5+}$ ions ($^3T_1(^3F)\rightarrow^3T_1(^3P)$ transition) have been studied.

The redox kinetics have been analyzed in the framework of different diffusion models. The origin of the absorption changes caused by the redox thermal treatments is discussed in terms of transport and point defect structure of the studied crystals.
F$^+$- and F-centres in $\alpha$-Al$_2$O$_3$ are assumed to be the most extensively studied defects [1]. However, their optical characteristics, which were measured over the period from 1970 till 1980, do not reflect comprehensively the set of properties predicted in [2]. F$^+$- and F-centres have the local symmetry C$_2$ and their electronic structure should include at least three excited states. But until recently one excited triplet state with $h\nu_{m} = 6.1$ eV and two singlet states with $h\nu_{m1} = 4.8$ eV and $h\nu_{m2} = 5.4$ eV were registered for F- and F$^+$-centres respectively. Many researchers believe (see the review [1]) that the third excited state of the F$^+$-centre is located at $\sim$6 eV and largely overlaps with the absorptive transition of the F-centre. For this reason, its exact spectroscopic parameters could not be determined.

Modern means of optical spectroscopy providing a subnanosecond resolution allowed us to obtain some unique results for F$^+$- and F-centres in $\alpha$-Al$_2$O$_3$ [3, 4]. Specifically, excited states with $h\nu_{m3} = 5.94$ eV and $h\nu_{m4} = 6.6$ eV were revealed for the F$^+$-centre. On the strength of results of the present study, they were related to transitions of the electron to the levels 2B and K respectively. It was confirmed that the lowest state 1B was emissive among the four excited states of the F$^+$-centre. Its lifetime was $2.1\pm0.1$ ns.

New information about the electronic structure of the F-centre was obtained. It includes not only triplet ($h\nu_{m1,tr} = 6.1$ eV and $h\nu_{m2,tr} = 6.3$ eV), but also singlet ($h\nu_{m1,s} = 4.8$ eV, $h\nu_{m2,s} = 5.3$ eV, $h\nu_{m3,s} = 5.9$ eV and $h\nu_{m4,s} = 6.4$ eV) excitation levels. Properties of the singlet-singlet luminescence of the F-centre at 3.3 eV were analyzed in detail. The decay time constant of this luminescence at $T = 8$ K was estimated at $1.6\pm0.2$ ns. Specific features of the excitation energy redistribution both in triplet and singlet states and between them were determined depending on the orientation and the temperature.

Polarization characteristics of absorptive and radiative transitions in F$^+$- and F-centres, which were highly accurately determined at $T = 8$-300 K, were processed and systematized. Parameters of the electron-phonon interaction were calculated and one-coordinate and band models of F$^+$- and F-centres were proposed using these polarization characteristics. The similarity of spectral and kinetic properties during singlet-singlet transitions, which was revealed for F- and F$^+$-centres in $\alpha$-Al$_2$O$_3$, confirmed the corresponding regularity detected in other wide-gap oxides.

References
PERMANENT BLEACHING OF F₂ COLOUR CENTRES IN LITHIUM FLUORIDE UNDER UV LIGHT ILLUMINATION

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Colour centres (CCs) in Lithium Fluoride (LiF) are extensively investigated, particularly because of their peculiar active properties, which found application in the realization of broad-band emitting lasers and amplifiers in the optical domain [1] operating at room temperature (RT). In the last decades a great interest has been devoted to propose [2] and investigate different irradiation methods and techniques for the development of miniaturised light emitting devices based on this interesting materials [3]. Recently F₂ laser emission in the red has been claimed in x-ray irradiated LiF crystals, combining Bragg gratings and waveguides induced by ultra-short infrared laser pulses [4].

We study the possibility to use a CW, frequency doubled, Ar laser light at 244nm, which is coincident with the peak of the F absorption band, to modify the concentrations of F₂ and F₃⁺ active CCs in LiF crystals coloured by γ rays. These aggregate defects possess almost coincident fundamental absorption bands located at 450nm (M band); they emit broad photoluminescence bands peaked at ≈675 and ≈540nm [5].

