FM&NT-2015
Functional Materials and Nanotechnologies
October 5th - 8th 2015

Abstract book

VILNIUS, LITHUANIA
ACKNOWLEDGEMENTS

The organizers would like to thank the following companies and institutions for generous support:

- Vilniaus Universitetas S.S.
- Bruker
- Raith Nanofabrication
- EX VII expertus Vilnensis
- Taylor & Francis
- Ekspla
- American Elements
- Altechna
- Linea libera
- Light Conversion

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</tbody>
</table>
Your challenge is our mission.

www.raith.com
Dear Colleagues,

On behalf of the Local Organising and Programme Committees we are delighted to welcome you to the conference Functional Materials and Nanotechnologies (FM&NT-2015) in Vilnius.

The general topic of the conference is devoted to advanced materials and nanotechnology which are essential for economic wealth and quality of life of humans. Materials science is an interdisciplinary field, bridging the fundamental science and applied engineering. The series of FM&NT conferences is aimed at the exchange of knowledge and cooperation among the experts within certain fields and across related topics, as well as at revealing new trends and problems.

FM&NT became an international forum attracting participants not only from the countries of Baltic sea region, but also from the rest of EU, Norway, Russia, Ukraine, Belarus, Kazakhstan, Taiwan, Korea, Georgia, Turkey, Serbia, etc. The diverse country list is an indication of the importance of the conference for scientists working in various fields.

The conference is an annual event started in 2006 in Riga (Latvia). For 7 years, it has been organized by the Institute of Solid State Physics, University of Latvia. In 2013, the event moved to Estonia, and was organized by the Institute of Physics, University of Tartu (Estonia), then returned back to Riga in 2014, where a joint conference RCBJSF–2014–FM&NT was organised.

This year the conference is held in the main campus of Vilnius University, which is one of the oldest universities in Europe, situated in the heart of the historical centre of Vilnius, the capital of Lithuania. The Old Town of Vilnius with numerous churches and baroque architecture is listed in the Unesco World Heritage List.

Welcome to Vilnius all the FM&NT participants, and we wish them a fruitful and pleasant stay in our country.

Conference Chair

Prof. Jūras Banys
About Brukier Corporation

How Bruker has been driven by the idea to always provide the best technological solution for each analytical task for more than 50 years now?

Today, worldwide more than 6,000 employees are working on this permanent challenge at over 90 locations on all continents. Bruker systems cover a broad spectrum of applications in all fields of research and development and are used in all industrial production processes for the purpose of ensuring quality and process reliability.

Bruker continues to build upon its extensive range of products and solutions, its broad base of installed systems and a strong reputation among its customers. Being one of the world's leading analytical instrumentation companies, Bruker is strongly committed to further fully meet its customers' needs as well as to continue to develop state-of-the-art technologies and innovative solutions for today's analytical questions.

### Infrared, Near Infrared and Raman Spectroscopy
- FT-NIR Spectrometers
- FT-IR Routine Spectrometers
- FTIR Research Spectrometers
- FT-IR Microscopes, Raman

### X-ray Diffraction and Elemental Analysis
- X-ray Fluorescence
- X-ray Diffraction
- Single Crystal X-ray Diffraction
- Small-Angle X-ray Scattering
- X-ray Micro-CT
- Handheld XRF
- LIBS
- Micro-XRF and TXRF
- X-ray Metrology
- EDS, WDS, EBSD, SEM Micro-XRF and SEM Micro-CT
- Optical Emission Spectrometry
- CS/ONH-Analysis

### Surface Analysis
- Atomic Force Microscopy
- 3D Industrial Optical Microscopy
- Stylus Profilometry
- Tribology and Mechanical Testing

### Magnetic Resonance
- NMR
- NMR FoodScreener
- EPR
- Preclinical MRI
- Compact MR
- TD-NMR
CONFERENCE COMMITTEES

International Steering Committee

Andris Sternbergs (Chairman) Institute of Solid State Physics, University of Latvia
Jūras Banys Vilnius University
Gunnar Borstel University of Osnabrueck
Niels E. Christensen University of Aarhus
Robert A. Evarestov St. Petersburg State University
Claes-Goran Granqvist Uppsala University
Dag Høvik The Research Council of Norway
Marco Kirm University of Tartu
Jiri Kulda Institut Laue-Langevin
Witold Łojkowski Institute of High Pressure Physics
Ergo Nõmmiste Institute of Physics, University of Tartu
Ingólfur Thorbjörnsson Icelandic Centre for Research

Local organising committee


Programme committee

J. Banys (Chairman) K. Arlauskas V. Balevičius R. Grigalaitis M. Ivanov J. Matukas V. Sirutkaitis V. Šablinskas J. Šulskus G. Tamulačiūtė L. Valkūnas V. Vansevičius
Laboratorijų technologijos

Medicinos technologijos

Vaizdinimo technologijos

Kriminalistinės technologijos

Artimi Jums, atviri pažangai

UAB „Expertus Vilnensis" Mokslininkų g. 12A, LT-08412, Vilnius,
Tel.: +370 5 2729374; El. paštas info@exvil.lt; Svetainė: www.exvil.lt
GENERAL INFORMATION

Conference Venue

Functional Materials and Nanotechnologies (FM&NT-2015) will take place at Vilnius University.

Vilnius University is one of the oldest and most famous establishments of higher education in Eastern and Central Europe, founded in 1579.

Main entrance to the Conference is through the Library Courtyard.

Address

Universiteto str. 3, Vilnius, Lithuania

Official Language

The official Conference language is English. No translation will be provided

Name Badges

All participants have been issued name tags, which must be worn to gain admission to the Conference facilities and social program.

Technical Instructions for Presenters

All meeting halls will be equipped with PC, LCD projector and microphones. The date/hour/room of your presentation(s) is available in the Conference Program. If you are using a slide presentation make sure that you bring it on the USB stick. Supported file types: ppt, pptx, pdf, avi.

Note! If you are planning to use your own computer for presentation, please inform secretariat about that in advance.
Coffee Breaks

Coffee, tea and other refreshments will be served next to the conference rooms.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
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<tbody>
<tr>
<td>October 6</td>
<td>9:50 – 10:20</td>
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<tr>
<td>October 7</td>
<td>9:50 – 10:20</td>
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<tr>
<td>October 8</td>
<td>9:50 – 10:20</td>
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<tr>
<td>October 6</td>
<td>15:20 – 15:40</td>
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<tr>
<td>October 7</td>
<td>15:20 – 15:40</td>
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</tbody>
</table>

Lunch

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
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<tbody>
<tr>
<td>October 6</td>
<td>12:40 – 14:00</td>
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<td>October 7</td>
<td>12:40 – 14:00</td>
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<tr>
<td>October 8</td>
<td>12:00 – 13:40</td>
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</tbody>
</table>

Internet Area

Wireless Internet access is available throughout the Conference venue.

Social Events

Excursion in the old town of Vilnius

October 7, 14:40 – 18:20

Excursion is free of charge for Conference participants.

Gala Dinner

October 7, 19:00 – 22:00

HBH Vilnius, Raudondvaris village, Vilnius County

Price: 50 € (on site)

Insurance

All participants are reminded that neither the Organisers nor the technical organizer ViaConventus are liable for any losses, accidents or damage done to persons or private property. Participants and accompanying persons are requested to make their own arrangements in respect of health and travel insurance.
<table>
<thead>
<tr>
<th>Time</th>
<th>Monday (5th October)</th>
<th>Tuesday (6th October)</th>
<th>Wednesday (7th October)</th>
<th>Time</th>
<th>Thursday (8th October)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00 - 08:50</td>
<td>Registration</td>
<td>A. Salak A. Ruseckas</td>
<td>A. Kuzmin M. G. S. Ferreira A. Sternberg</td>
<td>08:00 - 08:50</td>
<td>Registration</td>
</tr>
<tr>
<td>08:50 - 09:00</td>
<td>Coffee</td>
<td>R. Evarestov V. Porsev D.D. Khalyavin V. Dyakonov</td>
<td>T. Gutmann V. Sammelselg R. Österbacka</td>
<td>08:50 - 09:00</td>
<td>Jorge Morgado</td>
</tr>
<tr>
<td>09:00 - 09:50</td>
<td>Lunch</td>
<td>S. Marcinkevičius M. Tyunina A. Šarakovskis</td>
<td>Break</td>
<td>09:00 - 09:50</td>
<td>S. Marcinkevičius</td>
</tr>
<tr>
<td>10:00 - 10:50</td>
<td>Coffee</td>
<td>Coffee</td>
<td>A. Eckstein D. Karpinski P. Ščajev H. Stadler</td>
<td>10:00 - 10:50</td>
<td>G. Suchanek</td>
</tr>
<tr>
<td>11:00 - 11:50</td>
<td>Lunch</td>
<td>S. A. Gavrilov M. N. Popova S. A. Gavrilov</td>
<td>Excursion</td>
<td>11:00 - 11:50</td>
<td>G. Suchanek</td>
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<tr>
<td>12:00 - 12:50</td>
<td>Coffee</td>
<td>V. Artemov A. Nikolaenko N. Tsyuntsarė</td>
<td>Gala Dinner</td>
<td>12:00 - 12:50</td>
<td>Final refreshements</td>
</tr>
<tr>
<td>13:00 - 13:50</td>
<td>Lunch</td>
<td>V. Orlovskij J. Tedim O. Prentkovskis</td>
<td>Poster session I</td>
<td>13:00 - 13:50</td>
<td>Closing ceremony</td>
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<tr>
<td>14:00 - 14:50</td>
<td>Coffee</td>
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<td>14:00 - 14:50</td>
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<tr>
<td>15:00 - 15:50</td>
<td>Lunch</td>
<td>V. Artemov A. Nikolaienko N. Tsyuntsarė</td>
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<td>15:00 - 15:50</td>
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<tr>
<td>16:00 - 16:50</td>
<td>Coffee</td>
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<td>17:00 - 17:50</td>
<td>Lunch</td>
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<td>18:00 - 18:50</td>
<td>Coffee</td>
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<td>18:00 - 18:50</td>
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<tr>
<td>19:00 - 19:50</td>
<td>Lunch</td>
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<td>19:00 - 19:50</td>
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**LEGEND:**
- Advanced materials, nanomaterials, composites
- Functional oxides, ferroics
- Semiconductors, photovoltaics, organic electronics
- Alloys, Coatings
- Advanced spectroscopic techniques
- Sustainable energy
Altechna is a Lithuanian private capital leading company of international photonic and laser research working since 1996. It has been successfully following its mission to create competitive advantage and added value to the customers by innovative solutions in light technologies.

Altechna Instruments is one of the key company business fields dedicated to distribution of scientific cameras, spectrometers, nano-positioning and laser processing tools for academic and industrial clients.

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Tel. +370 5 27 25 738
Fax +370 5 27 23 707
instruments@altechna.com

Mokslininkų st. 6A
08412 Vilnius, Lithuania
instruments.altechna.com
## Tuesday (6th October)

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<thead>
<tr>
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<th>Location</th>
<th>Chair</th>
<th>Speaker</th>
<th>Title</th>
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<tr>
<td>08:00 - 08:50</td>
<td>Registration</td>
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<tr>
<td>08:50 - 09:00</td>
<td>Opening</td>
<td></td>
<td>Philippe Lambin</td>
<td>Plenary</td>
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<td></td>
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<td></td>
<td>Robert Evarestov</td>
<td>Elastic properties of graphene: a short review</td>
</tr>
<tr>
<td>09:00 - 09:50</td>
<td>S 1. Advanced materials, nanomaterials,</td>
<td>Theater Hall</td>
<td>Sigitas Tamulevičius</td>
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<td>composites</td>
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<tr>
<td>10:20 - 11:00</td>
<td>S 2. Functional oxides, multiferroics</td>
<td>Senate Hall</td>
<td>Jiri Kulda</td>
<td>Andrei Salak</td>
<td>Metastable perovskite multiferroics prepared at high pressure</td>
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<tr>
<td>11:00 - 11:20</td>
<td>S 3. Semiconductors, Photovoltaics, Organic</td>
<td>Seminar Room</td>
<td>Anatolijs Šarakovskis</td>
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<td></td>
<td>Electronics</td>
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<tr>
<td>12:40 - 14:00</td>
<td>Lunch</td>
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<td>14:00 - 14:40</td>
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**FM&NT | Vilnius, Lithuania, October 5 - 8, 2015**
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<thead>
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<th>Time</th>
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<th>Title</th>
<th>Chair</th>
<th>Room</th>
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</thead>
<tbody>
<tr>
<td>14:40 - 15:00</td>
<td>Vladislav Sadykov</td>
<td>Oxygen mobility in microwave sintered praseodymium nickelates-cobaltites and their nanocomposites with Y-doped ceria</td>
<td>Väino Sammelselg</td>
<td>Theater Hall</td>
</tr>
<tr>
<td></td>
<td>Alexandr Dejneka</td>
<td>Spectroscopic ellipsometry of ferroelectric nanofilms</td>
<td>Marina Tyunina</td>
<td>Senate Hall</td>
</tr>
<tr>
<td></td>
<td>Martins Zubkins</td>
<td>Structural, optical and electrical properties of ZnO:Ir thin films deposited by reactive magnetron co-sputtering</td>
<td>Mario G. S. Ferreira</td>
<td>Seminar Room</td>
</tr>
<tr>
<td>15:00 - 15:20</td>
<td>Abdulkarim Amirov</td>
<td>Anomalous magnetoelectric effect in three-layer Ni-PZT-Pt multiferroic composites</td>
<td>Marina N. Popova (Invited)</td>
<td>Theater Hall</td>
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<tr>
<td></td>
<td>Jiri Kulda</td>
<td>Neutron spectroscopy of functional materials with nano-scale inhomogeneities</td>
<td>Natalia Tsintsaru</td>
<td>Senate Hall</td>
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<tr>
<td></td>
<td>Svetlana Zazubovich</td>
<td>Luminescence and photo-thermally stimulated defects creation processes in PbWO₄:Bi³⁺ crystals</td>
<td>Natalia Tsintsaru</td>
<td>Senate Hall</td>
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<tr>
<td>15:20 - 15:40</td>
<td></td>
<td>Coffee Break</td>
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<tr>
<td>15:40 - 16:00</td>
<td>S 1. Advanced materials, nanomaterials, composites</td>
<td>表面限定自组装Janus tectons: a versatile platform for noncovalent HOPG and/or other substrates functionalization</td>
<td>Marina N. Popova (Invited)</td>
<td>Theater Hall</td>
</tr>
<tr>
<td></td>
<td>David Kreher</td>
<td>Optical Spectroscopy of Huntite Multiferroics</td>
<td>Sergey Gavrilov (Invited)</td>
<td>Senator Hall</td>
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<tr>
<td></td>
<td>S 2. Functional oxides, multiferroics</td>
<td>Periculiarity of the incommensurate phase in the TlInS₃ ferroelectric under X-ray irradiation</td>
<td>Natalia Tsintsaru</td>
<td>Senator Hall</td>
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<td>Marina N. Popova (Invited)</td>
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<tr>
<td>16:00 - 16:20</td>
<td>Stefan Sfilucci</td>
<td>Ballistic Ratchet effect on patterned graphene</td>
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<tr>
<td>16:20 - 16:40</td>
<td>Vladimir Artemov</td>
<td>FIB lithography of chiral plasmonic structures of various point symmetry</td>
<td>Alina Nikolaieinko</td>
<td>Senator Hall</td>
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<tr>
<td></td>
<td>Natalia Tsintsaru</td>
<td>Peculiarities of the incommensurate phase in the TlInS₃ ferroelectric under X-ray irradiation</td>
<td>Natalia Tsintsaru</td>
<td>Senator Hall</td>
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<td>Natalia Tsintsaru</td>
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<tr>
<td>16:40 - 17:00</td>
<td>Yuriy Orlovskii</td>
<td>Laser Heating of the Y₁₋ₓDyₓPO₄ Nanocrystals for Hyperthermia</td>
<td>João Tedim</td>
<td>Seminar Room</td>
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<td></td>
<td>Olegas Prentkovskis</td>
<td>Effect of ion, electron beam and ultrasound treatments on the structure and mechanical properties of steel 12Cr1MoV</td>
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<tr>
<td>17:00 - 19:00</td>
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<td>Poster Session</td>
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### Wednesday (7th October)

<table>
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<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>08:00 - 09:00</td>
<td>Registration</td>
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</tbody>
</table>
| Rainer Pärna (Plenary)  
Estonian-Finnish Beamline for Materials Science at MAX-IV Synchrotron Radiation research center  
Theater Hall  
Chair Vytautas Balevičius |
| 09:00 - 09:50 | Coffee Break                                |
| 09:50 - 10:20 | S 1. Advanced spectroscopic techniques  
Theater Hall  
Chair Rainer Pärna  
Alexei Kuzmin (Invited)  
Validation of material models using X-ray absorption spectroscopy | S 2. Sustainable Energy  
Senate Hall  
Chair Jūras Banys  
Andris Sternberg (Invited)  
Fusion – challenging issue on the agenda of Europe’s long-term energy strategy | S 3. Alloys, Coatings  
Seminar Room  
Chair Stefano Bellucci  
Mario G. S. Ferreira (Invited)  
Active Corrosion Protection by Nanoparticles and Conversion Films of Layered Double Hydroxides |
| 10:20 - 11:00 | Vytanas Balevičius  
Application of dynamic nuclear polarization as a powerful tool for structure determination of functionalized nanomaterials | Ivan Saldan  
Reversible hydrogen sorption for the infiltrated magnesium borohydride | Olegas Prentkovskis  
Structural self-organization of titanium alloys under impulse force action |
| 11:00 - 11:40 | Hartmut Stadler  
XPS and Mossbauer spectroscopy of LiFePO$_4$ and LiFePO$_4$/C ceramics | Jonas Reklaitis  
Nanocharacterization for complex scientific questions in material science - new approaches for nanomechanical, nanoelectrical, and nanooptical AFM techniques | Natallia Tsyntsaru  
Cobalt-tungsten alloys: multiscale engineering |
| 11:40 - 12:00 | Vytautas Balevičius  
FTIR and NMR spectroscopy of sol-gel derived calcium hydroxyapatites: correlation of experimental data and the size profiles of sub-nano spin clusters | Hartmut Stadler  
Validation of material models using X-ray absorption spectroscopy | Henrikas Cesiulis  
Electrodeposition and Corrosion Behavior of Nanostructured Cobalt-Tungsten Alloys Coatings |
| 12:00 - 12:20 | Draft | Hartmut Stadler  
Electrodeposition and Corrosion Behavior of Nanostructured Cobalt-Tungsten Alloys Coatings |
| 12:20 - 14:00 | Lunch                                      |
| 14:40 - 18:20 | Excursion                                  |
| 19:00 - 22:00 | Gala Dinner                                |
# Thursday (8th October)