Low power UV irradiation was performed at RT on LiF crystals irradiated at several doses from 5x10³ to 10⁴ Gy. An accurate comparison between absorption, photoluminescence and photo-excitation measurements, performed before and after laser irradiation, reveal a selective change in the CCs densities: a permanent bleaching of F₂ CCs was observed in all the investigated crystals, and a critical dependence from the used power density has been highlighted.

Further experiments are under way to better clarify the mechanisms responsible of complex F₂ centres destruction, but the results seem promising for the local modulation of CCs densities in a thin layer located at the surface of the investigated material trough well assessed interferometric methods, successfully used for Bragg gratings writing in optical fibres.

References

RADIATION-INDUCED PROCESSES IN SINGLE CRYSTALS OF Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ SOLID SOLUTIONS

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Borates are a peculiar class of materials for detection of thermal neutrons [1]. Lithium gadolinium orthoborate Li$_6$Gd(BO$_3$)$_3$:Ce$^{3+}$ (LGO:Ce$^{3+}$, $Z_{\text{eff.}}=46$) and lithium yttrium orthoborate Li$_6$Y(BO$_3$)$_3$:Ce$^{3+}$ (LYBO:Ce$^{3+}$, $Z_{\text{eff.}}=26$) are known as perspective scintillation detectors of thermal neutrons [2]. Recently we have shown that LGO:Eu$^{3+}$ and LYBO:Eu$^{3+}$ crystals possess an intensive thermally stimulated luminescence (TSL) and can be used as storage phosphors [3, 4]. Utilization of Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ solid solutions allows one to develop a storage material with variable sensitivity to ionizing radiation. However, origin of radiation defects in Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ crystals has not been described till present. Thus, the purpose of this work is to study radiation-induced processes in Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ single crystals.

Pure and europium-activated Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$ single crystals were grown using Czochralski method. Radiation defects in X-, γ-ray and β-irradiated Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ single crystals have been studied by means of TSL, photostimulated luminescence, photoluminescence (PL) and optical absorption methods. Radiation-induced transition Eu$^{3+}$$\rightarrow$Eu$^{2+}$ has been detected. But no PL of Eu$^{2+}$ ions has been observed, probably due to photoionization process. Additional optical absorption at $\lambda=320$-500 nm has been attributed to hole centres absorption. Two models of hole centres have been proposed: 1) O$^-$-centre and 2) $BO_3^-$-radical near stabilizing negative defect. The origin of optical transitions in the hole centre has been discussed. TSL of Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ crystals in the $T=300$-600 K range is presented by at least three peaks as a result of the presence of nonequivalent crystallographic position of radiation-induced defects. The trap parameters of main TSL peak at $T=455$ K have been determined: $E=1.1 \pm 1.2$ eV, $s \sim 10^{11}$ s$^{-1}$, first order kinetics. TSL spectra show that Eu$^{3+}$ ions act as radiative recombination centres.

Possibilities of application of Li$_6$Gd$_{1-x}$Y$_x$(BO$_3$)$_3$:Eu$^{3+}$ solid solutions with variable value of $Z_{\text{eff.}}$ for solid state dosimetry of ionizing radiation, in particular, for thermal neutrons detection are discussed.

References

Scintillation, energy transfer and storage, carrier trapping
INVESTIGATION INTO THALLIUM SITES AND DEFECTS IN DOPED SCINTILLATION CRYSTALS

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In recent years the need for advances in security systems has been highlighted, in particular the area of high speed scanning capability. Under new EU regulations one of the main scintillators utilised for these applications, CdWO₄, will be banned [1]. Many scintillation materials are being investigated as a replacement but they must have a combination of low cost, high conversion efficiency, rapid initial decay and emission in a desirable range to be feasible candidates. Two materials with great potential for this are thallium doped forms of caesium iodide, CsI(Tl), and sodium iodide, NaI(Tl). However, their use in fast applications has been hindered by a strong and persistent afterglow – a long term non-exponential decay of the luminescence pulse resulting in blurring and imaging artefacts. Afterglow has been generally accepted to be caused by a slow component in one of the several sequential steps in the kinetics of scintillation, with contributors likely to be impurities [2] and intrinsic stress caused by mechanical deformation [3]. The first step to understanding afterglow is to know the structure of the luminescent ions in the lattice but there have been very few systematic studies into the structure of these doped crystals, all utilising advanced optical techniques yielding little or no basic information such as concentration of defect types reported. Therefore we have embarked on a study of the activator thallium sites using Extended X-ray Absorption Fine Structure (EXAFS) measurements.

Initial studies in NaI(Tl) suggest that at 1000ppm the Tl is located on a Na site with a good fit to the face-centred cubic NaI model (figure1) with a local expansion around the central Tl⁺ ion due to the increased ionic radii (Na⁺ 1.16Å; Tl⁺ 1.64Å). Complementary structure and defect calculations are currently being performed using the General Utility Lattice Program (GULP), along with experimental calculations of the defect energies by conductivity measurements.

Figure 1 - Tl LIII-edge EXAFS (left) and Fourier Transform (right) of 1000ppm NaI(Tl). Solid lines are experimental data and dashed lines are theoretical patterns.

References

CREATION SPECTRA OF LONG-LASTING AFTERGLOW IN SrAl$_2$O$_4$:Eu AND SrAl$_2$O$_4$:Eu,Ln (Ln=Dy, Gd, La) PHOSPHORS

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The SrAl$_2$O$_4$:Eu,Dy phosphor shows an intensive afterglow which lasts for several hours. The function of Dy$^{3+}$ ions has been connected to the formation of photocarrier traps in host SrAl$_2$O$_4$ [1]. However, it is difficult with only the previous idea to explain the question why the afterglow is enhanced by such co-doping. Thus, the role of Dy$^{3+}$ ions on the afterglow processes still remain unresolved. Since the intensity of afterglow is increased with the concentration of photo-created electrons and holes, the incorporation of Dy$^{3+}$ may influence the change in the absorption feature. In this connection, it is worth while to note the experimental result that the afterglow is efficiently caused with photons in the energy region lower than the fundamental absorption edge of SrAl$_2$O$_4$ [2]. This suggests the existence of absorption bands resulting from Dy$^{3+}$ co-doping. The origin of the absorption bands has not yet been cleared.

In the present study, we have investigated the creation spectra of afterglow in the phosphors of SrAl$_2$O$_4$:Eu and SrAl$_2$O$_4$:Eu co-doped with Dy$^{3+}$, Gd$^{3+}$ or La$^{3+}$ ions. In order to obtain the creation spectrum of afterglow in each sample, the afterglow spectra were measured at various excitation photon energies by using a grating monochromator with a CCD detector. The creation spectra were corrected for the energy distribution of excitation light source. The cluster calculation has also been carried out using the discrete variational X$\alpha$ (DV-X$\alpha$) method [3] to clarify the origin of the absorption bands in the creation spectra of afterglow.

The creation spectra of afterglow in SrAl$_2$O$_4$:Eu and SrAl$_2$O$_4$:Eu,Ln (Ln = Dy, Gd, La) exhibit a prominent peak at 6.3 eV. This result indicates that the 6.3 eV peak is not be related to the $4f \rightarrow 5d$ absorption of trivalent Ln ions. In addition, the possibility of the $4f \rightarrow 5d$ absorption band at Eu$^{2+}$ ion is also excluded because the energy position of it does not coincide with that of the 6.3 eV peak. We suppose that the 6.3 eV peak is due to some lattice imperfection. According to Ref. 4, Dy$^{3+}$ ions substitute Sr$^{2+}$ sites. In this case, Sr$^{2+}$ vacancies are necessarily introduced owing to charge compensation. In many cases, they modulate the electronic states of host material, so that the perturbed absorption bands appear in the low energy tail of the fundamental edge. This situation can be seen in the present result.