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<th>Venue</th>
<th>Speaker(s)</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00 - 09:00</td>
<td><strong>Registration</strong></td>
<td></td>
<td>Jorge Morgado (Plenary)</td>
<td>Novel conjugated polymers for photovoltaics and hydrogen photogeneration</td>
</tr>
<tr>
<td>09:00 - 09:50</td>
<td><strong>Jorge Morgado</strong></td>
<td>Theater Hall</td>
<td>Chair Saulius Juršėnas</td>
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</tr>
<tr>
<td>09:50 - 10:20</td>
<td><strong>Coffee Break</strong></td>
<td></td>
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<tr>
<td>10:20 - 11:00</td>
<td><strong>S 1. Semiconductors, Photovoltaics, Organic Electronics</strong></td>
<td>Theater Hall</td>
<td>Maria. A. Diaz-Garcia (Invited)</td>
<td>Nanostructured thin-film organic lasers for sensing applications</td>
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<tr>
<td>10:20 - 11:00</td>
<td></td>
<td></td>
<td>Saulius Juršėnas</td>
<td>Tailoring the Physical Properties of Multifunctional Molecular Emitters</td>
</tr>
<tr>
<td>11:00 - 11:20</td>
<td><strong>S 2. Sustainable Energy</strong></td>
<td>Senate Hall</td>
<td>Donats Erts (Invited)</td>
<td>Bi$_2$Te$_3$ and Bi$_2$Se$_3$ nanostructures: synthesis, topological insulator and thermoelectric properties</td>
</tr>
<tr>
<td>11:00 - 11:20</td>
<td></td>
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<td>Javier Macías</td>
<td>Solid solutions in SrVO$_3$-SrTiO$_3$ system as ceramic components for solid oxide fuel cells anodes</td>
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<td>11:20 - 11:40</td>
<td><strong>S 2. Sustainable Energy</strong></td>
<td>Senate Hall</td>
<td>Donats Erts (Invited)</td>
<td>Bi$_2$Te$_3$ and Bi$_2$Se$_3$ nanostructures: synthesis, topological insulator and thermoelectric properties</td>
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<td>Aleksey Yaremchenko</td>
<td>Oxygen-deficient K$<em>2$NiF$<em>4$-type Nd$</em>{1-x}$Sr$</em>{1+x}$NiO$_4$ as prospective oxygen electrode materials for SOFC/SOEC</td>
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<td>11:40 - 12:00</td>
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<td>Development of Tetrathiotetraene Based Thin Films for Thermoelectrical Applications</td>
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<td>11:40 - 12:00</td>
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<td>Characteristics and sinterability of ceria stabilized zirconia nanoparticles prepared by chemical methods</td>
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<td>Scanning Near-Field Optical Spectroscopy of GaN-based Materials, Nanostructures and Devices</td>
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<td>Mitch M.C. Chou</td>
<td>Growth and optical properties of rock-salt Zn$_{1-x}$Mg$_x$O epilayers on MgO (100) substrate</td>
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<td>14:40 - 15:00</td>
<td><strong>Anna Kozlova</strong></td>
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<td>Improved quality of nonpolar m-plane ZnO on surface treated LiGaO$_2$ substrate by Molecular Beam Epitaxy</td>
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<td>15:00 - 15:20</td>
<td><strong>Gytis Juška</strong></td>
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<td>The lanthanum-gallium silicate group crystals as functional materials for optical and piezoelectrical application</td>
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<td>15:20 - 16:00</td>
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<td>16:00 - 17:00</td>
<td><strong>Final Refreshments</strong></td>
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Innovation with Integrity
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Jan Suchanicz  Structural, dielectric and ferroelectric behaviour of (1-x)Na_{0.5}Bi_{0.5}TiO_3-xSrTiO_3 ceramics (x=0, 0.02, 0.04 and 0.06)

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Krzysztof Konieczny  Influence of axial pressure on electric properties of Na_{1-x}Li_xNbO_3 (x=0.08, 0.1, and 0.2) ceramics

Maxim Ivanov  Observation of local Piezo- and Ferroelectricity in Lysozyme protein by means of PFM technique

Rubanik Vasili  Use of ultrasonic vibrations for mechanoactivation and compaction of ceramic powders

Jolanta Vamze  Characteristic of osteopontin, osteocalcin and osteoprotegerin expression in rabbit bone tissue after the implantation of hydroxyapatite-containing biomaterials

Abuova Alsuul  Effect of Ag catalyst atoms on adsorption, reduction and dissociation of oxygen molecules on LaMnO_3 (001) surface

Abuova Fatima  Non-Equilibrium Charge Dynamics in Functionalized Semiconductor Nanostructures

Beata Wodecka-Duś  Synthesis and sintering of the BLT ceramics doped with Fe^{3+}

Dariusz Bochenek  Technology and dielectric properties of the PLZT-ferrite composites

Dagmara Brzezinska  The properties of (1-x)(0.5PZT-0.5PFN-xPFN ceramics

Edita Palaimienė  Dielectric Investigations of Polycrystalline Dysprosium Bismuth Ferrite Ceramic

Mantas Šimėnas  A Monte Carlo study on coronene influence on self-assembly of tricarboxylic acids

Pawel Zieba  Three-component gyrotropic metamaterial

Maxim Silibin  Magnetic interactions in La_{1.2-x}Sr_2Mn_{1.5}Sb_2O_3 (x ≤ 0.2) solid solutions

Sarunas Svirskas  Electromechanical properties of Na_{0.5}Bi_{0.5}TiO_3SrTiO_3-PbTiO_3 solid solutions

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Malgorzata Adamczyk - Habrajska  Nano-indentation studies and macro-scale mechanical testing of calcium modified (Pb_{0.75}Ba_{0.25})(Zr_{0.35}Ti_{0.65})O_3 ceramics

Sergey Babailov  Lanthanide Complexes as Probes of Local Temperature by NMR PARACHEST

Gennady Vizdrik  A simple model of “negative capacitance” phenomenon in inorganic-organic heterostructures

Dzmitry Karpinski  Electromechanical properties of Bi_{1-x}Pr_xFeO_3 solid solutions within the phase boundary region
Femtosecond Ultrastable Tunable Laser Systems

1 kHz – 1 MHz
190 nm – 20 μm

30 fs
LightWire FF3000 is a very flexible femtosecond fiber laser designed with micromachining applications in mind. It can generate femtosecond pulses with energy up to 2 μJ sufficient for the modification of dielectric materials, thin film ablation or surface nano-structuring. If higher energy is required, bursts with energy of up to 10 μJ can be produced. By varying parameters of the burst (number of pulses, energy) one can optimize the laser for the specific process. The repetition rate of the laser can be changed between 2–40 MHz and pulse duration between 300 fs and 10 ps for further optimization. For high speed processing when very high pulse energy is not required (two-photon polymerization, glass modification) laser can be operated at high repetition rate up to 40 MHz with the same average power of 4 W. Integrated pulse-picker is available as an option for full control of the output pulse train.

**FEATURES**
- Up to 4 W output power
- Up to 2 μJ pulse energy
- Tunable pulse duration 300 fs – 10 ps
- Tunable repetition rate from 2 MHz to 40 MHz
- Burst mode operation with up to 10 μJ pulse energy with 20 ns between pulses
- Low maintenance
- Passive cooling
A good knowledge of the elastic properties of graphene is prerequisite to any practical application of it in nanoscopic devices. Although this two-dimensional material is only one atom thick, continuous-medium elasticity can be applied as long as the deformations vary slowly on the atomic scale and provided suitable parameters are used. The present paper aims to be a critical review on this topic. The basis for the paper is the classical Kirchhoff-Love plate theory. It demands a few parameters that can be addressed from many points of view and fitted to independent experimental data. The parameters can also be estimated by electronic structure calculations. Although coming from diverse backgrounds, most of the available data provide a rather coherent picture that gives a good degree of confidence in the classical description of graphene elasticity. The theory can than be used to estimate, e.g., the buckling limit of graphene bound to a substrate. It can also predict the size above which a scrolled graphene sheet will never spontaneously unroll in free space.
Thermodynamic Properties of Nanotubes: Zone-Folding Approach

R. Evarestov, A. Bandura, V. Porsev
Institute of Chemistry, St. Petersburg State University, University Prospekt 26, St. Petersburg, 198504, Russia
re1973@re1973.spb.edu

Zone-folding (ZF) approach allows the calculation of single-walled nanotube (SWNT) phonon frequencies by cutting the phonon dispersion in 2D reciprocal space of the layer used for SWNT rolling up. The total number of cutting lines is equal to the number of layer unit cells in the corresponding 2D supercell. The efficiency of ZF approach was demonstrated in the phonon dispersion calculations for carbon and boron nitride SWNTs [1, 2]. In this work we apply ZF approach for the thermodynamic properties calculations of SWNTs rolled up from the single layers of V$_2$O$_5$, Ti(Zr)S$_2$ and TiO$_2$ bulk crystals. Calculations have been made within the density functional theory using the hybrid exchange-correlation functional and localized atomic basis set [3]. The phonon dispersion was calculated using frozen phonon method [3]. For V$_2$O$_5$-based SWNTs with rectangular morphology the chiralities (4, 0) and (6, 0) were considered. Ti(Zr)S$_2$- and TiO$_2$-based zigzag (n, 0) and armchair (n, n) SWNTs with hexagonal morphology were considered for $n = 12$ and $n = 8$, respectively.

The obtained results show that the difference of the calculated Helmholtz free energy for the SWNTs and those found by ZF approach is about 2-5 kJ mol$^{-1}$ at the room temperature. The agreement in heat capacity is else better. The temperature dependence of SWNT free energy is well reproduced in ZF approach (as example, see Figure 1). The ZF approach seems to be especially efficient in calculations of thermodynamic properties of SWNTs with large diameters (more than hundred atoms in 1D-unit cell).

Acknowledgements
Authors are grateful to St. Petersburg State University for the financial support (Grants No. 12.38.273.2014 and 12.50.1566.2013) and for the computer center facilities.

Feasibility of formation of a perovskite structured polymorph from mixed oxides with the chemical formula $ABO_3$ is conditioned by both size and chemical nature of cations in positions $A$ and $B$. Based on numerous experimental data, the perovskite structure existence field has been estimated in terms of the geometrical tolerance-factor [1]. Outside the filed, a composition with the $ABO_3$ chemical formula either crystallizes in other structural forms: e.g., ilmenite, LiNbO$_3$-type, K-W bronze, or does not exist as a single phase. Under high pressure (typically from hundreds of MPa to tens of GPa), a perovskite phase appears to be the most favourable since it generally provides the closest-packed atomic arrangement. Thus, application of (quasi)hydrostatic pressure extends the perovskite field. Perovskite phase can be formed under high-pressure/high-temperature conditions by means of either directs synthesis or phase transformation from less compact $ABO_3$ polymorphs. In many cases, a quenching under pressure results in stabilization of perovskite polymorph as a metastable phase. Temperature of decomposition or reverse transformation of such phases at ambient pressure is usually high that opens up opportunities for comparative study of metastable and stable perovskites over wide temperature ranges.

It is well-known that ferroelectric activity is characteristic of compositions that contain lone-pair cations: as a rule, lead or bismuth in $A$-position. Lattice distortions caused by atomic displacements and/or oxygen octahedral tilting in a particular perovskite composition depend to a large extent on the relative size of the constituent cations. Magnetic properties can be controlled through manipulation of content and/or ordering of paramagnetic cations (e.g., Fe$^{3+}$, Mn$^{3+}$) in $B$-position. In such a way, new perovskite multiferroics can be designed. However, it turned out that most of bismuth- or lead-containing perovskites of promising chemical compositions can be prepared under conditions of high pressure (or high stress – for epitaxial films) only. Since these non-conventional preparation methods are not easily available, the number of studied metastable perovskite phases is relatively small. Besides, in the majority of cases, inferences on (anti)ferroelectric nature of high-pressure perovskite phases were made based on analysis of the crystal structure only, without dielectric measurements.

In this work, we report on results of about twenty-year experience of high-pressure synthesis of metastable perovskite multiferroics and complex study of their crystal structure, magnetic and dielectric properties. Scores of new compounds and solid solution systems including those with morphotropic phase boundaries were obtained and explored. Comparative analysis of the perovskite phases prepared by conventional methods and the metastable phases has revealed new regularities in compositional behaviour of crystal structure characteristics and dielectric properties and allowed to reconceptualise some phenomena previously considered as well-known [2, 3]. Novel structural phases with unusual combinations of elastic, dipolar and magnetic order parameters have been found in those metastable perovskites [4, 5].

Recent research in this area was done in the network of project TUMOCS. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 645660.

Dynamics of Charge Carrier Generation and Recombination in Organic Photovoltaic Solar Cells

A. Ruseckas¹, D. Amarasinghe-Vithanage¹, A.B. Matheson¹, S.J. Pearson¹, G.J. Hedley¹, I.D.W. Samuel¹, V. Pranculis², V. Gulbinas²

¹- School of Physics and Astronomy, SUPA, University of St Andrews, St Andrews, United Kingdom
²- Center for Physical Sciences and Technology, Savanoriu 231, Vilnius, Lithuania

ar30@st-andrews.ac.uk

Organic solar cells are thin, semitransparent and can be made on flexible substrates. They now achieve power conversion efficiencies of 11% yet higher efficiency and long-time stability are required for practical applications. Quantitative understanding of relevant physical processes is essential for further development. Low dielectric permittivity of organic semiconductors of ε~4 results in strong Coulombic attraction between electrons and holes and in significant losses of photovoltage and photocurrent.

We use broadband transient absorption spectroscopy, ultrafast optical probe of carrier drift using electric-field-induced second harmonic generation (EFISH) and time-resolved photocurrent measurements to study carrier generation, transport and recombination. We show that Coulombically bound and unbound electron-hole pairs have distinct absorption spectra which allows us to get quantitative description of charge pair dissociation. We show that pair dissociation strongly depends on nanoscale morphology of the active layer where the synergy of fine intermixing of electron donor and acceptor molecules and small-scale phase separation gives efficient charge separation [1,2]. Recombination of geminate and non-geminate charge pairs into a triplet state of the donor material is identified as the main loss channel in organic solar cells.

Charge carrier recombination and electronic trap states in perovskite solar cells

A. Baumann1, S. Väth1, P. Rieder1, M. Heiber1, K. Tvingstedt1, V. Dyakonov1,2

1. University of Würzburg, Institute of Physics, Am Hubland, Würzburg, 97074, Germany
2. Bavarian Center for Applied Energy Research (ZAE Bayern), Würzburg, Germany
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Hybrid perovskite solar cells are progressing very fast, showing extraordinary performance competing with inorganic thin-film technologies. Open-circuit voltages close to and even exceeding 1.0 V can be measured, which is closer to the maximum possible value defined by the Shockley-Queisser limit than many other PV technologies. [1] However, there is a lack of fundamental understanding of the photovoltaic properties and working principles of this class of solar cells. For example, anomalous current-voltage hysteresis is often observed in perovskite solar cells, being either an interface phenomenon or related to the bulk perovskite. Other interesting issues are polarization effects either related to the reorientation of organic molecules or due to trapped charges or migration of charged species.

Here, we present our studies on the charge carrier recombination in vapour deposited planar methylammonium lead iodide perovskite (MAPbI3) solar cells. In the open-circuit voltage decay, we observed two very different time domains in the transients. [2] On short time scales, we observed a voltage drop very similar to the reference polymer-fullerene solar cells. A second, much slower decay on longer time scales was observed only in perovskite solar cells. Interestingly, in perovskite devices, the recombination dynamics at all timescales were found to be dependent on the preconditioning of the devices by light illumination prior to measuring. We will discuss the potential origins of the voltage transients. To address the possible influence of electronic traps on the devices performance and to identify the energy levels of such states, we performed thermally stimulated current (TSC) measurements on solution processed MAPbI3 solar cells. [3] To separate between bulk and interfacial traps, we varied the device configuration using different transport layers in normal and inverted device geometry and also studied pure perovskite layers. We observed several peaks in the TSC measurements. The TSC peaks (T1, T2, see Fig. 1) at low temperature are indicative of very shallow traps near the conduction or valence bands, and the peak at high temperature (T4) is assigned to deep traps in the band gap of the perovskite. Finally, we observed an asymmetric peak at T=162 K (T3), which we assigned to the structural phase transition of the perovskite crystal from the orthorhombic to the tetragonal crystal structure. The origin of the T1, T2 and T4 TSC peaks and their impact on the performance of the solar cells will be discussed in detail.


Figure 1. Thermally stimulated current (TSC) for various devices with and w/o hole transport layers (HTL).
Reactive magnetron sputtering deposition and applications of diamond like carbon based nanocomposites

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Nanocomposite materials – materials including nanosized particles, due to interesting and promising electrical, optical etc. properties during last decade have attracted attention of many researchers. Engineering of materials in terms of type, size, shape and concentration of nanoparticles appears an efficient tool to tune properties of the nanocomposite materials that find multiple applications ranging from heterogeneous catalysis to gas sensing and non-linear optics.

In between of variety of the host materials, diamond-like carbon (DLC) films is the subject of considerable attention due to their extraordinary properties such as low friction coefficient and high wear resistance; high corrosion resistance and chemical inertness; high electrical resistivity; infrared-transparency and high refractive index. Therefore, many applications of DLC films have already been implemented for practical use such as mechanical elements, optical components or biomaterials. Metal nanoparticle containing DLC films showing excellent potential in various practical applications attract much attention as well. The nanocomposite films containing the nanometer range sized noble metal nanoparticles of silver, gold or other metals like copper, embedded in a matrix such as amorphous carbon have been studied intensively, since such type of films exhibit antibacterial properties, they demonstrate surface plasmon resonance (SPR) and are promising materials for developing the elemental base of laser physics, opto- and micro-electronics devices.

In this work we present a short review of recently performed research on structure and optical properties of DLC based silver/copper nanocomposites deposited by reactive magnetron sputtering and novel applications of this material. The deposition has been performed employing two modes: direct current (DC) and high-power impulse magnetron sputtering (HIPIMS). Influence of technological conditions like flux of reactive gas, bias voltage on the composition, properties of the nanosized filler and matrix components were studied systematically paying attention to the final properties of the nanocomposites. Plasmonic properties of thin films composed of silver/copper nanoparticles embedded in a diamond like carbon matrix are discussed versus concentration, size of nanoparticles and compared with the results obtained for the films deposited by other techniques. The analysis of the nanocomposites included grazing incidence angle XRD, SEM, ellipsometry, Uv-Vis spectrometry and pump-probe spectroscopy. Structuring of the nanocomposite films using plasma methods as well as applications of the nanocomposites in the development of novel biosensors combining resonance response of the wave guided structure in DLC based nanocomposites and plasmonic effect will be presented.
Obscure Effects of Epitaxy on Ferroelectric Properties

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Single-crystal-type epitaxial films of perovskite-structure oxide ferroelectrics are envisaged to enable numerous micro- and nanoelectronic applications. Compared to polycrystalline films, epitaxial films can bring improvements in device performance. Moreover, advanced or novel functions can be achieved in epitaxial heterostructures of ferroelectric films. Importantly, progress in growth of epitaxial perovskite oxide films on Si substrates makes it feasible to commercialize applications of such films. The superior properties stem from the microstructure of epitaxial films. Compared to ceramics-type polycrystalline films, single-crystal epitaxial films are free of grain boundaries, which usually possess non-stoichiometric composition and non-ferroelectric properties. The presence of boundaries can lead to suppression of ferroelectric polarization and response functions, to increased leakage, poor switching characteristics, and fast fatigue. The ceramics-type boundaries are absent in epitaxial films. Next, in contrast to random orientation of polar axes in polycrystalline films, controllable (usually – single) orientation of polarization is obtained in epitaxial films. This allows for enhancement of switchable polarization, or dielectric permittivity, or electro-mechanical properties. Moreover, when epitaxial films are grown on top of dissimilar single-crystal substrates, mismatch between film and substrate materials (in crystal symmetry, lattice parameters, thermal expansion, and chemical composition) enables the formation of new crystal phases and the emergency of properties which do not exist in bulk prototypes. Epitaxial control of lattice symmetry, strain, polarization, domains, and interfaces has been demonstrated theoretically and experimentally in various ferroelectric heterostructures. Heterostructures with enhanced polarization, huge permittivity, excellent electro-mechanical properties, or strong linear electro-optic effect have been implemented. Besides this, epitaxial growth of perovskite oxide films may also lead to less studied phenomena. In particular, a good film-substrate match is possible for a narrow selection of substrates and ferroelectrics only. Nevertheless, epitaxial films have been grown on variety of substrates despite very large mismatch. Here epitaxial growth and unusual dielectric and ferroelectric properties of mismatched heterostructures will be presented. Both improvements and degradation of performance will be demonstrated. Possible origin of the observed anomalous behavior will be discussed.
Upconversion luminescence in rare-earth doped oxyfluoride materials

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For some decades much attention has been paid for studies of upconversion processes in rare-earth doped materials, which involve the absorption of multiple photons (usually infrared) and subsequent emission of one single photon (visible or ultraviolet). Upconversion effect could be used in different applications such as lasers, infrared quantum counters, next-generation lighting or displays, biological nanolabels and others [1].