The electronic states of SrAl$_2$O$_4$ has been also calculated for the [Sr$_3$Al$_2$O$_{38}$]$^{34-}$ model cluster. From the result of calculations, the intrinsic absorption edge was determined to be 7.73 eV. The agreement between experiment and calculation is good. Now, calculations are proceeding for the cluster introducing a Sr$^{2+}$ vacancy.

References

Highly doped Yb:YAG crystals are very attractive for the application in the thin disk laser concept due to the good thermal properties of YAG host and small quantum defect and broad absorption band of Yb³⁺-ion. To date, impurities in the crystals have limited the viability of highly doped Yb:YAG active media. Due to the high concentration of Yb³⁺-ions, the excitation energy can effectively migrate until it is transferred to an impurity ion, leading to the generation of additional heat in the crystal and resulting in a reduction of the emission signal and shortening of the lifetime of the upper laser level. Yb²⁺-ions and impurity ions of nickel and iron coming from the iridium-crucible were determined as efficient quenching centers in Yb:YAG crystals grown by the Czochralski-method. We present the experimental investigations of the quenching effects caused by Yb²⁺-ion and nickel in Yb:YAG crystals as well as the theoretical model for the energy transfer processes to Yb²⁺- and Ni²⁺-ions.

We have investigated as-grown Yb(80%):YAG and YbAG as well as Ni(0,1%):YbAG crystals annealed in air atmosphere. As an indicator of the quenching process we measured the fluorescence lifetime of the investigated crystals and its dependence on the excitation power. Special experimental arrangements were used in the lifetime measurements in order to eliminate radiation trapping effect. The absorption spectra of Yb²⁺ and Ni²⁺ in Yb:YAG crystals were measured in order to find out which electron transitions of these ions are involved in the energy transfer process.

It was derived that the radiation quenching by Yb²⁺-ions occurs as a cooperative energy transfer process from two excited Yb³⁺-ions to an Yb²⁺-ion in the ground-state. This process shows a high efficiency: The presence of 0.005 at.% of Yb²⁺-ions in YbAG leads to the reduction of the fluorescence lifetime by a factor 100.

The energy transfer to the Ni²⁺-ions is a resonant one-step process from one excited Yb³⁺-ion to a Ni²⁺-ion in the ground-state.
LUMINESCENCE AND SCINTILLATION PROPERTIES OF Y₃Al₅O₁₂:Pr SINGLE CRYSTAL.

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Analogous to fast 5d-4f luminescence of Ce³⁺ can be obtained also from Pr³⁺ ion in suitable crystal hosts. Comparing to Ce³⁺ the luminescence is high energy shifted and even faster. Pr³⁺-doped Y₃Al₅O₁₂ (YAG) crystal was investigated in the past as a potential solid-state laser material [1]. Some luminescence and scintillation properties were studied later [2]. Recently high quality single crystals showed surprisingly high light yield [3]. Comparative study of absorption, luminescence and scintillation properties of several Pr-doped materials was performed in [4].

We investigated Czochralski-grown YAG:Pr single crystal as a potential novel scintillator. The principal fast 5d-4f emission band is peaking at 318 nm and is accompanied by slower 4f-4f line emissions. We studied a set of samples with various concentrations of Pr together with the undoped crystal used as a reference. Optical characteristics including absorption, photoluminescence, radioluminescence, scintillation decay, radiation damage and thermoluminescence were measured. Their dependence on the dopant concentration was followed.

The radiation damage results show that with increasing concentration of Pr the radiation damage reduces. Thermoluminescence above room temperature shows the dominant glow curve peak around 250 °C. Comparing to YAG:Ce scintillator an advantage of YAG:Pr is its much faster scintillation decay (16-17 ns at room temperature) and an absence of slow components in the decay. Therefore YAG:Pr appears as potentially interesting scintillator material.