Complex fluorides, especially rare-earth doped NaREF₄ (RE=Y³⁺, La³⁺ or Gd³⁺), are promising materials for the upconversion luminescence mostly due to low phonon energy of their matrices and multisite nature of the crystalline lattice allowing for efficient energy transfer between the sites [2].

In this paper, a short introduction into upconversion luminescence will be given followed by a review of some recent results obtained in our group related to site-selective spectroscopy of Er³⁺ in NaLaF₄ [3] and erbium doped β-NaYF₄ for the first time obtained in transparent oxyfluoride glass ceramics by melt-quenching and subsequent heat treatment of the precursor glass (Figure 1.) [4].

Figure 1. Upconversion luminescence in oxyfluoride glass and glass ceramics samples under excitation at 980 nm.

References
Spectroscopy of Phonons in Huntite Multiferroics

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Rare-earth (RE) borates with general formula \( RM_3(BO_3)_4 \), where \( R \) stands for a rare earth or yttrium and \( M = Al, Ga, or Fe \), crystallize in the trigonal noncentrosymmetric \( R32 \) structure of the natural mineral huntite. They attract a considerable attention because of their good luminescent and nonlinear optical properties combined with excellent physical and chemical characteristics. \( YAl_3(BO_3)_4 \) and \( GdAl_3(BO_3)_4 \) doped with neodymium or ytterbium are used for self-frequency doubling and self-frequency summing lasers. Concentrated \( NdAl_3(BO_3)_4 \) crystals are efficient media for minilasers. Iron borates incorporate two interacting magnetic subsystems, Fe and RE ones, and demonstrate a great variety of interesting magnetic and optical properties and a series of phase transitions occurring with variation of both temperature and external magnetic field. A coexistence of at least two of the three order parameters (elastic, magnetic, and electric ones) and a coupling between them (which is the definition of a multiferroic), have been reported for a majority of iron borates and, unexpectedly, for several aluminum and gallium borates. In multiferroics, magnetic properties can be controlled by an electric field and vice versa which has an application potential.

Our laboratory carries out systematic studies of \( RM_3(BO_3)_4 \) functional materials. A complete information on the energies and symmetries of the RE crystal-field levels and lattice phonons is essential for a theoretical description of multiferroic properties. In my talk, I’ll report on our recent studies of lattice phonons in \( RFe_3(BO_3)_4 \) and of electron-phonon and magnetoelastic interactions in these multiferroic compounds. Interactions between magnetic, electronic, and lattice degrees of freedom are typical for multiferroics and one could expect to observe some spectral signatures of these interactions.

A brief summary of our results is as follows.

1) Far infrared (FIR) reflection measurements at room temperature combined with earlier Raman scattering data [1] enabled us to find all by symmetry allowed phonons in \( RFe_3(BO_3)_4 \), \( R = Pr, Nd, Sm, Gd, and Tb \), and to determine their parameters [1,2]. Dispersion analysis and FIR reflection spectra modeling were used to extract these parameters for the infrared active modes.

2) The temperature-dependent FIR reflection and Raman spectra clearly evidence a structural phase transition at \( T_c = 199 \text{ K} \) and \( T_d = 148 \text{ K} \) in gadolinium and terbium iron borates, respectively. The temperature \( T_c \) was found to depend upon the quality of a crystal. A hysteresis and a quasi-soft mode were observed in both FIR and Raman spectra testifying a weak first-order phase transition at \( T_c \).

3) At the magnetic ordering temperature \( T_N \) (which lies between 31 and 41 K for the studied iron borates) a well defined peculiarities are observed in the temperature dependences of some phonon frequencies. Those are spectral signatures of the magnetoelastic, or spin-phonon, interaction [3].

4) Spectral signatures of an interaction between phonons and crystal-field excitations of the RE ion are observed in the FIR spectra of the neodymium [3] and terbium iron borates. The temperature dependence of some phonon frequencies are those of the magnetoelastic, or spin-phonon, interaction [3].

5) A temperature-dependent interference between two types of excitations was observed in \( PrFe_3(BO_3)_4 \) in which the frequency of 4f crystal-field electronic excitation of \( Pr^{3+} \) falls into the TO – LO frequency interval of the optical phonon mode near 50 cm\(^{-1}\) (1.5 THz). Experimental data were explained on the basis of a theoretical model of coupled electron-phonon modes. The fitting procedure revealed the value 14.8 cm\(^{-1}\) for the electron-phonon coupling constant. This rather large value points to an essential role played by the electron-phonon interaction in physics of multiferroics [4].

I would like to thank my colleagues who participated in the studies [1-4]. A part of this research was supported by the Russian Scientific Foundation under Grant No. 14-12-01033.

Porous anodic oxides as model matrices for synthesis and investigation of 1-D nanostructures

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This report describes the procedures for the highly ordered porous anodic oxides preparation, which are comfortable and effective templates for the synthesis and study of one-dimensional nanostructures. The various nanomaterials synthesis methods in porous matrices and such structures various properties research results.

Great interest in nanostructured materials is caused by perspective of new device with enhanced properties design. The fabrication of structures with feature sizes smaller than 100 nm is an expensive using conventional (e-beam and photo) lithographic methods. Therefore, nonlithographic methods may be better suited for mass production of nanoscale materials. Most approaches fall into one of three main categories: template methods; self-organized nanostructures; and direct growth.

Electrochemical processing is a simplest way to produce nanostructured materials. One of the interesting nanostructures are porous anodic oxides. Porous anodic alumina, titania, tungsten oxide and oxides of other valve metals are promising structures or already found their application in various fields, such as medicine, construction, energy, functional electronics, MEMS, sensing and others. Either self-organized highly ordered porous oxide structures obtained by electrochemical oxidation presents the big interest for use them as a matrices for synthesis various 1-D nanostructures, mainly nanowires, as well. Such nanostructures can be obtained by various methods such as AC, DC or pulsed electrodeposition, SILAR technique, metal sulfidization of metals etc.

Also such porous matrices allows to investigate electro-physical, thermo-chemical, mechanical and optical properties of one-dimensional structures formed within anodic oxide pore arrays effectively and with ease.
Estonian-Finnish Beamline for Materials Science at MAX-IV Synchrotron Radiation research center

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MAX IV laboratory is a new synchrotron radiation research center located in Lund Sweden. When MAX IV facility starts operation, it will be the brightest synchrotron source worldwide. Currently 13 beamlines are funded for the MAX IV facility, FinEstBeaMS is one amongst them.

FinEstBeaMS beamline is a materials science beamline to be built at the 1.5 GeV storage ring of the MAX-IV facility. FinEstBeaMS beamline has two branch lines dedicated for research of matter in its various forms: gases and liquids but also nanoparticles and solids. Investigation probes at FinEstBeaMS are vacuum ultraviolet light and soft X-rays (4.3 eV - 1000 eV), produced by elliptically polarizing undulator and selected by plane grating monochromator. At endstation for gases and liquids electron and ion spectrometers will be installed.

Information gained at FinEstBeaMS will be extremely valuable and helps to understand process occurring in the upper part of atmosphere, where clouds are formed and were ozone layer protects us, but also radiation damage of organic molecules like ones forming DNA. It will be possible to investigate nanoparticles and nanomaterials for self-cleaning surfaces and environment remediation using sunlight; nanomolecular layers on alloy surfaces for biotechnological applications involving biosensors and biomedical implants; electrochemical double layer capacitors for efficient energy usage; and semiconductor based power electronic devices for better energy utilization.

Funding for the basic equipment and instrumentation, materials, and personnel costs during the construction phase has been obtained by Estonian and Finnish consortium supported by the European Union through the European Regional Development Fund and the Academy of Finland (FIRI2010, FIRI2013, FIRI 2014 [1,2]).

Validation of material models using x-ray absorption spectroscopy

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The popularity and possibilities of x-ray absorption spectroscopy (XAS) have been significantly grown during the last decades with the rapid progress in synchrotron radiation sources. Being element-selective and short-range order sensitive technique, XAS is well suited for an investigation of complex crystalline and disordered compounds as well as nanostructured [1] and biological materials [2]. Moreover, time-resolved XAS experiments can be realized to follow in-situ modifications of the material structure under extreme conditions [3] and on a time scale down to femtoseconds [4]. At the same time, the analysis of the extended x-ray absorption fine structure (EXAFS), containing structural information on the local environment around absorbing element [5], is usually limited to a few nearest coordination shells due to the difficulties associated with shell overlap, structural and thermal disorder as well as many-atom contributions. Therefore, a significant amount of structural information contained in the experimental EXAFS spectra gets lost.

To address this challenging problem, several approaches, based on a combination of numerical simulations such as Monte Carlo and molecular dynamics (MD), have been developed in the past. In particular, the MD-EXAFS method [6] allows one to perform not only an interpretation of total experimental EXAFS spectrum, but also a validation of the force-field models. In this report recent advances in the development and application of the MD-EXAFS method will be presented on an example of oxide materials as SrTiO$_3$, NiO, ZnO and Y$_2$O$_3$ [6-9].

Application of dynamic nuclear polarization as a powerful tool for structure determination of functionalized nanomaterials

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In the last decades, a large number of catalytically active hybrid systems, as well as inorganic/organic composite materials organized on the meso- and nanoscale have been developed and their structure has been determined. Such materials are important due to their widespread application potential, ranging from heterogeneous catalysis for environmental friendly organic transformations, over inorganic-organic hybrid model systems for real life structures such as bones, to multi-stimuli responsive materials. In recent years, solid-state NMR spectroscopy has evolved into an important tool for the structure determination of such mostly amorphous materials, as well as to study their surface chemistry.[1]

However, standard NMR suffers from its low intrinsic sensitivity due to the low population difference of the nuclear spin states. This disadvantage restricts for example the detection of nuclei containing a low gyromagnetic ratio and low natural abundance such as $^{15}$N. Since many of the above mentioned functional materials include nitrogen containing groups which are very difficult to spin-label, methods for sensitivity enhancement which are not based on chemical routes have to be utilized. Dynamic Nuclear Polarization (DNP) is one method to overcome sensitivity problems in NMR at high magnetic fields. [2] This technique allows the detection of low sensitive nuclei such as $^{15}$N even in natural abundance, and thus opens new perspectives for structure determination of hybrid materials and catalysts. [3]

The presentation will give an introduction to DNP and will show recent examples applying this technique for structure determination of functional nanomaterials. As first example, the characterization of a novel heterogeneous dirhodium catalyst is presented, where it was possible to perform a detailed analysis of binding sites based on DNP measurements.[4] In a second example DNP is employed as tool to study the switching behaviour of rhodamine grafted on crystalline nanocellulose (CNC). [5] Such composite material can be used as multi-stimuli responsive material. Finally, first insights are given, how DNP can be utilized to look on binding sites of immobilized peptides which serve as model systems for bone like structures.

Figure 1: Schematic representation of the immobilized dirhodium catalyst (left). Natural abundance $^{15}$N DNP NMR of the immobilized dirhodium catalyst (right). (depicted from ref.[4])

Nanocharacterization for complex scientific questions in material science - new approaches for nanomechanical, nanoelectrical, and nanooptical AFM techniques

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Modern material science on complex functional nanostructured materials requires analytical techniques with sufficient resolution and correlated multimodal data output. True pN-level force-controlled AFM-imaging based on kHz-distance modulation coupled with intelligent extraction of low-noise ultrafast force distance cycles (Peak Force Tapping Mode) has scientifically proven to be a very powerful technique for this purpose. Multi-component surfaces can be non-destructively imaged with up to atomic resolution independent from surrounding media. At every image pixel the complete distance-dependent interaction between tip and surface is revealed. Fully correlated topographic and quantitative nanomechanical information can be extracted (Peak Force QNM). Simultaneous high-bandwidth current amplification and electrostatic force gradient detection adds nanoelectrical properties to the data set (Peak Force TUNA/KPFM). Recent extensions of the Peak Force Tapping family combine optical nearfield detection with force based imaging and crosslink nanoelectromechanical measurements with nm-resolved chemical identification (Peak Force IR). Physical background and instrumental aspects of these exciting new imaging modalities will be discussed and highlighted with application examples.
Fusion – challenging issue on the agenda of Europe’s long-term energy strategy

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The European Union has agreed on ambitious Energy and Climate targets for 2020 and beyond: to reduce greenhouse gas emission, to increase the share of sustainable renewable energies, as well as proceed with development of fusion energy reactors as strategic future energy option. ITER is a fascinating project holding the stage, the only large-scale global project in which seven key partners from across the globe work together. ITER is also contributing to exceptional challenge to provide energy to our citizens and at the same time to decarbonize the economy.

Nanotechnology and advanced functional materials have the potential to help achieving these ambitious targets. Latvian EUROfusion Organization – heading Institute of Solid State Physics University of Latvia (ISSP UL) – is composed of several parts – ISSP UL, Institute of Physics University of Latvia (IP UL) and Institute of Chemical Physics University of Latvia (ICP UL). The research topics are compatible to the European Fusion Programme and to the international ITER Project in our focus areas. Effective implementation of results can be achieved only in close collaboration with other EU Member States EUROfusion Organizations (Laboratories).

Some of the following research projects accomplished by EUROfusion Organization ISSP UL will be discussed during presentation:

- Ab initio simulations of the reduced activation steels strengthened by yttria precipitates;
- When and how ODS particles are formed. X-ray Absorption Spectroscopy (XAS) and atomic scale modelling of ODS steels. Theoretical modelling of first stages of ODS steel production;
- Regions of azimuthal instability in gyrotrons;
- Fusion related liquid metal MHD research. Stability of metal droplets jets in tokamak environment;
- LIBS spectroscopy of the impurity concentration depth profile in wall tiles;
- Analysis of accumulated tritium and microstructure of carbon based JET divertor tiles;
- Tritium release from high dose neutron irradiated beryllium pebbles;

The model of the γ-Fe crystalline lattice with 2 Y substitutes and 1 O impurity atom in the 1st nearest neighbours positions (a) and the corresponding charge redistribution around the 2 Y substitutes and O atom inside the (110) splitting plane (b). The latter is defined as the total electron density of γ-Fe lattice including the two Y substitutes and O impurity atom minus the sum of those for γ-Fe lattice with 2 vacancies, 2 Y and O atom in vacuum.
Paper Electronics Using Environmentally Friendly Devices

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Paper electronics is rapidly evolving and the possibility of extending the available information beyond the printed graphic is very interesting [1]. Many of the suggested approaches are for example to improving logistics or disposable sensing, e.g. as food sensors on packages to minimize food spoilage. However, for paper electronics to be truly recyclable and/or disposable the components need be environmentally friendly and bio-compatible, and preferably operating at low voltages. Here we propose an environmentally safe approach to such active circuits and electronic functionalities, by making ion-modulated transistors on paper.

By blending the semiconductor poly(3-hexyl thiophene) (P3HT) with a biodegradable poly-lactic acid (PLLA), we have increased the operating speed of ring oscillators manufactured on rough and absorptive paper substrates with four orders of magnitude [2]. The reason is the spontaneous phase-separation between the P3HT and PLLA leading to thin but continuous semiconductor films.

A range of ionic liquids (ILs) based on choline chloride (ChoCl) were used as the electrolytic layer in the IMTs. Different organic compounds were mixed with ChoCl to create solution-processable deep eutectic mixtures that are liquid or semiliquid at room temperature. In the final, solid version of the IMT, the ILs are also solidified by using a commercial binder to create printable transistor structures operation at ~1V [3].

Furthermore, we will also address issues with making CMOS-type logic circuitry on the paper substrate.

![Fig. 1. An SR latch in component form (left upper corner) was built by using four transistors and two resistors. The truth table for the SR latch with the inputs S and R and outputs Q_S and Q_R is shown in the lower left corner. The inputs and outputs of the latch with the raw data in the upper graph and the four channels separated in the lower graph.](image)

Furthermore, we have made simple digital circuits on the recyclable paper substrate using the developed environmentally friendly transistor structure. In Fig. 1 a one-bit memory latch (SR-latch) is constructed using four p-channel transistors and two resistors and the output is shown [3].

Active corrosion protection by nanoparticles and conversion films of Layered Double Hydroxides

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The active corrosion protection of metallic substrates can be achieved by addition of corrosion inhibitors to protective coatings. However, direct mixing of an inhibitor with coating formulations can lead to important drawbacks decreasing barrier properties of the coating and diminishing activity of the inhibitor. Also, soluble inhibitors can cause phenomena like osmotic blistering or be leached out spontaneously to the environment, which limits long-term performance and is environmentally pernicious. To overcome this problem and have controlled release of inhibitor different strategies of inhibitors storage in nanocontainers have been developed in order to produce smart self-healing coatings.

The use of nanocontainers for organic and inorganic corrosion inhibitors is described, especially the most promising from industrial point of view, based on Layered Double Hydroxides (LDH). LDHs are able to release corrosion inhibitors in a controlled way by anion-exchange. The combination of nanocontainers in the same coating system has proved in many cases an important synergistic effect avoiding deactivation of inhibiting compounds.

Similarly to their powder counter-parts, LDH films can be obtained by different routes, including chemical and electrochemical assisted ones.

In this work we explore the anion-exchange ability of LDHs to intercalate different active species and impart differentiated functionalities.
New carbon and oxide based protective and anti-corrosion nanocoatings

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Corrosion inhibition of metallic substrates is an important and crucial step for great economical as well as environmental savings. In this presentation, we introduce an extra thin effective corrosion inhibitive material having layered structure designed for protection and functionalization of Ti Grade 5 alloy or AISI 304 stainless steel substrates. The coating consists of a first layer made of thin graphene nanoplatelets, on top of which a multilayer Al2O3 and TiO2 films (the laminate) is applied by low-temperature atomic layer deposition (ALD). The amorphous structure of the laminate was confirmed by micro-Raman and X-ray diffraction analysis, the structure of the coating is studied with high-resolution scanning electron microscopy methods, supported with focused ion beam technique, allowing to prepare and characterize cross-section structures of the samples. Corrosion inhibition ability of the prepared coatings was analyzed by open circuit potential, Tafel plot, and by voltammetric analysis, in aqueous salt solutions. The open circuit potential of the graphene-metal oxide coated substrates showed much passive nature than bare substrate or graphene coated or only metal oxide coated substrates [1, 2].

Figure 1. Example of (a) Al2O3/TiO2 nanolaminate surface after 40 days immersion in 1 M KBr aqueous solution and (b) voltammetry plots of the bare, rGO coated, Al2O3/TiO2 laminated, and rGO/Al2O3/TiO2 laminated Ti-5 substrates measured in the electrolyte.

A new composite graphene-metal oxide anti-corrosion coating with a thickness of ≤100 nm is prepared and tested extensively in this study, and showed good anti-corrosion properties when coating light metals, like titanium alloys or common ferroalloys, like low-priced stainless steels. The developed coating technology is environmentally friendly, and the protective coating is also biocompatible because the outer sublayer of the coating is titania, which is a well-known biocompatible material. In the presentation both the coating technology and the tests will be introduced in more detail.

Novel conjugated polymers for photovoltaics and hydrogen photogeneration

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Conjugated polymers are remarkable materials for various electronic, optoelectronic and bioelectronic applications. An impressive progress has been observed over the last three decades, supported by the preparation of new systems whose design has followed the progressive unravelling of processes and devices working fundamental steps.

In this communication, I will focus on the use of these materials for energy generation, in photovoltaics (OPVs) and in photoelectrochemical cells for hydrogen generation. In particular I will address the development of cross-linkable conjugated polymers that we have been exploring in the fabrication of OPVs with nanostructured interfaces and how the devices performance correlates with the nanostructuring dimensions. The more recent work on the preparation of novel low energy gap polymers and polymers with high electron affinity for such applications will be also described.

Finally I will address the synthesis and characterization of conjugated polymers for the hydrogen photogeneration as an alternative energy production scheme. I will focus on both regular conjugated systems and in conjugated polymers functionalised with catalysts.

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Nanostructured thin-film organic lasers for sensing applications

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In the last years extensive research has been devoted to the investigation of optically-pumped solution processable thin film organic lasers, due to their advantages of chemical versatility, wavelength tunability, mechanical flexibility and low cost [1]. Particularly attractive for applications in the fields of optical communications, biosensing and chemical sensing are distributed feedback (DFB) lasers, consisting of nanostructured active organic waveguides. In this context, our research group has performed extensive work on DFBs with different types of organic active materials and laser resonators [2-9]. In this presentation our last advances in improving both, the active laser material and the laser resonator will be discussed. Results on novel high performing laser dyes of various families (perylenediimides, oligophenylenevinylene and oligothienoacenes), dispersed in thermoplastic polymer films, emitting in a wide range of wavelengths within the visible spectrum (Fig. 1a), as well as progress in the development of different device geometries based on one dimensional second-order DFB resonators fabricated by holographic lithography and nanoimprint lithography, will be presented (Fig. 1b). The capability of these lasers to be used as label-free refractive index sensors, as well as sensors for the specific detection of biomolecules of clinical interest will also be discussed.

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Bi$_2$Te$_3$ and Bi$_2$Se$_3$ nanostructures: synthesis, topological insulator and thermoelectric properties

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Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are narrow band gap semiconductors composed by layered structures where each charge-neutralized layer is formed by five covalently bonded atomic sheets. These layers are bonded together by van der Waals forces, thereby enabling mass production by both bottom-up (chemical synthesis) and top-down (mechanical exfoliation) methods. The synthesis and physical properties of these materials have been widely studied because of their pronounced room temperature thermoelectric properties finding applications as active elements in thermoelectric micro-generation, local micro-cooling and infrared detectors [1].

Recently, Bi$_2$Te$_3$ and Bi$_2$Se$_3$ were discovered to be three-dimensional (3D) topological insulators (TI) – materials with gapped insulating bulks and metallic conducting surfaces. In TI, the strong spin-orbit coupling reduces the probability of the electrons backscattering by surface defects, which lowers the surface resistivity and leads to the formation of topologically protected surface states [2]. The unique properties of the topological surface states makes TIs promising for novel applications such as spintronics and quantum computing.

Making these materials into nanostructures became a challenging task as it is believed that the efficiency of thermoelectric materials can be improved by creating of structures where one or more dimensions are reduced, for example, thin films, nanoribbons or nanowires. At the same time, nanostructuring of TI materials is a possible way to detect merely surface effects by significant enhancing their surface-to-volume ratio and thus reducing an impact of bulk transport which can mask the peculiar properties of the surface states.

Here we present two-stage method for catalyst-free vapour-solid (VS) synthesis of highly-crystalline nanoplate-seeded free-standing, above the substrate surface, bismuth telluride and bismuth selenide nanostructures. The advantages of this method in comparison with widely used Au-catalysed vapour-liquid-solid synthesis technique [3] are rapid growth times, exclusion of H$_2$ gas, as well as the absence of contamination of deposited structures with catalyst residues.

For the investigation of topological insulator properties the magneto transport characterisation was performed at low temperatures. The $\pi$ Berry phase was identified in quantum oscillations confirming the topological surface states.

For the thermoelectric study, Bi$_2$Te$_3$ and Bi$_2$Se$_3$ and graphene were combined in layered structures. Graphene is a substrate, allowing epitaxial growth of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ [5]. At the same time, graphene is perfect candidate for use as a top electrode in optoelectronic devices due to unique combination of properties – mechanical strength, excellent heat and electrical conductivity and transparency for visible and near-infrared spectrum.

Graphene/Bi$_2$Se$_3$ nanostructures were synthesized by combination of chemical vapour deposition (CVD) and catalysis-free vapour-solid deposition methods. Thermo- and opto-electrical properties of fabricated layered structures were investigated under ambient conditions. Such structures may have applications in flexible infrared sensors, thermo-power and local cooling microdevices as well as in Li-ion batteries anodes.

A common feature for ternary nitride semiconductors is band potential fluctuations, related to spatial variations of alloy composition, strain, extended defects, and cation clustering. Such fluctuations may have different consequences on nitride device performance. In some cases (polar InGaN quantum wells (QWs)), localization separates carriers from dislocations reducing the rate of the nonradiative recombination [1]. In other materials, e.g. AlGaN, localization occurs at domain boundaries with a larger defect concentration and a higher rate of nonradiative recombination [2]. In photonic devices, such as lasers and LEDs, the presence of lower potential sites may lead to current crowding and premature device degradation [4]. Carrier localization broadens the emission spectrum, reducing modal gain in lasers. In addition, for emitters of polarized light based on non- and semipolar QWs, carrier localization may reduce degree of the linear polarization [5], which is not desirable for applications. Thus, a detailed understanding of potential fluctuations and their relation to properties of material growth and defects is important for development of efficient light emitting devices. Since band potential fluctuations occur on the nanoscale, optical techniques with resolution overcoming the diffraction limit should be used. Photoluminescence (PL) measurements using scanning near-field optical microscopy (SNOM) is a proper technique for this purpose.

In the presentation, results of SNOM investigations on AlGaN epitaxial layers [2,3], AlGaN QW-based deep UV LEDs [4], as well as on nonpolar and semipolar InGaN QWs [6-9] will be reviewed. Recent results on spatial distribution of the degree of linear PL polarization as well as on lateral carrier transport will be presented. The experimental data were obtained using a SNOM apparatus working in different configurations: illumination, collection, illumination-collection, or a combination of those. Typically, the data were obtained with 100 nm spatial resolution at 300 K. During scans, the whole emission spectra were measured at each point of a scan, which allowed plotting and analyzing maps of peak emission wavelength, intensity and spectral width, and performing correlations and statistical analysis of these maps.

Different nitride materials and nanostructures were found to possess very different properties of band potential fluctuations, with different dependencies on ternary nitride composition, crystallographic orientation, growth regime and surface morphology. The rich data of the SNOM measurements have not only provided a deeper understanding of phenomena behind the band potential fluctuations, but also pinpointed directions towards improvement of device efficiency and stability.

Nondestructive evaluation of embedded piezoelectric transducers by thermal wave and pulse methods

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Piezoelectrics are functional materials transforming electrical energy into mechanical energy and vice versa. Nowadays, they find wide application in smart systems used for the health-monitoring of safety components, for actively changing the component strength in case of crashing, for damping the vibration in order to increase the machining quality and machine dynamics or to reduce disruptive noise, for pumps, valves and regulatory, for smart prostheses etc. An important role in fabrication of such smart systems is dedicated to performance inspection during laminated module processing.

Thermal methods are a promising approach for the non-destructive evaluation of integrated piezoelectric sensors and actuators. The polarization distribution of the piezoelectric can be determined from the pyroelectric response generated by a modulated laser beam (the so-called laser intensity modulation method – LIMM) [1, 2] or by a laser pulses [3].

In this work, we demonstrate that LIMM is a promising approach for non-destructive evaluation of the polarization state and thermal interfaces of embedded piezoelectrics in integrated sensor-actuator modules. In the case of thermal pulses, the recorded time dependence of the pyroelectric current is Fourier-transformed and divided by the complex gain spectrum of the measurement system in order to compensate the measurement-induced signal distortion. The calculated frequency spectrum is then analyzed in the same way as conventional LIMM data. The thermal-pulse method yields similar results as the LIMM technique, but it is faster by about one order of magnitude than LIMM measurements of similar bandwidth and quality.

For our measurements, four types of samples were evaluated: (i) piezoelectric Pb(Zr,Ti)O_3 (PZT) plates embedded in low temperature co-fired ceramics (LTCC) [4], (ii) macro-fiber-composite (MFC) actuators consisting of PZT rods embedded in epoxy resin, placed between two copper electrodes and covered by a Kapton film [5], (iii) PZT plates coated with polyimide and embedded in casted aluminum [6], and (iv) thermoplastics-compatible piezoceramic modules (TPM) consisting of a metalized PZT functional layer (fiber arrays or monolithic wafers) which is positioned between two transparent thermoplastic carrier films of polyamide 6 (PA6) comprising a meandered electrode [7].

At low modulation frequencies, the pyroelectric response of PZT is governed by thermal losses to the embedding layers. Here, the sample behavior can be described by a harmonically heated piezoelectric plate exhibiting heat losses to the environment characterized either by a single thermal relaxation time or by a continuous distribution of relaxation times. The spatial polarization distribution of the PZT plate was shown to provide a small contribution to the imaginary part of the pyroelectric current in the frequency range confined by the inverse of the thermal relaxation time of the PZT plate (the time for reaching thermal equilibrium with the environment) and the inverse of its heat transit time (the time required to establish internal thermal equilibrium).

Analyzing the frequency response by means of a Nyquist plot provides insight into the transfer functions of linear time-invariant systems. Advanced models of frequency response (several relaxation times, a relaxation time distribution, etc.) were considered to describe the pyroelectric response. Thermal relaxation times or relaxation time distributions of the embedded piezoelectrics were derived. They characterize the thermal contact conductance and thus enable disclosure of lamination failures.

Theoretical Study of $\alpha$-$V_2O_5$ Double-Walled Nanotubes

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Tubular nanostructures of $V_2O_5$ are promising materials for future industrial applications. At the present time there is a lack of theoretical investigations of atomic and electronic structure of these materials. Their properties can strongly deviate from those of the bulk phase and require a careful study for further engineering research.

Previously we studied the structural, electronic and vibrational properties of single-walled nanotubes (SWNT) folded from $\alpha$- and $\gamma$-$V_2O_5$ monolayers [1]. The electronic and phonon properties of $\alpha$- and $\gamma$-phase nanotubes appeared to be similar to those of the parent layer. It was found that nanotubes of the same chirality are energetically equivalent for both considered phases. The strain energies calculated for [100]-oriented nanotubes folded from layers of both phases are close to zero. This reflects the unique flexibility of the layers for folding in the [100] direction. It should be noted that experimentally synthesized tubular nanostructures are multi-walled and the interactions between walls need to be taken into account for their proper modeling.

Here we present the results of DFT calculations of double-walled nanotubes (DWNT) of $(n_1, 0)@(n_2, 0)$ chirality formed from monolayers of $\alpha$-$V_2O_5$. Calculations were made by CRYSTAL09 program using PBE0 exchange-correlation functional and the atomic basis set. Semiempirical Grimme correction was used in order to account the dispersion interactions between walls. DWNTs were constructed by coaxial insertion of the narrower (with smaller diameter) SWNT into the wider one (with larger diameter). In order to avoid too close disposition of NT walls we consider DWNTs with the difference $n_2 - n_1 = 3, 4$. All atomic positions in DWNTs were fully optimized.

After geometry optimization we observe the formation of two types of local regions extended along the DWNTs (Fig. 1). The first one is the interwall adhesion region with structure close to that of the bulk $\alpha$-$V_2O_5$. The second one is layer-puckering region which arises from the mismatch between the circumferences of inner and outer wall. The formation of kinks is possible due to large flexibility of $\alpha$-$V_2O_5$ monolayer.

Although the total density of states (DOS) of DWNTs is close to the sum of DOS of two initial SWNT constituents, the formation of small shoulders on edges of valence and conduction bands results in considerable decrease of band gaps of DWNTs (up to 1 eV relative to the monolayer). The main reason of the formation of such shoulders is the shifting of DOSs of inner and outer walls in opposite directions on energetic scale. The electronic density of shoulder at conduction band edge is localized on vanadium atoms in bulk type regions, while the formation of DOS shoulder at valence band edge is the cumulative effect of all oxygen atoms.

Figure 1. The view of $(8,0)@(12,0)$ $\alpha$-$V_2O_5$ DWNTs along nanotubes axis (left) and corresponding electronic DOS of inner and outer walls (right). The circle marks adhesion region. Legend: V, large balls; O, small balls.

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Redistribution effects in graphene nano platelets / epoxy resin composite

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Microcleavage exfoliation procedure of expanded graphite was employed to obtain GNP particles. As raw material, was used Asbury expandable graphite. EPIKOTE Resin 828 was used for composites fabrication. Composites with the concentrations 0.25 – 4 wt. % of well dispersed GNP particles were prepared. Electromagnetic properties of composite materials have been studied in the wide frequency range (from 20 Hz to 2 THz). It was demonstrated, that at room temperature the percolation threshold in such system is 2.87 wt. %. According to the low temperature analysis, the conductivity occurs due to the electron tunnelling mechanism. During the annealing of composites above the epoxy resin glass temperature we have observed the dramatic increasing of both permittivity and conductivity. The phenomenon was studied with the impedance formalism. The frequency dependence of impedance cannot be described by a single RC circuit $Z=R/(1+i\omega C)$. To describe such behaviour the impedance spectra were modeled as infinite chain of RC circuits connected in series, and corresponding distribution of relaxation times was calculated by solving an integral equation [1] (1)

$$Z = Z_{\infty} + \Delta Z \int_{-\infty}^{\infty} \frac{f(\tau)}{1-i\omega \tau} d(\log \tau)$$

Figure 1. Distribution of relaxation times on heating (a) and on cooling (b) of composites with 2wt.% of GNP

On heating the maximum of distribution of relaxation times shifts to the shortest relaxation times and distributions becomes narrower, while on cooling the distributions of relaxation times are almost temperature independent (Fig. 1). We can conclude, that redistribution of GNP particles is observed. Due to this process the average size of GNP particels, and consequently the mean distance between conductive clusters decreases, as a result the potential barrier for tunneling decreases. This leads to the huge rise of the conductivity and shifts the percolation threshold to the lower concentrations (down to 1.38 wt. %).

Modelling and simulation of CNTs- and GNRs-based nanocomposites for nanosensor devices

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The main objective of the current study is to demonstrate the implementation of advanced simulation models providing a proper description of the electronic properties, electrical conductivity, electromagnetic and electromechanical phenomena of functionalized CNT- and GNR-based nanostructures of different morphologies and their interconnects for nanosensor and nanomemory systems. The sensitivity of the local electronic density of states to external influences (mechanical, chemical, magnetic, etc) on the fundamental electromagnetic properties of CNTs, GNRs and their metal interconnects have been analyzed from the point of view of nanosensor applications [1-3]. We develop a set of prospective models of nanocarbon-based nanomaterials and nanodevices based on the various interconnects and interfaces (see Figure 1).

In particular, nanoporous systems are considered as complicated ensembles of basic nanocarbon interconnected elements (e.g., CNTs or GNRs with possible defects and dangling boundary bonds) within the effective media type environment (Fig.1a,1b). The model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric polymer environments (e.g., epoxy resins) is regarded as a disordered system of fragments of nanocarbon inclusions with different morphologies (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric environment. Presumably, the electrical conductivity of a nanocomposite material will depend on the concentration of nanocarbon inclusions (in fact, carbon macromolecules). Isolated nanocarbon inclusions will provide conductivity due to the hopping conductivity mechanism through dangling bonds up to the percolation threshold, when at high concentrations (some mass %) a sustainable ballistic regime appears, which is characteristic of pure carbon systems. The hopping mechanism is regulated by the hopping of electron between ‘nanocarbon macromolecules’:

$$\sigma_C = \sigma_0 \cdot \exp(-\frac{4}{3} \left(\frac{4\pi r_{c0}}{a}\right)^{1/4} \left(\frac{W_0}{kT}\right)^{1/4})$$

where $r_{c0}$ - is the length of the tunnel ‘jump’ of the electron equal to the distance between ‘nanocarbon’ clusters, $\sigma_0$ - normalization constant which means the conductivity of monolithic dielectric medium. The simulation of nanocomposite conductivity via the volume part of nanocarbon inclusions is presented in Figure 2. Natural applications of this kind of nanocomposite materials can be found in nanosensors of pressure and temperature.

Ceramic composite material with carbon nanotubes fabricated by spark plasma sintering

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Spark plasma sintering was used for produce nanocomposite alumina oxide ceramic containing carbon nanotubes (0-50%vol.) as reinforcing element. The structure of material was investigated by optical and electron microscopy. The modulus of elasticity and fracture toughness are in three times more than characteristic pure alumina oxide Al₂O₃.

Examination of the samples shows that their structure is a densely sintered alumina oxide grains surrounded by carbon nanotubes. Carbon nanotubes are uniformly distributed throughout the volume of the composite and form a reticulate framework structure along the facets of the grains. This type of firing ceramic blanks as spark plasma sintering does not result to evident grain growth, it size in the sintered grain material does not exceed 2 microns.

Composite microhardness decreases with increasing of carbon nanotubes content from 16.5 to 15.2 GPa. It agrees with the fact that the microhardness of the pure material is always higher than its composite. The stress intensity factor for samples with 50% vol. nanotubes is higher in about 3.3 times than for the sample of pure alumina, and the modulus of elasticity is higher in 2.8 times.

The research results are shown in Table.

Table. Value of modulus of elasticity, crack resistance and microhardness of samples sintered at 1550 °C.

<table>
<thead>
<tr>
<th>Carbon nanotubes content, %vol.</th>
<th>Medium sintering</th>
<th>Microhardness, GPa</th>
<th>Crack resistance, MPa·m¹/²</th>
<th>Modulus of elasticity, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 argon</td>
<td>16.5 ± 0.35</td>
<td>2.7</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>20 argon</td>
<td>15.8 ± 0.35</td>
<td>4.8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>30 argon</td>
<td>15.6 ± 0.51</td>
<td>6.5</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>50 vacuum</td>
<td>15.2 ± 0.61</td>
<td>8.9</td>
<td>780</td>
<td></td>
</tr>
</tbody>
</table>

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Ultrafast Excitation migration and quenching in a PFO-PBy-single-wall carbon nanotube hybrid system

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Single-walled carbon nanotubes (SWNTs) are potential materials for future electronic devices because of their unique electronic properties. The fast carrier relaxation make them a promising component in ultrafast photonic devices. There were also attempts to use them in solar cells. Wrapping the tubes with polymers selects SWNTs with particular chiralities. However, polymers used for wrapping also change electronic properties of nanotubes.