References

Main types of structural disturbances, which are induced in nominally pure wide-gap oxides by thermochemical or radiation effects, are oxygen vacancies in different charge states (F- and F+-centres). These defects cause considerable changes in many radiation-optical properties of materials modified by this means.

One of effects, when the changes are most vivid, is thermoluminescence (TL) of single crystals of aluminum oxide grown or thermally treated under reducing conditions or exposed to high-energy electrons. A series of TL peaks is recorded over the temperature interval of 300 to 900 K. The peak at 450 K, which is called the main peak, is most convenient for the use in practical thermoluminescence dosimetry. However, detailed studies of this peak revealed some regular features of its behaviour, which were unusual in terms of the conventional formal kinetics. The most significant of those features were the dependence of the illuminated light sum on the heating rate, the drop of the average activation energy during fractional glow technique, and the superlinearity of the dose characteristic.

Later studies demonstrated a profound relationship between parameters of the main peak and the energy distribution and the occupancy of other traps. Mechanisms of the occupancy of traps in aluminum oxide during excitation with light or electrons and heating were considered. It was shown that the capture of charge carriers in deep traps led to the aforementioned anomalies in the behaviour of the main peak, the change of its shape and the luminescence spectrum, and thermal quenching of the luminescence of F-centres. The occurrence of interactive processes was confirmed by observation of phototransferred TL involving shallow and deep traps and the presence of analogous features of TL in aluminum oxide crystals having radiation-induced oxygen vacancies. One may think therefore that the aforementioned processes of the interaction between trapping centres are responsible for the general features of TL properties in anion-defective \(\alpha\)-\(\text{Al}_2\text{O}_3\) crystals.

The set of experimental results, which was obtained in this study, was interpreted in terms of model representations, which describe competing processes of the redistribution of charge carriers between different trapping and luminescence centres. The model is based on an interactive trap system, which differs from the known system by the temperature dependence of the probability that charge carriers are captured on deep trapping centres. The data of computer simulation confirmed specific features of luminescence properties of anion-defective \(\alpha\)-\(\text{Al}_2\text{O}_3\) crystals.
We have synthesized and studied the excitation-emission properties of erbium-coordinating porphyrin-based solid state films for emission in the 1530-nm band. In such organometallic materials the overall quantum yield of the NIR emission relies on at least three factors [1, 2]: the singlet-triplet intersystem crossing in the organic (ligand) part, the resonant transfer to the rare-earth ion, the lack of quenching of the NIR emission by vibronic excitations of the surrounding C-H and O-H bonds. In the present compound, a relatively strong visible emission from the singlet state shows that intersystem crossing is not very effective and this can account for a value of quantum yield as low as $\phi \approx 10^{-4}$. On the other hand, time-resolved phosphorescence measurements (see Fig. 1) demonstrates that the triplet state is efficiently depleted by transfer to the higher energy levels of the erbium ion with respect to non-resonant Gd films. Measurements on the decay rate of the NIR emission have also assessed the significant role of the vibronic quenching. Within this framework, suitable substitution of the organic groups has been carried out which has led to the increase of intersystem crossing and the decrease of quenching by C-H bonds with a higher quantum yield at 1530 nm.

![Graph showing time decay profiles of triplet and singlet states of Er films compared to Gd films](image)

**Figure 1:** Time decay profiles of the triplet and singlet states of Er films compared to that of the triplet state of Gd films.

References

ENERGY TRANSFER IN RE$^{3+}$ DOPED FLUORIDE CRYSTALS

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Pure and rare earth doped LiLuF$_4$ and LiCaAlF$_6$ crystal developments were directed to potential applications in scintillators, tuneable lasers and X-ray storage phosphors [1-2]. Luminescence properties and transfer losses of these crystals significantly depends on the RE centre structure and charge compensative defects. LiLuF$_4$ and LiCaAlF$_6$ crystals are the typical examples of scheelite and colquirite structure accordingly. In the first case RE$^{3+}$ doping ion replaces Lu$^{3+}$ ion in lattice. Both bi- and trivalent RE ions occupy Ca$^{2+}$ site in LiCaAlF$_6$ lattice. This study devoted to the analysis of luminescence and energy transfer for these crystals in relation with the luminescence centre and compensative defects structure.