We address excited state dynamics in SWNTs that are wrapped with poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6-(2,2-bipyridine))] (PFO-BPy) in order to select tubes with the (6,5)-chirality [1]. Because of narrower energy gap of the SWNTs the energy levels form a so-called type-I heterojunction where energy transfer is possible, however not necessarily fast and efficient.

Fluorescence measurements show a significant drop of intensity comparing pure polymer and conjugated SWNT. However the decay components of solutions show no significant difference. Therefor we assume that the fluorescence of the conjugated solution is dominated by the remaining free polymer or their fractions less tightly wrapped around SWNTs. On the other hand solid films show significant quenching of the polymer fluorescence due to the SWNTs and lead to the conclusion of efficient energy transfer. The quenching is faster than the time resolution of about 3 ps of our measurements.

In conclusion the energy transfer is very fast despite very weak overlap of absorption and fluorescence spectra. To get more information about the transfer mechanism different contents of PFO-BPy were added to the conjugated SWNTs and the decay times and anisotropy of the polymer fluorescence both in solutions and thin films were investigated. Furthermore transient absorption, electrical and carrier drift measurements address ultrafast dynamics of carrier mobility in conjugated SWNTs.

This work has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under the Grant Agreement n° 316633.


Coupling between the order parameters in multiferroic phases of the perovskite Bi$_{1-x}$La$_x$Fe$_{0.5}$Sc$_{0.5}$O$_3$ system


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Atomic substitutions offer obvious and efficient way of modification of both crystal structure and physical properties of the “classical” multiferroic BiFeO$_3$. There compositions derived from bismuth ferrite by means of substitutions of Bi$^{3+}$ and Fe$^{3+}$ by rare earth cations and by appropriate trivalent cations, respectively, are the most studied. In such a manner, rich “temperature-composition” phase diagrams have been revealed with a variety of compositionally driven structural phase transitions. However, broad substitutions in the iron sublattice are hardly possible even in the case of cations which are similar in ionic size to octahedrally coordinated Fe$^{3+}$. It restricts the tuning capability of chemical modification in BiFeO$_3$ in relation to magnetic properties. Application of the high-pressure synthesis technique allows a considerable extension of the atomic substitution ranges in BiFeO$_3$-based systems. Series of perovskite solid solution systems with gradual substitution of Fe$^{3+}$ by Cr$^{3+}$, Co$^{3+}$, and Ga$^{3+}$ have been produced [1, 2].

The perovskite BiFe$_{0.5}$Sc$_{0.5}$O$_3$ composition, which is the equimolar solid solution of BiFeO$_3$ and BiScO$_3$ where the latter is a metastable compound, has recently been synthesized under high pressure [3]. Crystal structure of the as-prepared phase of BiFe$_{0.5}$Sc$_{0.5}$O$_3$ was shown to differ from the structures of the end members. Further chemical modification of this composition was done through substitutions of bismuth by lanthanum. As a result, the entire series of perovskite solid solutions Bi$_{1-x}$La$_x$Fe$_{0.5}$Sc$_{0.5}$O$_3$ has been formed. Crystal structures of the obtained phases and their temperature behaviour were studied using powder x-ray diffraction, neutron diffraction and transmission electron microscopy. Results of the diffraction experiments were considered in comparison with the magnetization measurements data and analysed based on a general phenomenological approach.

At room temperature, the as-prepared phase at $x \leq 0.05$ is an antipolar Pnma with the $\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$ superstructure. An incommensurately modulated structural phase with the Imma(00$\gamma$) superspace group is observed for 0.1 $\leq x \leq 0.3$, while a non-polar Pnma phase ($\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$) is stable at $x \geq 0.35$. All the obtained phases were found to combine all three types of the ferroic order parameters: elastic, dipole, and magnetic. Below $T_N \sim 220$ K, the phases exhibit the same long-range G-type of antiferromagnetic order with a weak-ferromagnetic component; however, directions of the magnetic moment in the primitive unit cells of the particular structural phases are different.

Analysis of the coupling between the dipole, magnetic, and elastic order parameters revealed that the weak ferromagnetism in both phases is mainly caused by the presence of the antiphase octahedral tilting whose axial nature directly represents the relevant part of the Dzyaloshinskii vector. Besides, it follows from the analysis that the incommensurate displacive mode in the Imma(00$\gamma$) phase is dictated by the symmetry to couple a spin-density wave. The propagation vectors of the structural modulation and the spin-density wave are interrelated as $(a,a,0)$ and $(\sqrt{2}a-a,a,2a)$, respectively (a=$\gamma$/2) [4]. The obtained results demonstrate a crucial role of the antisymmetric exchange in magnetic properties of Fe$^{3+}$-containing distorted perovskites.

This work was supported by project TUMOCS. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 645660.

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Interface exchange coupling associated with phase separation in mixed-valence oxides

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Mixed-valence oxides are compounds where phase separation plays a crucial role determining their low-temperature properties. The colossal magnetoresistive perovskites \((\text{Nd}_{\text{1-x}}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3\) \((x = 0; 0.1)\) are spontaneously phase separated at low temperatures due to a sequence of phase transformations; they represent an antiferromagnetic (AFM) matrix with embedded ferromagnetic (FM) clusters \([1]\). At low temperatures, magnetic behavior of these manganites is consistent with a cluster-glass magnetic state. When the compounds are cooled through both the Neél and the Curie temperatures in static magnetic fields, the magnetization hysteresis loops exhibit horizontal shift (Fig. 1 a). The magnetic field induced shift of the hysteresis loop defines the exchange bias (EB) effect and the coercive field are determined as

\[
H_{\text{EB}} = \frac{H_1 + H_2}{2},
\]

\[
H_{\text{C}} = \frac{H_2 - H_1}{2},
\]

respectively, where \(H_1\) and \(H_2\) are the magnetic field values corresponding to a zero magnetization. The shift of the hysteresis loop \(H_{\text{EB}}\) is absent when cooling in zero magnetic field. The EB phenomenon is evident of an interface exchange coupling between the coexisting AFM/FM magnetic phases \([2]\). The effect vanishes above the Curie temperatures \((T_c \sim 70\ \text{K} \text{ and } \sim 50\ \text{K} \text{ for } \text{Nd}_{\text{2/3}}\text{Ca}_{\text{1/3}}\text{MnO}_3 \text{ and } \text{(Nd}_{\text{0.9}}\text{Y}_{\text{0.1}})_{\text{2/3}}\text{Ca}_{\text{1/3}}\text{MnO}_3\text{, respectively}}\) with the disappearance of FM phase. Magnetic training effect also has been observed. The exchange field \(H_{\text{EB}}\) and coercive field \(H_{\text{C}}\) are found to be strongly dependent on temperature and the cooling magnetic field (Fig. 1 b). The temperature and cooling magnetic field evolution of the EB effect is closely related with the evolution of the phase segregated state of the compounds. In cooling magnetic fields \(H_{\text{cool}} > 5\ \text{kOe}\) the \(H_{\text{EB}}\) appeared to be strongly different for \(\text{Nd}_{\text{2/3}}\text{Ca}_{\text{1/3}}\text{MnO}_3\) and \((\text{Nd}_{\text{0.9}}\text{Y}_{\text{0.1}})_{\text{2/3}}\text{Ca}_{\text{1/3}}\text{MnO}_3\) compounds, which implies the different FM phase content and the FM clusters size.

The exchange bias effect can be used for detection of impurity phases in complex oxides that is generally a challenging task in Material Science.


Magnetic resonance study of EuTiO$_3$ thin film, ceramics and a polycrystal

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EuTiO$_3$ is a frequently investigated material in the last decade due to the discovery of relatively strong magnetoelectric (ME) effect below the antiferromagnetic (AFM) phase transition temperature $T_N$=5.3-5.5 K, where the dielectric permittivity decreases almost 5% on cooling below $T_N$ and increases 7% with rising magnetic field [1]. EuTiO$_3$ is an incipient ferroelectric, like SrTiO$_3$ because quantum fluctuations suppress possible ferroelectric phase transition at low temperature. However, recently, it was found that both ferroelectric and ferromagnetic order can be induced by biaxial strain in thin EuTiO$_3$ films [2]. This opens a new route for construction of novel multiferroic nanostructures with a strong ME coupling. Presently, there are numerous studies on this material in the form of ceramics, crystals and thin films grown on different substrates (see e.g. [1-4]). In particular, ceramic samples of EuTiO$_3$ were also studied by electron paramagnetic resonance [3], but only in the paramagnetic phase down to about 50 K. To the best of our knowledge, this material was never studied using conventional magnetic resonance technique in the magnetically ordered phase. Since many principal questions related to intrinsic properties of EuTiO$_3$ are non-completely resolved yet and magnetic resonance, in general, provides important information on microscopic level, such as spin-spin interactions and their thermal fluctuations, magnetic structure, magnetic anisotropy, exchange frequencies and so on, we decided to perform a detailed magnetic resonance investigation of this material in wide temperature region from 400 K down to 3 K at microwave frequencies 9.2-9.8 and 34 GHz. The studied samples were ceramics, polycrystals and 100 nm thick epitaxial film deposited on (110) oriented DyScO$_3$ substrate. For comparison, magnetic susceptibility measurements were also done for ceramic sample at the temperatures 2-300 K.

Figure 1. Temperature dependence of the magnetic resonance spectra measured in epitaxial EuTiO$_3$ film with the magnetic field applied in film plane. a) spectra at temperatures 6, 5.6, 5.2, 4.9 and 4.55 K: with temperature decrease the spectral line shifts towards larger fields. b) spectra at 4.3, 4.05, 3.8, 3.6, 3.4, 3.2 K: with temperature decrease below the Neel temperature $T_N$ =4.5 K, the spectral line splits into several components.

The magnetic resonance spectrum in the paramagnetic phase is very broad (~290 mT) because the exchange frequency is comparable with the magnetic dipole broadening. However, the linewidth essentially narrows at approach the AFM phase transition showing distinct minimum at the Neel temperature. This indicates that the spin-spin correlations are predominantly isotropic like in the simple cubic AFM RbMnF$_3$. Below the Neel temperature the spectrum corresponds to the AFM resonance and it splits due to magnetic anisotropy. This anisotropy was in detail studied in single-crystalline film, where the spectrum is distinctly split into several components (Fig. 1). Besides, additional resonance peaks appear at the right-hand side of the spectrum. They steeply shift towards the high magnetic fields (Fig. 1). This suggests that magnetostatic or standing-spin-wave AFM modes are excited. The obtained results are discussed and compared with other published data [3-4].

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Phase formation and functional properties of lead-free ceramics

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Development of lead-free piezoelectric ceramics comprises a task stimulated by both ecological problems and demands of various industries. Moreover, the compositions with high Curie temperature \(T_C\) value \(\sim 700\) K are very perspective for applications at high temperatures. The perovskite structure lead-free compounds \((K_{0.5}Na_{0.5})NbO_3\), \((Na_{0.5}Bi_{0.5})TiO_3\), \((Bi_{0.5}Mg_{0.5})TiO_3\), and BiFeO_3 reveal high \(T_C\) values, so they may be used as basic oxides for the development of new materials for high temperature applications [1-3].

However, preparation of dense ceramics is rather difficult due to the Bi\(^{3+}\), K\(^+\) and Na\(^+\) oxides losses during sintering at high temperatures, so various additives with low melting temperatures may be useful [4, 5].

In this work, ceramic solid solutions with compositions close to the Morphotropic Phase Boundaries (MPB) in the systems \((1-y)(1-x)(Na_{0.5}Bi_{0.5})TiO_3 - x(K_{0.5}Na_{0.5})NbO_3 - BiFeO_3\) (system I) and \((1-y)(1-x)BiFeO_3 - xBaTiO_3 - yBi(Mg_{0.5}Ti_{0.5})O_3\) (system II) \((x, y < 0.25)\) were prepared by the solid-state reaction method at temperatures \(800 – 1200\)°C. To improve sintering various additives with low melting temperatures (Bi\(_2\)O\(_3\), KCl, V\(_2\)O\(_5\), etc.) were used.

To control phase formation, crystal structure, microstructure, dielectric and ferroelectric properties of ceramics, the X-ray Diffraction, Scanning Electron Microscopy, Second Harmonic Generation and Dielectric Spectroscopy methods were used.

Depending on composition, type and amount of additives, and synthesis conditions, formation of solid solutions with different relative contents of rhombohedral (pseudocubic) and/or tetragonal perovskite phases was proved. The influence of phase content, structure parameters and microstructure of ceramics in the systems I and II on Curie temperature \(T_C\) value and effects of dielectric relaxation was revealed, the possibility of the piezoelectric properties enhancement in modified ceramics discussed.

The results obtained confirmed advantages of the new functional materials development for high temperature applications using the compositions studied.

References


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Structural and high-temperature thermoelectric properties of \( \text{Ca}_{2.8-x}\text{Dy}_{0.2}\text{Bi}_x\text{Co}_4\text{O}_{9+\delta} \) prepared by sol–gel method

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Misfit-layered \( \text{Ca}_3\text{Co}_4\text{O}_{9+\delta} \) has attracted considerable attention as a thermoelectric material due to its high thermoelectric performance as well as thermal and chemical stability at high temperature in air. The layered structure consists of two alternating subsystems: a distorted \( \text{NaCl-type CaO-CoO-CaO} \) layer and a \( \text{CdI}_2 \)-type \( \text{CoO}_2 \) layer, which are stacked along the \( c \)-axis. For practical thermoelectric applications, a large dimensionless figure of merit, \( ZT=S^2T/\rho\kappa \) is necessary, where \( S \), \( \rho \), \( T \), and \( \kappa \) are the Seebeck coefficient, the electrical resistivity, the absolute temperature, and the thermal conductivity, respectively. In this study, high-textured \( \text{Ca}_{2.8-x}\text{Dy}_{0.2}\text{Bi}_x\text{Co}_4\text{O}_{9+\delta} \) ceramics with small grain sizes were fabricated by combining the sol-gel method and solid-state reaction method. Their structural and high-temperature thermoelectric properties were investigated. All of the XRD peaks were indexed with a monoclinic lattice. A very small amount of \( \text{Co}_3\text{O}_4 \) phase was detected. SEM images showed that most grains had plate-like morphology along with high-textured structure, which is indicative of high-quality polycrystals with a large crystallographic anisotropy. The \( \text{Ca}_{2.8-x}\text{Dy}_{0.2}\text{Bi}_x\text{Co}_4\text{O}_{9+\delta} \) showed a semiconducting behavior and p-type conduction. It is believed that \( \text{Ca}_{2.8-x}\text{Dy}_{0.2}\text{Bi}_x\text{Co}_4\text{O}_{9+\delta} \) ceramics may be promising thermoelectric materials for high-temperature applications.
Low Band Gap Polymer PCPDTBT/ PC$_{61}$BM Bulk Heterojunction Solar Cells Investigated by MIS-CELIV Technique

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During the last five years the performance of organic bulk heterojunction (BHJ) solar cells has been improved considerably [1, 2]. Light absorbance in BHJ, effective charge carriers’ separation and collection at the electrodes describes solar cell’s efficiency. In order to identify BHJ fabrication parameters that determine the highest power conversion efficiency it is very important to properly measure charge carriers mobility. There have been used various different techniques to measure the mobility in organic solar cells, such as time-of-flight (TOF), charge extraction by linearly increasing voltage (CELIV), photo-CELIV, injection-CELIV (i-CELIV), plasma extraction and double injection. However, certain errors may occur due to Langevin recombination and the influence of the initial distribution of the photogenerated charge carriers [3]. i-CELIV method overcomes those limitations and allows to estimate separately the mobility of the holes and electrons [3, 4]:

$$\mu = \frac{2e^2 A (j_0 - j_0^* (t/T)^{1/2})}{k_0 j_0}$$

(1)

where (insulator), $A$ is voltage slope, $e_o$ is the dielectric constant of the semiconductor, $t_0 = 1.63 t_1$, where $t_1$ is time, when current reaches $1.5 j_0$. $j_0$ is initial displacement current step, $j_0^*$ is saturated current maximum at voltage offset.

In this work i-CELIV technique was used to study low band gap polymer PCPDTBT, fullerene derivative PC$_{61}$BM separate layers and these materials BHJ combination at various blend ratios and different annealing temperatures. MIS structure (Si/SiO$_2$ (270 nm)/Organic semiconductor/Metal contact) shown in Figure 1 b) was measured using i-CELIV technique. Reverse polarity linearly increasing voltage pulse with the slope $A$ was applied to the sample. Gold contacts have been used in case of holes mobilities measurements and silver or aluminum contacts for electrons mobilities measurements. Different voltage offset was applied (Figure 1 (a) and (c)) to inject. By using Equation (1) holes and electrons mobilities were calculated. Measured results indicate that electrons and holes mobilities depend on BHJ blend ratio similar to PCDTBT and PC$_{61}$BM BHJ [4].

![Figure 1](image.png)

**Figure 1.** (a) CELIV triangle pulses with varying offset voltage on forward bias. (b) Schematic of measured samples in the case of hole-only configuration. The injected charge carriers are distributed near the interface of the semiconductor/insulator. (c) i-CELIV transients for PCPDTBT hole-only devices with different or without a voltage offset.

Modeling charge separation dynamics at the interface of donor and acceptor materials using the stochastic Schrödinger equation

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Organic solar cells offer several advantages, such as flexibility and low manufacturing cost, over their non-organic analogues. However, organic photovoltaic devices in general still have lower energy conversion efficiency than the best commercially available non-organic solar cells. In organic photovoltaic devices incoming photons mostly create bound electron and hole states - excitons. The energy conversion efficiency in organic devices greatly depends on how effective is the process of exciton dissociation into holes and electrons and their subsequent separation [1]. Usually the organic solar cells are made of electron donor and acceptor materials, thus, the charge separation process mainly occurs at their interface.

In this work we model the process of charge separation at the interface of the donor and the acceptor using the stochastic Schrödinger equation [2]. The model of this interface consists of a single donor site and a 3D lattice representing the acceptor material with external electric field applied across it (Figure 1). Each site models a molecule with two energy levels (ground state and excited state) which can be identified as HOMO and LUMO levels in organic molecules. In this work we assume that the exciton was created in the bulk of the donor material and managed to arrive at the donor - acceptor interface. We also make the assumption that during the charge separation process the hole remains on the donor site.

The initial state of the electron in our calculations is localized on the donor site, thus, representing a Frenkel exciton state. Using the stochastic Schrödinger equation we propagate the system state and calculate the charge separation distance between the electron and the hole in the direction of the external electric field and also the absolute separation distance. We fit the obtained results to experimental data and extract microscopic parameters of the system which cannot be measured experimentally.

Figure 1 Donor - acceptor interface model. Big ball denotes the donor site where the hole resides; smaller balls denote the acceptor sites where the electron moves; grey plane is the donor - acceptor interface; $\vec{F}$ denotes the direction of the external electric field; $J_{\text{DA}}$ denotes the interaction energy between the donor site and the nearest acceptor site; $J_{\text{A}}$ denotes the nearest neighbor interaction energy between acceptor sites.


Light-induced charge carrier transients in black-Si

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Optimization of plasma or chemical etching conditions of black-Si (b-Si) production opens possibilities to control surface area, aspect ratio of nanoneedles, hydrophobicity of the surface, change of the surface recombination rate and antireflection properties all very useful parameters for solar cell and sensor applications [1, 2]. High > 18 % black Si solar cell efficiency was achieved even without antireflection coating [3].