Luminescence spectra at direct photo-excitation as well as at X- and $\gamma$-ray irradiation Ce, Eu and Pr doped LiLuF$_4$ crystals were measured at RT. Ce$^{3+}$ doped crystal exhibits the typical fast radiative $d$-$f$ transitions in UV region. Pr$^{3+}$ containing sample shows both fast $d$-$f$ and slow visible $f$-$f$ emissions. Eu$^{3+}$ doped one reveals only $f$-$f$ spin forbidden transitions in red-orange region. It was found that energy transfer and storage losses are not similar for pure and Ce, Eu and Pr doped crystals. Glow curves are independent on the type of RE$^{3+}$ impurity whereas TL spectra are specific for each of dopants. It directs to the intrinsic nature of the main radiation defects. At the same time the degree of colourability depends essentially on the RE type. Pr-doped LiLuF$_4$ possesses the highest coloration. Ce-containing crystal demonstrates much less radiation damage. The colourability and TSL intensity is negligible for Eu-doped samples.

The main difference between LiCaAlF$_6$ crystals doped by Eu$^{2+}$ or Ce$^{3+}$ is related to a case of charge compensation necessity. A bivalent europium ion does not need any compensation. LiCaAlF$_6$:Eu possesses the typical $f$-$d$ Eu$^{2+}$ emission (370 nm, 1 $\mu$s) and high scintillation yield ($\sim 11.10^3$ ph/MeV). Radiation induced absorption and TSL efficiency are insignificant. Contrary to Eu$^{2+}$-ion, the surplus charge of Ce$^{3+}$ ion is compensated by point defects (vacancy and/or interstitial fluorine). In this case the scintillation output was found to be many fewer (<$10^3$ ph/MeV). LiCAF:Ce crystal is a promising base for TL phosphor and dosimeter development.

The energy transfer and storage in both systems are discussed in respect of the typical for Ce$^{3+}$, Pr$^{3+}$ and Eu$^{3+}$ ions redox reaction and their level positions within bandgap.

References

ESR INVESTIGATION OF S-TYPE IMPURITY DEFECTS IN PbWO4 SCINTILLATING CRYSTALS


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Scintillating PbWO4 (PWO) with scheelite structure has been the subject of intense scrutiny during the past decade due to its applications in high energy and nuclear physics and, more recently, for medical imaging, radiation defectoscopy, safety sector, etc.

Impurity ions in the PWO crystal lattice influence the energy balance in the crystal and affect the scintillating properties and the energy transfer, as well as the radiation hardness. Information about the defects properties is paramount for an educated choice of dopants in order to design and control specific material properties. Electron Spin Resonance (ESR) is one of the best suited techniques to provide such essential information about the local interactions, microstructure and quantum properties of defects.

We report here a comparative ESR study of Mn$^{2+}$ and Gd$^{3+}$ impurity ions doped in very low concentrations (less than 1 ppm) in PWO single crystals. The behaviour of the two ions was found to be similar in many respects. Both ions substitute Pb$^{2+}$ host ions in unperturbed $S_4$ tetragonal sites, the extra positive charge compensation in the case of Gd$^{3+}$ ions taking place very likely at distance . The strong temperature dependence of the EPR parameters of both ions was found to be determined by the presence of a local vibrational mode, with frequency 3.5 times larger in the case of the Gd$^{3+}$ ions than for the Mn$^{2+}$ ions [1,2].

We discuss further the ESR line broadening effects, in terms of spin-lattice relaxation mechanisms and presence of local strains.

References

Investigations of thermoluminescence (TL) and optically stimulated luminescence (OSL) of AlN ceramics have shown that this material reveals properties favourable for application as a dosimetric material for UV detection: high sensitivity, large dynamic range and spectral sensitivity close to human skin and others. However, practical application is hampered by a high fading rate of the accumulated signal during storage of the material at room temperature.

Analysis of UV light induced luminescence processes allows distinguish 3 regions in the excitation spectra of photoluminescence (PL), TL and OSL: I (190-210 nm) - host absorption; II (230-270 nm) - absorption of oxygen related centres; III (280-340 nm) - absorption of other defect centres. Regions I and II fall into UV-C range, while region III corresponds mainly to UV-B range, which is the most actual for protection against harmful influence of UV light on living beings.

Emission spectra of TL and OSL contain both 400 nm and 470 nm bands. Although these luminescence bands are excited within a wide spectrum, their relative intensity depends upon the excitation area: excitation in region II gives mainly the 400 nm luminescence band, in region III – mainly the 470 nm band, while excitation in region I gives both of them. In our previous studies of dosimetric properties we detected the 400 nm band for recording the TL and OSL signal.

TL studies allow understand the reasons of the observed low stability of the accumulated signal. TL is observed in a wide temperature range up to 500 °C, TL curves containing two main thermal peaks: at 120 °C and 250 °C. The lower peak is excited in the II region, its emission contains mainly 400 nm and the higher peak is connected with excitation in the III region and 470 nm emission. Evidently, the accumulated TL and OSL signal corresponding to the 400 nm band is less stable and is characterized with higher fading rate than that corresponding to the 470 nm band.

An attempt was made to use the 470 nm band for detection of the accumulated OSL and TL signal induced by UV irradiation. The preliminary results are encouraging: its fading rate is much lower compared to that of the 400 nm detection, besides, its excitation falls mainly into UV-B range, which is the most interesting spectral area for UV dosimetry. Additional improvement of the dosimetric properties was obtained by using oxygen ion implantation of the ceramics samples, which caused the growth of the 470 nm band.
PHOSPHORESCENCE OF SiO₂ OPTICAL FIBRES DOPED WITH Ce³⁺ IONS

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The dosimetric properties of a prototype radio-luminescence (RL) detector based on a Ce³⁺-doped optical fibre were recently tested in view of its possible application in radiation therapy as in-vivo dosimeter [1, 2]. The response of the system, irradiated with photon and electron beams commonly used in radiation therapy, showed a good reproducibility, linearity with increasing dose and dose rate, and a satisfactory independence of radiation energy. By contrast, further investigations and improvements in the luminescence properties of the device are deserved, in particular regarding the presence of a slow phosphorescence component. This component influences the signal monitored during irradiation, since a systematic increase of the output with increasing irradiation time was observed. This effect is particularly evident when the detector is irradiated with high frequency pulsed electron beams, like those employed in intra-operative radiation therapy, as shown in Figure 1.

![Fig. 1: RL signal of a Ce³⁺ doped fiber during irradiation with a Mobetron mobile electron linac operating at 12 MeV with dose rate of 10 Gy/min.](image)

The aim of this study is the investigation of the origins of such phosphorescence and its characterization. The defects in the Ce-doped glass are therefore studied by means of thermoluminescence measurements on the active fibre and on its parent bulk material. The results of the glow curves analysis are then correlated with the RL spectra of the Ce³⁺-doped optical fibre, and of the commercial optical fibre spliced to the detector.

References

Recently it has been discovered that $\text{K}_2\text{YF}_5$ crystals singly doped with rare earth (RE) ions are promising phosphors for thermoluminescence (TL) dosimetry. TL phosphors based on such combinations show relatively high sensitivity to ionising radiation and low fading, while for some $\text{K}_2\text{YF}_5$:RE combinations the shape of the TL glow curves depends on the type of radiation field, which offers possibilities for discriminating mixed radiation fields [1-3].