Reflectivity changes of black-Si (b-Si) upon optical excitation were measured by pump-probe technique using picosecond laser pulses at 532 (pump) and 1064 nm (probe) wavelengths. The specular reflection from random pattern of b-Si nano-needles was dominated by photoexcited free-carrier contribution to the reflectivity. Reflectivity was rather low, with characteristic minimum at 700-1000 nm, and being in 10⁻² - 10⁻¹ range. The SEM images of b-Si and experimentally measured decays are shown in Figure 1; the inset describes the used experimental setup layout.

Experimental kinetics of reflectivity was found consistent with the surface structural and chemical analysis data. Surface recombination velocity was estimated to be as low as ~10 cm/s. Temperature measurements provided faster decays and stronger DR signals due to increase of Auger recombination rate, caused by increase of Si absorption coefficient. Modeling of b-Si reflectivity signal versus probe wavelength and needle length was elaborated. Photo-induced reflectivity is shown to change sign depending on the height of b-Si needles. These large variations of reflectivity by needle length can be used for designing sensors and engineer light harvesting.

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Oxygen mobility in microwave sintered praseodymium nickelates-cobaltites and their nanocomposites with Y-doped ceria

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PrNi$_{1-x}$Co$_x$O$_{3-\delta}$ composites are promising as IT SOFC cathodes provided their sintering conditions are optimized [1]. In this work effect of microwave sintering (MS) on properties of such materials is studied.

Perovskite (P) PrNi$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ (PNC) and fluorite (F) Ce$_{0.9}$Y$_{0.1}$O$_2$ (YDC) oxides were synthesized by Pechini route. PNC-YDC composites were prepared by ultrasonic dispersion. Pellets were sintered at 870 – 1100 °C using specially designed microwave set-up. Samples were characterized by XRD and TEM with EDX. Oxygen mobility was estimated by O$_2$ TPD and oxygen isotope heteroexchange with $^{18}$O$_2$ and C$^{18}$O$_2$.

MS provides dense materials (porosity < 10 %) even at the lowest temperatures. PNC is single-phase P. Composites are comprised of P+F phases with Pr$_6$O$_{11}$ admixture, strong elements redistribution between P and F domains occurs (Figure 1). The total amount of oxygen desorbed is up to 20 monolayers for PNC and 70 monolayers for PNC–YDC, being ~ 1.5 times higher as compared to conventionally sintered (CS) samples. This is due to a higher disordering of P and F domains as well as their boundaries. The oxygen isotope exchange is characterized by R$^2$ mechanism with the surface exchange constant $k_{ex}$ ~ $10^{-6}$ cm/s and the oxygen tracer diffusion coefficient $D_O$ ~ $10^{-8}$ cm$^2$/s at 700 °C (Table 1), being close to CS samples made at higher temperatures [1].

Hence, MS at lower temperatures provides even better functional characteristics of PNC-YDC nanocomposite cathodes.

Table 1. Surface exchange constants, oxygen tracer diffusion coefficients at 600 K and their activation energies.

<table>
<thead>
<tr>
<th>Sample, $T_{sint}$</th>
<th>$k_{ex}$, cm/s</th>
<th>$E_{act}$, kJ/mol</th>
<th>$D_O$, cm$^2$/s</th>
<th>$E_{act}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNC, 1000 °C</td>
<td>1.2 $10^{-7}$</td>
<td>80</td>
<td>8.6 $10^{-12}$</td>
<td>70</td>
</tr>
<tr>
<td>PNC – YDC, 930 °C</td>
<td>2.4 $10^{-7}$</td>
<td>65</td>
<td>6.0 $10^{-12}$</td>
<td>65</td>
</tr>
</tbody>
</table>

Anomalous magnetoelectric effect in three-layer Ni-PZT-Pt multiferroic composites.

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The structures on base of zirconate titanate (PZT) is one of the popular multiferroic composites for technical application where use a magnetoelectric conversation [1]. PZT often used as a piezoelectric component because it exhibits good dielectric and piezoelectric properties.

In the present paper the direct magnetoelectric effect was studied experimentally in samples of zirconate titanate with their two sides metallized with thin nickel film and platinum film (Ni-GaAs-Pt). The ME effect was studied by measuring a voltage $U$ generating across a sample under both alternating and bias magnetic fields. Generally, the ME effect is characterized by a ME voltage coefficient $\alpha = \frac{dU}{b \cdot dH}$, where $dU$ is an alternating voltage arising between electrodes of a sample, $b$ is a thickness of a sample, $dH$ is an alternating magnetic field intensity.

A resonance significantly increasing of the ME-coefficient was observed at a frequency 84 kHz in zero bias magnetic fields. The maximum of output voltage signal under resonance is 24.5 mV in 20 Oe alternating and zero bias magnetic fields. This corresponds to the giant magnetoelectric effect at room temperature for such types of systems [2]. The dependence of the magnetoelectric coefficient on the bias magnetization field in a Ni-GaAs-Pt structure has an anomalous shape that is uncharacteristic of known composite magnetoelectric materials based on ceramic piezoelectrics. This anomaly may be associated with nature of coupling of Ni and Pt films to the zirconate titanate substrate, inhomogeneity of the films and their properties. This type of effect was detected in work [3] in similar Ni-GaAs-Au structures. The dependence of ME-coefficient from thickness of Ni film also was observed. For this experiment, samples were manufactured with the thickness of the Ni film l=0.4, 0.8, 1.2 and 1.8 micron.

Spectroscopic ellipsometry of ferroelectric nanofilms

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A good potential of wide bandgap perovskite-type ferroelectrics for applications in thin-film photonic and optoelectronic devices stimulates studies of optical properties of ferroelectric thin films. Here we report on the ellipsometric study of optical constants in epitaxial ferroelectric (FE) nanofilms of KTaO₃, KNbO₃, and NaNbO₃ grown on SrTiO₃ (001) substrates. Spectroscopic ellipsometry allowed us to investigate films with a thickness of 10–30 unit cells only. Determining optical constants in such ultrathin films of wide bandgap insulators is a challenge. However, use of spectral range extended to vacuum ultraviolet enabled good accuracy which was significantly improved owing to high optical homogeneity of crystallographically perfect epitaxial films with atomically smooth surfaces. Room temperature ellipsometric data were collected using a variable-angle rotating-analyzer spectroscopic ellipsometer over a wide spectral range from 0.74 to 9.0 eV at two angles of incidence (Θ = 65°, 70°). Spectra of ellipsometric angles (Δ, ψ) were acquired with the accuracy sufficient for reliable extraction of optical constants. The experimental ellipsometric spectra were fitted using a model consisting of a stack of a semi-infinite substrate, a thin film, a surface roughness layer, and ambient air. The parameterization of the initial dielectric functions of the films was based on the multi-oscillator model. The optical properties of the surface roughness layer were represented by a Bruggeman effective medium approximation. The measurements and data processing ensured accurate and reliable spectra of optical constants and absorption coefficient. Analysis of absorption spectra revealed that positions of the main absorption maxima and absorption edges in the films differ significantly from those in single-crystal samples. Compared to crystals, the blue-shifts are observed in the KTaO₃ film, and the red-shifts are detected in the NaNbO₃ and KNbO₃ films. Also the temperature evolution of the index of refraction in the transparency range in the films is found to differ from the behavior in the crystals. The results are discussed in terms of epitaxially induced lattice strain and strain-enhanced ferroelectric polarization in the films. The possibilities and limitations of ellipsometric analysis applied to ferroelectric nanofilms are summarized.
Neutron spectroscopy of functional materials with nano-scale inhomogeneities.

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The understanding of collective behavior in systems composed of nano-scale components at the edge between order and disorder is a problem common to a wide range of modern materials, reaching from strongly correlated electron systems via superionic conductors to relaxor ferroelectrics.

Although scattering techniques using X-rays and neutrons cannot investigate individual objects on the nanometer-scale, they provide a highly efficient tool to establish energy spectra and correlation functions in space and time characterizing the collective behavior of ensembles of nano-objects. Any departure from perfect periodicity broadens the observed Bragg peaks and gives rise to diffuse signal between them in function of the scale length of the perturbation. Similarly, disorder leads not only to broadening of phonon and magnon lines, but perturbations of crystal periodicity and the presence of vacant potential energy minima may lead to spectacular effects like the "waterfall" phonon dispersion anomaly observed e.g. in relaxor ferroelectrics.

The progress in neutron instrumentation brings more and more adequate tools to investigate such systems by collecting scattering data over large areas in the momentum and energy space, which can be confronted with results of realistic model calculations as a function of external parameters, temperature in particular.

In addition to ab-initio based molecular dynamics, which permits to reproduce the observed data by models containing known ingredients, it is important to look for phenomenological concepts permitting to understand the qualitative behavior of inhomogeneous systems and to discern its similarities across different materials classes.

In this contribution we will present a review of recent activities on the ILL time-of-flight and triple-axis spectrometers addressing systems of technological interest and exhibiting nano-scale inhomogeneities.
Structural, optical and electrical properties of ZnO:Ir thin films deposited by reactive magnetron co-sputtering

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One of the obstacles to further developments of transparent electronics based on transparent conductive oxide (TCO) thin films is lack of p-type conductors. Polycrystalline spinel ZnIr$_2$O$_4$ thin films with appropriate acceptor defects are shown as p-type conductors by experimental and theoretical studies [1,2]. Light ZnO doping with Ir has been studied only with first principles DFT calculation [3] without any experimental investigation. This study investigates properties of ZnO:Ir thin films deposited by reactive magnetron co-sputtering and how iridium incorporates in this system in these circumstances.

ZnO:Ir thin films were deposited by reactive magnetron co-sputtering from a metallic Zn and Ir targets in an Ar+O$_2$ atmosphere (Fig. 1a). Working pressure was kept constant at 10 mTorr (Q(Ar) = 20 sccm, Q(O$_2$) = 10 sccm) by gate valve for all deposition processes. Zn target was sputtered in constant 200 W (DC) mode, but Ir in low power (from 6 to 25 W) and low frequency (100 Hz) pulse mode with additional grid above the target in the order to decrease the sputtering and deposition rate of Ir. A set of samples was deposited at different Ir target (cathode) powers to vary the Ir concentration in the films (Fig. 1b). Thin films were deposited on different type of substrates (glass, Ti, Si) so that they would be suitable for different type of measurements.

Composition and structural, optical and electrical properties of the ZnO:Ir thin films were studied by XRF, XRD, SEM, Raman, FTIR techniques, as well as Hall effect measurements and two beam optical spectrophotometry.

Composition study of the thin films showed that reactive magnetron co-sputtering is suitable technique to dope thin films very accurately. XRD measurements showed that light doped ZnO thin films with Ir are oriented in the c-axis direction. Lattice constant $c$ as well as strain and stress are increasing with iridium concentration. However, the grain size is not changing significantly. Thin films are not conducting until iridium concentration reaches approximately 10 at. %. Absorption in the visible range increases significantly with iridium concentration and it seems that thin films contain two optical band gaps.


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Luminescence and photo-thermally stimulated defects creation processes in PbWO$_4$:Bi$^{3+}$ crystals

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Single crystals of lead tungstate (PbWO$_4$) is a well-known scintillation material used, e.g., in the electromagnetic calorimeter at the Large Hadron Collider, where the Higgs boson has recently been discovered. PbWO$_4$ crystals were also chosen for several other projects, e.g., for ALICE project at CERN and for electromagnetic calorimeter of the PANDA detector at the future Facility for Antiproton and Ion Research in Darmstadt, Germany, where hadron physics in antiproton annihilation processes will be investigated. The significant improvement and optimization of the production technology and codoping with trivalent rare-earth ions (La$^{3+}$, Y$^{3+}$) allowed to considerably improve scintillation characteristics of PbWO$_4$ crystals.

In recent years, some Bi$^{3+}$-doped compounds were found to have rather attractive characteristics suitable for their possible applications in scintillation detectors. However, the luminescence of Bi$^{3+}$-doped PbWO$_4$ crystals was not studied. The present work is devoted to the investigation of (i) the photoluminescence characteristics of PbWO$_4$:Bi crystals by the time-resolved spectroscopy methods in the 4.2-300 K temperature range and (ii) the photo-thermally stimulated defects creation processes under selective irradiation of the crystals at different temperatures $T_{irr}$ (20-200 K) with different energies $E_{irr}$ (3-5 eV) and irradiation durations $t_{irr}$ (1-60 min). Optically created electron and hole centers are detected by the thermally stimulated luminescence (TSL) and electron spin resonance (ESR) methods. From the dependences of the TSL intensity on $E_{irr}$, $T_{irr}$ and $t_{irr}$, creation spectra of the corresponding electron or hole centers, activation energies of their creation, and dose dependences, respectively, are obtained. Thermal stability parameters are determined for the corresponding electron and hole traps.

In the luminescence spectrum of PbWO$_4$:Bi, besides the known blue, green - G(I) and G(II), and ultraviolet emissions (see, e.g., [1, 2]), the Bi$^{3+}$-related emission is observed at 2.1 eV. Its lowest-energy excitation band is located at 3.55 eV. At 4.2 K, the decay curve of this emission consists of two exponential components with the decay times of 30 µs and 165 µs. The decay time of the slower component decreases with the increasing temperature starting at least from 4.2 K. A relatively large width (FWHM=0.75 eV) and Stokes shift (S=1.45 eV) of the 2.1 eV emission band as well as temperature dependence of its decay kinetics indicate that the 2.1 eV emission is of exciton origin. We ascribe this emission to the radiative decay of an exciton localized around a Bi$^{3+}$ ion. The phenomenological model is proposed for description of the exciton states dynamics, and the parameters of the triplet exciton state (the separation between the metastable and emitting levels) are determined.

The mechanisms of photo-thermally stimulated creation of various electron and hole centers in PbWO$_4$:Bi and the origin of these centers are investigated. It is suggested that under 3.55 eV excitation, the thermally stimulated electron transfer from the valence band to the excited Bi$^{3+}$ center takes place during the excited state lifetime of this center, resulting in the creation of a stable electron Bi$^{2+}$ center (see, e.g., [2]). The mobile hole released in this process can migrate along the valence band and be trapped at the regular oxygen ion O$^{2-}$ located close to some crystal lattice defect, e.g., the Bi$^{3+}$ ion associated with a lead vacancy, producing the O(I)-type hole center. The hole centers of this type have been observed by EPR in PbWO$_4$:Mo, La(Y) crystals [3]. Recombination of electrons and holes close to the Bi$^{3+}$ ions results in the appearance of the luminescence of excitons localized around the Bi$^{3+}$ ions. As a result of these investigations, the location of Bi$^{3+}$ levels with respect to the valence band and the conduction band of PbWO$_4$ is also defined.

The concentration of single-vacancy-related electron and hole centers in PbWO$_4$:Bi crystals is found to be small. The tunneling green G(II) emission, accompanying the recombination of these centers, is strongly suppressed. These data indicate that similar to the PbWO$_4$: crystals doped with trivalent rare-earth ions, the doping of PbWO$_4$:Bi with trivalent Bi$^{3+}$ ions also results in the considerable suppression of the number of single (non-compensated) oxygen and lead vacancies as the traps for electrons and holes, respectively.

’Surface-confined self-assembled Janus tectons: a versatile platform for noncovalent HOPG and/or other substrates functionalization’

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Beyond the well-mastered two-dimensional (2D) supramolecular self-assembly at surfaces by physisorption of flat molecular building-blocks (tectons)1, the next challenge consists in providing a universal strategy exploiting the room above the substrate, i.e. the direction perpendicular to the surface, in order to add a functionality which mustn’t disturb the 2D self-assembly and be preserved from possibly-detrimental substrate influences. This issue is particularly relevant for sp2-hybridized carbon based supports where the tecton physisorption leads to a noncovalent functionalization of the surface, offering the possibility of attaching functional groups without disturbing the electronic substrate properties2, opening opportunities for example in molecular electronics and sensors3, molecular spintronics4 or fast DNA sequencing in the field of bioinformatics5. In this context, we reported the first example of a general strategy for generating physisorbed monolayers on flat sp2-carbon based substrates, exposing a wide range of external interfacial composition6a,b. More precisely, two family of tectons have been recently synthesized in view of forming physisorbed adlayers exposing either a wide variety of small terminal chemical group (-CN, -CO2Me, -CHO, -CO2H, -Br, -PhCN) or functional moiety, in this first attempt diamino triazine, terpyridine, and ferrocene units: this approach is validated through the supramolecular self-assembly study by scanning tunneling microscopy (STM) at the liquid/HOPG and graphene interface and molecular mechanics modeling6c. Moreover, here we will present as well some unpublished results related to i) the long-Range and 3D Linear Noncovalent Functionalization of Fullerene Derivatives7, ii) the Extension of the Janus Concept to Other Substrates by modifying the chemical strategy involved8 (replacing Van der Waals interactions by hydrogen bondings) and iii) the use of such a platform to self-assemble in the future nanoparticules in a controlled manner.

Ballistic Ratchet effect on patterned graphene

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In the present work, we develop a theoretic analysis, propaedeutic to the optimization of the photogalvanic current induced by a high frequency radiation in monolayer graphene [1-3], patterned with asymmetric nano-defects. Specifically, the latter are given by clusters of atomic vacancies of triangular shape. We propose a completely ballistic picture of the Ratchet effect, where the main contribution to the collective and cumulative charge displacement is due to ballistic scattering. Numerical simulations are performed in the framework of the Scattering Matrix (SM) approach, described elsewhere [4], which is conceptually analogous to the non-linear Green’s function formalism (NEGF). The main difference is that it provides a convenient description of the graphene lattice in terms of propagating and evanescent modes. Triangular holes are analyzed as paired defects in monolayer graphene, as depicted in figure 1(a). The shape of the holes affects the charge scattering and changes the charge distribution induced by an external applied voltage. The latter is given by a plane-wave impinging on the plane of graphene in the normal direction: the electric field $E$ is assumed as polarized along the y-axis, in order to promote charge displacement in this direction. The resulting voltage can varied continuously in the interval from $-\Delta V$ to $\Delta V$, with $\Delta V=|E_y| \cdot L$ and the resulting charge distribution can mediated in this interval, in order to reproduce an average charge distribution over a period $2\pi/\omega$ of the electromagnetic excitation:

$$Q = \int_{\mu_c + \Delta V}^{\mu_c} \sum_{j=1-N^V} |\psi_i|^2$$  \hspace{1cm} (1)

In the present framework, the lateral metal contacts are replaced by Dirichlet conditions for the electron wavefunctions. More rigorously, absorbing boundaries, mediated by the metal-graphene discontinuity, could be assumed, but this is largely beyond the purpose of the present work. Figure 1(b) shows an example of simulated distribution $|\psi|^2$ - namely charge per unit area and per unit energy, after Landauer normalization, at energy $\mu_c$.

Figure 1. a) Triangular vacancy defect in paired configuration. (b) Top view of surface charge density $Q$. Here, $\mu_c=0.22$ eV, with $d=3$ nm, $a=7$ nm, $h=2$ nm, $s=9$ nm, $t=13$ nm.

FIB lithography of chiral plasmonic structures of various point symmetry

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Focused ion beam (FIB) lithography is a powerful tool for fabricating optical submicron- and nano-structures [1-3]. This technology allows fabrication of 3D chiral nanostructures: single elements and periodic arrays. Chiral metamaterials – artificial subwavelength structures with broken mirror symmetry – demonstrate extreme optical activity and circular dichroism [2,4].

We report on FIB fabrication of chiral plasmonic structures of various rotational point symmetries (C3, C4, and C6) and the dependence of their linear optical properties on the order of the point symmetry, which is also very important for the nonlinear optical properties of these structures [4,5].

The specimen was prepared by thermal evaporation of silver on glass substrates, the silver film thickness obtained was 260 nm. The dual beam microscope software allows performing FIB milling with the digital templates – stream files. These templates consist of x,y coordinates and a dwell-time parameter responsible for the milling depth of each point. The total round shape of the patterned area was chosen to fit the optical ellipsometer characterization beam area of 300 μm². Using the FIB lithography techniques we have patterned larger areas with periodic arrays with controlled period, unit cell shape and dimensions. Every stream file was formed by unit cells of the 3-, 4- and 6-fold point symmetry providing the structure shapes shown in Fig. 1(a,b,c). The observed deviations of the unit cell shape are due to the silver film grain structured.

On the basis of the experimental data we have concluded that the C4 symmetric structures possess the largest optical activity and ellipticity that reach extreme values at the wavelength of 440 nm as shown in Fig. 1(d). The other two fabricated arrays of C3 and C6 symmetric chiral shapes have proved to possess lower optical chirality.

The work was supported by the Russian Science Foundation (project 14-12-00416). We are grateful to A.L. Vasiliev for the equipment provided.

Laser Heating of the $Y_{1-x}Dy_xPO_4$ Nanocrystals for Hyperthermia

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We propose a novel material, the solid solution $Y_{1-x}Dy_xPO_4$ ($x = 0.01 - 1$) with tetragonal xenotime-type structure, which may be suitable for laser-induced local heating of cancer tumors for hyperthermia. We prepared the material by microwave-hydrothermal treatment and heated a powder consisted of the nanoparticles by focused quasi-CW laser irradiation at different wavelengths in the near IR spectral range fitting the transparency window of biological tissues. The local temperature on the surface of the powder in the place of irradiation increases linearly with increasing laser power and increasing the Dy$^{3+}$ concentration (Fig. 1a). At the same time the efficiency of local heating $\Phi = \Delta T / (P f)$ ($\Delta T$ is a local temperature increase, $f$ is an oscillator strength of absorption transition, and $P$ is the quantity of laser power) is proportional to the energy of the initially excited electronic level (Table 1). The proposed method allows for high rates of heating and cooling (Fig. 1b). The laser power used for heating was rather low, tens of milliwatts that together with short heating time to required temperature may result in extremely low doses of laser irradiation for heating.

![Figure 1](image-url) 

(a) 

(b)

Figure 1 (a) The local temperature increase $\Delta T$ of the $Y_{1-x}Dy_xPO_4$ powder taken from the hottest pixel of the image of the powder surface on the IR camera after laser irradiation versus laser power. Excitation was done into the $^6F_{5/2}$ (811 nm) and $^6F_{7/2}$ (914 nm) levels of Dy$^{3+}$ in the scanning microscope spot mode during one minute. We excited the Dy$^{3+}$ ion by pulsed tunable femtosecond laser Coherent Chameleon Ultra II with 140 fs pulse duration, repetition frequency 80 MHz, and maximal average power up to 140 mW.

(b) The local temperature kinetics of the hottest area of the DyPO$_4$ nanocrystals powder (0.425 x 0.425 mm) taken from the hottest pixel of the image on the IR camera of the powder surface under laser irradiation in the scanning microscope spot mode with the average power of 30 mW at different excitation wavelengths excited directly into the $^6F_{5/2}, ^6F_{7/2}$, or $^6F_{3/2}$ level, and between the $^6F_{5/2}$ and $^6F_{7/2}$ levels, from top to bottom 811, 914, 760, and 850 nm. The laser switched, on and off, every second.

Table 1. The heating efficiency $\Phi = \Delta T / (P f)$ of the $Y_{1-x}Dy_xPO_4$ nanocrystals depending on the number ($N$) of multiphonon transitions with $p \leq 3$ in the cascade nonradiative relaxation process ($h\omega_{\text{eff.}} \approx 1000$ cm$^{-1}$).

<table>
<thead>
<tr>
<th>Multiphonon transition</th>
<th>$\lambda_{\text{exc}}$, nm</th>
<th>$x$, %</th>
<th>$\Delta T$, K</th>
<th>$P$, mW</th>
<th>$f$, $10^6$</th>
<th>$\Phi = \Delta T/(P f)$, [K/mW]</th>
<th>$\Delta E$, cm$^{-1}$</th>
<th>$p$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6F_{3/2} \rightarrow ^6F_{5/2}$</td>
<td>760</td>
<td>47.5</td>
<td>23</td>
<td>100</td>
<td>0.32</td>
<td>0.72</td>
<td>1.22</td>
<td>816</td>
<td>1</td>
</tr>
<tr>
<td>$^6F_{5/2} \rightarrow ^6F_{7/2}$</td>
<td>811</td>
<td>47.5</td>
<td>52</td>
<td>100</td>
<td>1.35</td>
<td>0.39</td>
<td>0.54</td>
<td>1232</td>
<td>2</td>
</tr>
<tr>
<td>$^6F_{7/2} \rightarrow ^6H_{3/2}$</td>
<td>914</td>
<td>47.5</td>
<td>57</td>
<td>100</td>
<td>3.3</td>
<td>0.17</td>
<td>0.22</td>
<td>713</td>
<td>1</td>
</tr>
</tbody>
</table>

Peculiarities of the incommensurate phase in the TlInS$_2$ ferroelectric under X-ray irradiation

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The TlInS$_2$ crystals attract attention due to the possibilities their using as functional optoelectronics materials. They are characterized by the existence of a sequence of phase transitions (PT) with a creation of incommensurate (ICP) and commensurate (CP) phase in temperature range T=190–240 K. Furthermore, these crystals are characterized by a large density of localized states near the Fermi level ($10^{17}$-$10^{18}$ cm$^{-3}$), indicating about high defect concentration of different types. The defect system affects on formation and properties of ICP significantly through modulation wave pinning on defects. The state of the defect system can be changed by irradiating the crystals of electrons, γ and X-ray photons that is manifested in a changing of a shape of permittivity and conductivity temperature dependences [1]. However, there is no information about structural characteristics of ICP and CP in irradiated samples in these experiments. Therefore, in the present study the parameters of ICP and CP (modulation vector, the temperature range of ICP existence, the relative volume fraction of ICP) were determined by X-ray four-circle diffraction in X-rays irradiated TlInS$_2$ crystals of polytypes $c$ and $2c$. The samples were sequentially irradiated with polychromatic radiation of BGV-12 Pd tube; absorbed doses were 80 Gy and 240 Gy.

In present work it was established that during the cooling in irradiated samples of polytype $c$ the beginning of the active formation of ICP correspond to the temperature T≈220K, and the wave vector of ICP is the same as in unirradiated samples $q(\mu 0.04, 0, \pm 0.25)$. In Fig. 1 the typical 2D intensity distribution of such satellites taken around the "forbidden" Bragg point (4,0,5) is presented. Fig. 2 shows the ratio of the satellite $q(-0.04, 0, +0.25)$ intensity to the intensity of (4,0,5) reflection $\gamma=I_{sat}/I_{(405)}$. This parameter defines the volume fraction of ICP in the sample. As can be seen, the higher the absorbed dose, the less the amount of ICP in the temperature range T=197 K-220 K, where occurs the heat generation of ICP. Also, we observed at the first time the formation of modulated structure under the irradiation dose of D = 240 Gy at room temperature (circles in Fig. 2). It is important to note that an annealing the samples at T=430 K during 10 hours totally destroys this structure (triangles). Consequently, the generation of radiation defects is accompanied by appearance of the modulation wave, which might be not due to displacements of atoms, but due to periodic defect distribution in the anion sublattice of sulfur. Regarding polytype $2c$, the satellites of ICP were not observed either in the irradiated or non-irradiated samples. The reasons of this effect are discussing.


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Layered double hydroxides (LDHs) are a class of synthetic nanostructured anionic exchangers, which can be synthesized in a relatively inexpensive and potentially recyclable manner. Typically, they have the general formula \([\text{M}^{2+}_{1-x}\text{M}^{3+}_x\text{(OH)}_2]^x\text{A}^{n-}\cdot m\text{H}_2\text{O}\), where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) are di- and trivalent cations, respectively, and \(\text{A}^{n-}\) is an anion. Combining different cations and anions through different synthetic routes, a large number of tailored LDH compositions with desirable physical and chemical properties can be obtained.

The positively-charged layers of LDHs are relatively weakly bound to charge-balancing anions in the interlayer region. This weak interlayer bonding allows them to expand and intercalate, for example, different functional organic molecules, which makes them ideal inorganic-organic host-guest hybrid materials with applications in catalysis, pharmaceuticals, photochemistry, electrochemistry and functional polymers.

The synthesis of Zn(2)-Al LDH-NO₃, an intermediate material for the intercalation of different functional molecules used in a wide range of applications [1,2], was investigated considering the time, temperature and pH of the co-precipitation and/or hydrothermal treatment steps involved in the synthesis. By examining the crystallite size (powder X-ray diffraction), morphology (atomic force microscopy and scanning transmission electron microscopy), hydrodynamic radius (dynamic light scattering), colloidal stability (zeta potential), molecular structure (periodic DFT calculations) and chemical species in solution (hydrogeochemical calculations combined with high performance liquid chromatography), it was possible to understand the crystallization and dissolution processes involved in the mechanisms of crystallite and particle growth (Figure 1) and verify a growth pattern. In addition, the hydrogeochemical computational tool rendered insights on the speciation of different metal cations in solution. Therefore, this technique can be a promising solution to model and optimize the synthesis of LDH-based materials for industrial applications.

Figure 1. General tendencies obtained and approach used in this work.

Macro- and nanoporous anodized aluminium

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Properties of nanomaterials often differ from ones of macrosized materials, and many of them have to be investigated. As one of example is formation of nanoporous anodic metal oxides. An oxide film can be grown up on certain metals – sometimes so-called valve metals, e.g. aluminum, titanium, hafnium niobium, tantalum, tungsten, vanadium, and zirconium – by an electrochemical process called anodization. For each of these metals there are conditions established enable to promote the formation of thin, dense, barrier or porous oxide having uniform thickness at whole surface. Among valve metals aluminum is unique because of its ability to form in a thin barrier oxide, as well as to form in certain acidic electrolytes a thick oxide films, containing a high density of microscopic pores. This coating has diverse and important applications including architectural finishes, prevention of corrosion of automotive and aerospace structures, and electrical insulation. The best known porous anodic oxide, anodic aluminium oxide (AAO), was first reported 50 years ago and is now commercially available [1 - 3] because its pores can be used as template for preparing various nanoparticles, nanowires and nanotubes. Porous oxide grows in acid electrolytes in which oxide simultaneously can deposits and partially dissolves. The most widely used bath contains dilute sulfuric acid, typically about 1 molar or 10 weight percent concentration. Other baths used for particular applications contain oxalic acid or phosphoric acid. It has been widely accepted mechanism that the formation of pores in anodized metal oxides is based on two continuous processes, one is oxide dissolution at the electrolyte/oxide interface and the other is oxidation of metal at the oxide/metal interface. This work presents a description of the research on fabrication, application and understanding the formation mechanism of anodic metal oxides (Fig.1).

Fig.1.a- SEM images of nanoporous AAO coatings from sulfuric (inset) and oxalic acids; b- nanoindentation tests of AAO produced from oxalic acid (SEM images after nanoindentation -inset); c- SEM images in top view (upper row) and cross-sectional view (middle row) of AAO and 1 μL water droplets (lower row) on AAO formed after 30 min of anodizing in 5 wt % phosphoric acid.

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Effect of ion, electron beam and ultrasound treatments on the structure and mechanical properties of steel 12Cr1MoV

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The vast majority of products and parts of machines in operation are affected by variable loads that can cause their fatigue failure. In this regard, one of the most actual problems in engineering is to develop methods to increase the fatigue life of materials. Increasing functional properties by hardening a surface layer brings to a simultaneous reduction in fatigue characteristics. This occurs as a result of surface embrittlement, and is a danger of early fatigue crack initiation. Optimization of coating deposition mode allows improving as fatigue properties so and mechanical ones of structural products that currently is an urgent practical problem. Ion treatment has long been used to improve the fatigue properties by modifying a surface layer to a depth of a few micrometers. In ISPMS SB RAS a processing mode has been developed, which allows to modify the structure of a surface layer of the material by the effect of metal ion beam to a depth of over 100 µm. This effect is expressed in the surface heating of steel during the treatment and forming the gradient layered structure. Heat-resistant steel 12Cr1MoV has been used for developing modes and study the effect of the ion beam treatment. The choice of the steel for ion modification was caused by the fact that it is able to keep its mechanical properties obtained after standard heat treatment at high temperature. This property is extremely important when using ion-beam treatment heating the surface of a specimen to high temperatures. It has been revealed that as a result of ion-beam treatment of steel specimens 12Cr1MoV by zirconium beam the structure modification occurs over the entire cross-section. Gradient layered structure being characterized by a lower microhardness of the surface layer to a depth of 130 µm and an increase in the mechanical properties of the core has formed in the material. It is fixed an increase in the tensile strength by 15%. It is shown that under the fatigue tests, modification of the structure leads to prevent the growth of localized plastic deformation at the origin and propagation of the main fatigue crack, resulting in increasing the fatigue life by 2–3 times.

To compare the effect of different type of treatment on steel 12Cr1MoV an electron-beam treatment (EBT) and ultrasound one (UST) have been carried out, too. The main difference of electron-beam treatment from the ion-beam one is that the surface layer is not subjected to the alloying by other chemical elements. Here, the effect of the treatment is fulfilled due to thermal heating during the process that leads to an increase in fatigue life by 30%.

The advantage of UST is to increase the strength of the surface layer, formation of compressive stress and the possibility of prior use of another type heat treatment. With the additional use of tempering steel 12Cr1MoV loses heat resistance, getting high mechanical properties. EBT effect is related to the thermal influence on the steel surface which levelled mechanical properties improved by tempering to naught. For this case a hardening is useless. UST leads to modification of the surface layer, while keeping the mechanical properties improved by tempering.

Thus, the possibility of hardening and UST combination is the best way to improve mechanical properties, combining the increase in the core properties and the surface layer strengthening. It is found that ultrasonic treatment results in improving the fatigue life by 40%. After tempering to enhance the mechanical properties of steel 12Cr1MoV its fatigue life increases by 14 times, and after the subsequent UST – by 40 times.

It is revealed that the thermal effect combined with the possibility of forming a surface modified layer, as for the ion-beam treatment and tempering with following UST significantly increase fatigue life. This is due to the specific origin of plastic deformation in a surface layer which should not only be characterized by the gradient nature of the changes in microhardness, but also delay start of microcracks.
FTIR and NMR spectroscopy of sol-gel derived calcium hydroxyapatites: correlation of experimental data and the size profiles of sub-nano spin clusters

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Materials based on calcium phosphates have found many applications in implantology, orthopedic and periodontal surgery. A special place in these areas occupies calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), further CaHA), which shows close similarity to the mineral of hard tissues (bone, enamel, dentin, etc.) and therefore has high biocompatibility with them [1]. The functional properties of phosphates strongly depend on details of their structure at the molecular/atomic level.

FTIR and NMR spectroscopy techniques provide the unique information on the local short-range (nano- and mezo-) scale effects. Therefore these methods are most perspective to study structure and dynamical changes in the above mentioned systems [2, 3]. These techniques have been applied in the present work studying very fine structural details, viz., the characteristic size profiles of sub-nano ³¹P–¹Hₚ spin clusters.

For the preparation of CaHA having different morphological features the sol-gel synthesis routes using four complexing agents (glycerol (I), ethylene glycol (II), tartaric acid (III), EDTA (IV)) were selected. The steps and conditions are detailed in Ref. 2. The synthesis products were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX).

The size profiles of sub-nano ³¹P–¹Hₚ spin clusters in the synthesized materials have been obtained processing ¹H →³¹P CP kinetic curves for static (no magic angle spinning) samples and following the Fourier transform formalism developed in Ref. 2. The FTIR bands have been attributed correlating NMR and FTIR data in the series of CaHAs (Figure 1).

Since the static CP NMR experiments are long-lasting and thus are hardly applied in technological routes, the obtained correlation allows to apply FTIR spectroscopy as a very rapid and powerful tool searching for the best complexing agents, controlling fine structural features and the perfectness (uniformity) of synthesized nanostructures in series of related materials.

Reversible hydrogen sorption for the infiltrated magnesium borohydride

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Magnesium borohydride is the high-capacity hydrogen complex hydrides (14.9 wt% of H₂) although its potential for reversible hydrogen sorption is still a challenge. Thermodynamics of Mg(BH₄)₂ is calculated to be near ideal for effective hydrogen storage but experiments reveal competing decomposition pathways with formation of very stable intermediates which limits cycle life. In practice, reversibility of 11 wt% of H₂ was demonstrated at very high pressures and temperatures [1] while only 2.5 wt% of H₂ at reasonable conditions [2]. Solid-state synthesis of Mg(BH₄)₂ has been developed [3] and decomposition products have been identified as well as methods to improve hydrogen sorption performance, including catalysis addition [4, 5] and nanoscience. The reversibility of complex hydrides may be enhanced if the system is enclosed by a nanoscale void which prevents the reaction partners on the dehydrogenated side from diffusing away from each other. Moreover, the generally enhanced diffusivity in nanocrystalline systems may lower the kinetic barriers for the material's transformation and, thus, facilitate hydrogen absorption and desorption [6]. Therefore, nano-engineering to introduce Mg(BH₄)₂ as nanoparticles in highly porous materials and avoid their aggregation during hydrogen cycling might be one of the solution [7]. The present work shows some approaches to improve reversible hydrogen storage capacity of Mg(BH₄)₂. Melting infiltration and wet impregnation were used as the main methods to prepare Mg(BH₄)₂ nanoparticles inside scaffold. Nanoporous silica and composites made of polyaniline and MWCNT were used as “dispersing agent” of the hydride powder. Experimental results in term of storage capacity and reversibility have been obtained and will be presented.

XPS and Mössbauer spectroscopy of LiFePO$_4$ and LiFePO$_4$/C ceramics


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LiFePO$_4$ crystallizes in olivine structure. It is a mixed electronic-ionic conductor and has been proposed as an attractive cathode material for Li-ion secondary batteries [1]. The conductivity values increased with increasing the amount of carbon in the LiFePO$_4$/C composites [2]. It is known [3] that in this compound Fe$^{2+}$ can be oxidized to Fe$^{3+}$. The material has a high reversible capacity (~160 mAh$^{-1}$) and the intercalation potential for Li/Li$^+$ is 3.5 V [4]. The redox behavior of the iron in this compound also makes it an interesting candidate for X-ray photoelectron spectroscopy (XPS) and the Mössbauer spectra study in the pure LiFePO$_4$ and carbon containing LiFePO$_4$/C ceramics. The LiFePO$_4$ powders for the XPS and Mössbauer spectra study have been synthesized by solid state reaction and LiFePO$_4$/C composites were synthesized by a sol-gel method and later sintered in argon gas. The ceramics of LiFePO$_4$ was sintered in air. The binding energies of Fe 2p, P 2p and O 1s core level of the LiFePO$_4$ ceramics and LiFePO$_4$/C composite surfaces have been determined by XPS at room temperature. The analysis of Fe 2p, P 2p and O 1s core level XPS deconvolution is presented in this work. Mössbauer spectroscopy in the temperature range from 10 K to 700 K has been applied in order to determine phase transition temperatures, the Debye-Waller factor and typical ionization states of iron in compounds. Behavior of Li$^+$ ions was evaluated in the second coordination sphere of iron based on changes in hyperfine parameters of Mössbauer spectra.