In the context of designing long-persistent phosphorescent materials, X-ray and optical storage phosphors and scintillators, considerable efforts are made to identify the structure of radiation-induced defects as well as the mechanisms of recombination and energy transfer between the defects and RE ions in RE-activated phosphors. The exact role of the RE dopant in these processes, in particular, its capability to trap electrons or holes, is a much debated issue. Taking into account that the TL glow curve structure of $\text{K}_2\text{YF}_5$ also depends on the RE dopant [3], this host is a very attractive system for investigating the above processes. On the other hand, electron paramagnetic resonance (EPR) spectroscopy is ideally suited to determine the structure of trapped electron and hole centres, and it also allows to detect changes in the valence states of the RE ions.

In this contribution, we present the first results of our EPR study of X-ray irradiated $\text{K}_2\text{YF}_5$ crystals singly doped with $\text{Ce}^{3+}$, $\text{Dy}^{3+}$ and $\text{Tb}^{3+}$. Prior to irradiation, the EPR spectra reveal the initial valence state of the RE dopant ions and allow identifying unintentional paramagnetic impurities. After X-ray irradiation at RT, EPR lines near the free electron resonance ($g = 2.0023$) are detected, which appear to be due to several trapped electron and/or hole centres. The decay of these centres upon step annealing in the 400 – 800 K range is monitored and correlated with TL glow curves. In X-ray irradiated $\text{K}_2\text{YF}_5$:Tb$^{3+}$, additional low-field EPR signals, presumably due to Tb$^{4+}$, indicate a valence state change of the RE dopant. The effects of RE concentration and applied radiation dose are studied as well.

References

TEMPERATURE DEPENDENCE OF DECAY CURVES OF LONG-PERSISTENT PHOSPHORESCENCE IN Ce$^{3+}$- OR Eu$^{2+}$-DOPED OXIDES

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Matsuzawa et al. found SrAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$ showing long-persistent phosphorescence in the green region [1]. Many long-persistent phosphors have been found in crystals and glasses doped with rare-earth ions (Ce$^{3+}$ [2], Tb$^{3+}$ [3], Eu$^{2+}$ [4]). These host crystals form regular networks of AlO$_4$ or SiO$_4$ tetrahedra, whereas glasses form random networks of the tetrahedra. The network structure is very important for mechanisms of storing and releasing optical energy in long-persistent phosphors [4]. In order to obtain new long-persistent phosphors with strong intensities and long-persistent times of several hours, it is required to examine a mechanism of long-persistent phosphorescence in the above phosphors.

We report temperature dependence of decay curves of phosphorescence intensities for Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$, Ba$_3$SiO$_5$:Eu$^{2+}$, and SrAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$. Decay curves of the phosphorescence intensities near room temperature and above 383 K for Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$/Ba$_3$SiO$_5$:Eu$^{2+}$ crystals satisfy the equation of $I(t)=I_0 t^{-n}$ with $n=0.3-0.5$ and 1, respectively [2,4]. On the other hand, the decay curves for SrAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$ satisfy $I(t)=I_0 t^{-1}$ in the wide temperature range of 200-350 K. The function of $t^{-1}$ deduces that trapped electrons and holes recombine radiatively through tunnelling. The function of $t^{-0.5}$ representing longer decay time suggests an additional process other than tunneling for the recombination.

An ESR study for Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$ reveals that after UV excitation, electrons are trapped in the form of F$^-$ centre (an electron trapped at an oxygen vacancy), whereas holes are self-trapped at Al sites [4]. According to the ESR results, AlO$_4$ tetrahedra in the crystal play an important role in trapping holes.

Enhancement of the phosphorescence intensities and the change of decay functions from $t^{-0.5}$ to $t^{-1}$ for Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$ (Ba$_3$SiO$_5$:Eu$^{2+}$) with an increase of temperature deduce that holes in the crystals move to Ce$^{3+}$ (Eu$^{2+}$) sites through thermal hopping assisted by networks of the AlO$_4$(SiO$_4$) tetrahedra in two dimensional and that electrons and holes recombine radiatively at Ce$^{3+}$ (Eu$^{2+}$) through tunnelling.

References