Figure 1. Dependence of the hyperfine field on temperature for the LiFePO$_4$/C composite. Line shows the estimated phase transition temperatures $T_m$=50 K

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Structural self-organization of titanium alloys under impulse force action

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In previous experiments [1,2], the authors found for the first time that under impact-vibration loading of the statically pre-stretched specimens from polycrystalline materials to various stages of deformation, self-organized processes occur in materials, which result in the formation of new spatial finely-banded structures interconnected at different levels of scale, which resemble in appearance the adiabatic shear bands. The revealed structural transformations occur exclusively in the impact-vibration mode of loading, which the authors call a dynamic unbalanced process (DUP), and depend primarily on the extent of previous static deformation of materials, under which the process is implemented, and on the magnitude of the force pulse. As a result of DUP implementation, the initial polycrystalline material actually becomes a hybrid material: “base – dissipative structure – gaps between the base and dissipative structure”. During the next static stretching, every new structural state of the material after a specific action of force impulse acquires new, often better mechanical properties, including fracture toughness. In this paper, the basic regularities in the variation of the mechanical properties under impulse force action due to impact-vibration loading were established based on the results of tests of titanium alloys with different initial structures.

Mechanical tests conducted on superhard titanium alloy VT22 with a polycrystalline structure showed that due to the implementation of DUP in the elastic region of the statically pre-strained alloy, it is possible to achieve a significant increase in ductility of the alloy by 2.75 times, with virtually no decrease in strength properties. Physical experiments showed that under impact-vibration loading, a significant fragmentation of the initial structure of the alloy takes place. This process of “self-organization” of the metallic material structure ensures a stable development of deformation under a short-term surplus application of the force energy to the material, and manifests itself in the formation of a fine-grained alloy structure. This is the main reason for a significant increase in ductility of the alloy.

Experiments conducted on submicrocrystalline titanium alloy VT1-0 revealed essentially the negative effect of the impact-vibration loading on the variation of the mechanical properties of the alloy as compared to the coarse titanium alloy. This reaction of the submicrocrystalline titanium to the impact-vibration loading causes the mechanical properties of the alloy to deteriorate significantly under further static stretching, compared to the mechanical properties under standard static stretching. In this case, during the test of the coarse titanium alloy, the energy that comes from outside is spent mainly on the formation of dissipative structures, and during the test of the alloy with the prepared (as a result of complex manufacturing operations) submicrostructure, probably only on its destruction.

Thus, for coarse titanium alloys the impact-vibration loading can be used as a simple technological method of improving the initial mechanical properties, in particular, ductility. On the contrary, for the titanium alloys with the initial submicro- and nanostructure this mode of loading is very dangerous during operation.

Cobalt-tungsten alloys: multiscale engineering

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Applying electrochemically deposited coatings is a convenient way to improve surface properties of substrate metal. Today materials for applications are frequently selected according to their functional properties. Nowadays theoretical and practical studies on the codeposition of tungsten with iron group metals are conducted worldwide, and interesting for study increases \cite{1-3}. Tungsten alloys of iron group metals have a high melting point and are often considered as superalloys or high-performance alloys, and the interest in those has been driven by its outstanding properties and multiple possible applications \cite{1}. That research is encouraged by the pronounced mechanical, tribological and magnetic properties as well as the corrosion resistance of tungsten alloys \cite{3}. The magnetic properties of electrodeposited Me-W alloys are of interest in recording media \cite{4, 5} and remotely-actuated micro-/nano-electromechanical systems (MEMS/NEMS), such as microactuators, micromotors, sensors, microgears or micromechanical magnetometers \cite{6, 7}. In other words, electrodeposited tungsten alloys are suitable candidates to meet many technological demands at macro-, micro- and nano-scale as coating films, microbumps and nanowires. The given research presents the overview of versatile possibilities of Co-W alloys at different scale electrodeposited from citrate-borate solution at pH 5-8; t=20 - 60 °C (Fig. 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{a- SEM images of electrodeposited Co-W coatings at 20\textdegree C (inset) and 60 \textdegree C; b- FIB SEM images of deposited double layered Cu/Co-W microbumps (inset) and triple layered microbumps; c- TEM image of Co-W nanowire.}
\end{figure}

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\begin{thebibliography}{10}
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Electrodeposition and Corrosion Behavior of Nanostructured Cobalt-Tungsten Alloys Coatings

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Electrodeposited nanostructured cobalt-tungsten alloys have potential in a number of applications because of diversity of crystal growth (from coarse crystalline to “amorphous-like”), extremely smooth surface, magnetic and tribologic properties. Due to a large surface area to volume ratio for thin electrodeposited films as compared to that of bulk materials, thin film properties are normally significantly different from its bulk material properties. The variation of the corrosion rates and other properties of the surfaces with their fabrication method and structure are well known. Therefore, the examination of corrosion properties of obtained materials is the integrated part of the modern materials science.

Coatings of Co-W alloy containing tungsten 3 to 30 at.% were electrodeposited onto stainless steel substrates from citrate electrolyte at various cathodic current density (5 to 15 A/cm²) and pH (5 to 8). The thickness of samples was at least of 10 μm.

The electrodeposits were obtained at stationary and various hydrodynamic conditions. The increase in the tungsten content in the alloy (up to 24 at.%) leads to the transformation from crystallographic texture into nanocrystalline (“amorphous-like”). It should be noticed that electrodeposition at 20 °C temperature leads to the “amorization” of structure at lower content of W (13 at.%).

The corrosion behavior of prepared Co-W deposits were studied at room temperature in 0.01M H₂SO₄ and in 0.012M Na₂SO₄ + 0.027M NaCl (90 °C) solutions by electrochemical techniques (voltammetry, electrochemical impedance spectroscopy). The differences in corrosion behavior of electrodeposited alloys are depending on the preparation conditions rather than the composition of obtained alloys. Among the various Co-W deposits studied here, the coatings deposited at 60 °C temperature show better corrosion behavior compared to Co-W deposits obtained at room temperature. The corrosion undergoes via intermediate adsorbed stage by forming oxygen-containing compounds; the relative content of oxygen increases after corrosion-anodization test up to 10-15 times. The estimated thickness of adsorbed layer varies in the range 0 to 1.6 Å. The differences in corrosion behavior of obtained alloys dependently on hydrodynamic conditions are discussed.

The crystalline Co-W alloy coatings exhibited lower values of corrosion resistance in the 0.012 M Na₂SO₄+ 0.027 M NaCl (90 °C) solution, and it is comparable with ones obtained for pure Co deposits. Meanwhile, the “amorphous-like” Co-W coating showed a quite compatible corrosion resistance in this solution.

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Tailoring the Physical Properties of Multifunctional Molecular Emitters

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Search for the new materials with advanced properties is one of the major tasks of the rapidly developing field of organic optoelectronics. Currently much attention is being focused on the multifunctional compounds, i.e. molecules composed of several fragments carrying different functionalities. Multifunctional materials are expected not only to increase the device performance but also to simplify their architectures and fabrication procedures.

On the other hand, multifunctionality unavoidably involves an increase in complexity of molecular properties giving rise to new collective effects, such as intramolecular charge transfer, intramolecular twisting and isomerization, formation of complexes etc. In a solid state, molecular complexity results in different packing morphology, and thus, in various intermolecular interactions, which considerably affect excitation localization, energy transfer and emission properties. Hence, further development of the multifunction molecular compounds for device applications requires thorough analysis and optimization of the emerged collective properties.

Here we review our recent work on tailoring the physical properties of various multifunctional emitter systems targeted for organic electronics devices. We show fine-tuning of the electronic states of anthracene by substituting at the 2-, 9-, ant 10- positions leading to excellent emissive and charge transport properties of the molecules for OLED applications. We also present features of multifragment donor-acceptor emitters capable of harvesting 100% triplet excitons (theoretically) via thermally activated reversed intersystem crossing mechanism utilized in the latest generation OLEDs. We present optimization of singly-bonded carbazole and fluorene triads for lasing applications by emphasizing an importance of the linking position and alkyl spacers. Furthermore, we discuss possibilities for tailoring the photophysical properties of intramolecular charge-transfer systems based on naphtalimide compounds by introducing various polar substituents, by varying intramolecular twisting angles and polarity of the surrounding medium. Finally, highly selective metal ion detection system based on fluorescence enhancement in naphtalimide derivatives is presented.
Light amplification in benzo[c]fluorenes

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Strong interest in laser sources based on low-cost organic semiconductors is provoked by their attractive electronic and optical properties combined with the mechanical flexibility and ease of processibility [1-3]. Simple fabrication of optoelectronic devices via solution processing is one of the key advantages of organic semiconductors. Although the breakthrough in material and device design has enabled to reduce lasing thresholds considerably, organic lasers with direct electrical pumping still remain a challenge. The main issues relate to low carrier mobility, singlet exciton annihilation, polaron absorption, quenching by electrodes, etc. Importantly, most of these issues are mediated by intermolecular coupling [2,3]. Typically, at high concentrations or in the solid state intermolecular interactions are enhanced leading to the formation of poorly emissive aggregate or excimer species. A straightforward way to preserve high emission efficiency and low stimulated emission threshold is to reduce intermolecular coupling by increasing the distance between neighboring molecules. Unfortunately, realization of efficient laser requires high chromophore density [2] and high carrier mobility, i.e., the features that are barely consistent with a necessity to decrease intermolecular coupling. This imposes a certain tradeoff in the properties of lasing materials and also points out the importance of developing new compounds featuring not only low amplified spontaneous emission (ASE) threshold, but also weak concentration quenching of emission and high carrier mobility.

![Figure 1](image.png)

Figure 1 (a) Emission peak intensity vs excitation power density for the benzo[c]fluorene neat film measured in the edge emission (mirrorless) configuration. (b) ASE threshold as a function of compound concentration in a polystyrene matrix.

To this end, a series of low-molecular-weight compounds utilizing benzo[c]fluorene core and twisted peripheral groups for prevention of concentration quenching were synthesized and investigated as potential lasing materials. The suitability of the benzo[c]fluorenes for light amplification was assessed by evaluating concentration quenching of spontaneous and amplified emission, by establishing relationship between pump thresholds of ASE and compound concentration (see Figure 1) as well as by quantifying radiative decay rates, photostability and carrier drift mobility. The weak concentration quenching accompanied by high fluorescence quantum yield and radiative decay rate enabled to attain the lowest ASE threshold (900 W/cm²) in the neat amorphous film of benzofluorene bearing dihexylfluorenyl peripheral moieties. Although the bulky groups at periphery ensured formation of glassy films with low ASE threshold, they adversely affected carrier drift mobility implying a tradeoff between ASE and charge transport properties for the lasing materials utilized in the neat form. Such low ASE threshold attained in air is among the lowest reported for solution-processed neat films. It shows great potential for benzofluorene-cored molecular glasses as active media for lasing applications.

DEVELOPMENT OF TETRATHIOTETRACENE BASED THIN FILMS FOR THERMO-ELECTRICAL APPLICATIONS

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Growing emission of CO₂ due to increased energy production has become one of most important obstacles for further economic development. To solve that problem major attention is paid to replace fossil resources by “green” energy production based on renewable sources – sun, wind, tide, hydrogen energetics and etc. At same time it is estimated that mankind approximately 20% of total power consumption (15 TW/year) loses as low level heat (<200 °C). This globally lost amount of 1020 J/year is greater than the total annual energy usage of all EU member states. It is obvious that direct conversion of this wasted energy in to electrical power by means of devices exploiting thermo electrical (TE) effect will have huge impact on energy production. Wider usage of such TE convertors for harvesting of waste energy is limited by cost and availability of TE active materials. Therefore within a last decade huge attention of research community is paid for search of low-cost and effective TE materials. Organic materials attract increasing attention due to the advantages of mechanical flexibility and low-cost synthesis.

Due to high electrical conductivity promising candidates for TE devices are ion radical salts containing tetrathiotetracene (TTT) [1–3]. The electrical conductivity of TTT iodide (TTTxIy) monocrystals strongly depends on crystal axis. Large and good quality monocrystals are necessary for TE applications and it is a challenging task to grow them in sufficient quantities. Much easier is to obtain smaller, needle like crystals and at the same time to orient them in necessary direction for best performance of the TE device, however, it is also a challenging task. Thin film preparation by thermal sublimation in vacuum could be a solution of the problem if one could control the orientation of TTT iodide crystallites within polycrystalline film.

In this contribution pure TTT thin films as well as TTT layers doped with iodine were studied. Two methods of doping were applied – post deposition doping and co-deposition of TTT and iodine. Impact of preparation conditions on morphology, electrical and TE properties of obtained thin films were studied. SEM was used to obtain morphology of the films. Electrical conductivity up to 2S/cm was measured by four probe technique. The values of Seebeck coefficient in thin film plane and perpendicular to the film were measured by custom made setup. Best value of Seebeck coefficient reached 128 μV/K.

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References
Solid solutions in SrVO$_3$-SrTiO$_3$ system as ceramic components for solid oxide fuel cells anodes

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Limitations of conventional Ni-based solid oxide fuel cell (SOFC) cerments anodes, such as microstructural instability, or fast coking and sulfur poisoning in hydrocarbon fuels, motivate the search for alternative anode components, in particular, suitable ceramic materials mostly based on perovskite-like phases. Strontium vanadate and strontium titanate were demonstrated to exhibit a good sulfur tolerance and resistivity to carbon deposition [1]. However, while perovskite-type SrVO$_{3-\delta}$ has a limited phase stability domain [2], SrTiO$_3$-based compositions shows conductivity ~ 10 S/cm under prospective operation conditions of fuel electrodes, implying significant current collection limitations [3-4]. The present work focused on SrVO$_3$-SrTiO$_3$ system aiming to find a compromise between high electrical conductivity of vanadate and high stability of titanate lattice.

Sr$_{1-x}$Ti$_x$O$_{3-\delta}$ ($x = 0$-1.0) ceramics were prepared by solid-state synthesis and sintered either in 10%H$_2$-N$_2$ atmosphere or in air. XRD analysis confirmed the formation of single-phase materials with cubic perovskite structure for entire compositional range under reducing conditions, while under oxidizing conditions the solid solution formation range was limited to Ti-rich end of the series. The characterization of materials included structural and microstructural studies, measurements of electrical conductivity as function of temperature and oxygen partial pressure, controlled-atmosphere thermogravimetry and dilatometry, and assessment of redox behavior on cycling between reducing and inert or oxidizing atmospheres. For reduced ceramics, increasing Ti concentration was found to reduce gradually electronic conductivity (Figure 1), but also to improve thermomechanical compatibility with solid electrolytes and to extend the perovskite phase stability domain towards higher p(O$_2$). In the case of oxidized compositions, the particular attention was given to reduction behavior at temperatures ≤ 1000°C relevant for in-situ fabrication of porous anode layers.

Figure 1. Temperature dependence of electrical conductivity of Sr$_{1-x}$Ti$_x$O$_{3-\delta}$ ceramics in 10% H$_2$-N$_2$ atmosphere.

Oxygen-deficient $K_2NiF_4$-type $Nd_{1-x}Sr_{1+x}NiO_{4+\delta}$ as prospective oxygen electrode materials for SOFC/SOEC

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Perovskite-related nickelates with layered Ruddlesden-Popper (RP) structure and general formula $Ln_{1+n}NiO_{3n+1}$ ($Ln = La, Pr, Nd; n = 1-3$) and their derivatives combine redox stability with oxygen stoichiometry changes, yielding enhanced mixed transport and electrocatalytic properties [1-3]. These unique features are promising for applications as oxygen electrodes with good electrochemical performance in reversible SOFC/SOEC (solid oxide fuel/electrolysis cell) systems. The present work was focused on the assessment of neodymium-strontium nickelates with $K_2NiF_4$-type ($n = 1$ RP) structure as prospective reversible oxygen electrodes.

$Nd_{1-x}Sr_{1+x}NiO_{4+\delta}$ ($x = 0-0.6$) ceramics were prepared by Pechini method with repeated annealings at 650-1000°C, and sintered at 1150-1200°C for 15 h under oxygen atmosphere. Variable-temperature XRD studies confirmed that all studied compositions retain tetragonal RP structure in the temperature range 25-1000°C and $p(O_2) = 0.21-1.00$ atm. The characterization of ceramic materials included microstructural studies, controlled-atmosphere dilatometry and thermogravimetry, and measurements of electrical conductivity as function of temperature and oxygen partial pressure. The absolute values of oxygen nonstoichiometry were determined thermogravimetrically from the mass changes on total reduction to $Nd_2O_3$, SrO and metallic Ni in 10%H_2-N_2 atmosphere.

The results demonstrated that, contrary to parent $Ln_2NiO_{4+\delta}$ compounds, $Nd_{1-x}Sr_{1+x}NiO_{4+\delta}$ exhibit oxygen deficiency under oxidizing conditions in high-temperature range (Fig.1A). Comparatively high $p$-type electronic conductivity show metallic-like behaviour at temperatures above 500°C and decreases with reducing $p(O_2)$ from 1.00 to $10^{-4}$ atm. Highest conductivity was demonstrated for $x = 0.8$ (Fig.1B). Thermochemical expansion, electrical and electrochemical properties of the studied materials were analyzed in correlation with defect chemistry, oxygen nonstoichiometry and structural parameters.

![Figure 1. Temperature dependence of oxygen nonstoichiometry (A) and electrical conductivity (B) of $Nd_{1-x}Sr_{1+x}NiO_{4+\delta}$ oxides in air.](image)

Characteristics and sinterability of ceria stabilized zirconia nanoparticles prepared by chemical methods

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Ceria stabilized zirconia polycrystalline ceramics due to their better stability in moist environment have been investigated extensively. However, for manufacture of dense zirconia based ceramics with submicron grains nanosized powders with high specific surface area are required. For preparation nanosized ceria stabilized zirconia nanopowders promising are developed chemical methods such as hydrothermal, coprecipitation, sol-gel or gel-combustion. The phase composition and particles size as well as sinterability of the obtained products depends strongly on the preparation method.

The aim of the present work was comparison of properties and sinterability of ceria stabilized zirconia prepared by microwave (MW), molten salts (MS), and gel-combustion (SG) methods using ZrOCl$_2$$\cdot$8H$_2$O and Ce(NO$_3$)$_3$$\cdot$6H$_2$O as precursors. The MW synthesis was carried out in a Masterwave BTR, Anton Paar, apparatus by heating salt solution with CH$_2$N$_2$O in water at 170–200 $^\circ$C during 20 min. The MS synthesis was carried out by heating mixture of zirconia and cerium salts with NaCl and NaNO$_3$ at temperature in the range of 400–800 $^\circ$C during 2 h at different ratio of MeO/NaCl+NaNO$_3$. The gel-combustion synthesis was performed by adding to water solution of salts glycine and HNO$_3$ and calcination at 500 $^\circ$C during 2 h.

The as-prepared by all methods ceria stabilized zirconia (CSZ) nanoparticles containing 10–15% cerium consisted from t-, c-ZrO$_2$ phases. The specific surface area of the nanoparticles prepared by MW, MS, and SG methods was in the range of 120–133 m$^2$/g, 54–123 m$^2$/g, and 24–48 m$^2$/g respectively depending on the synthesis parameters.

The crystallite size of CSZ nanoparticles prepared by MW and MS synthesis methods was in the range of 4–5 nm but crystallite size of SG nanoparticles was in the range of 10–15 nm because the higher synthesis temperature. The additional calcination of the samples up to 1000 $^\circ$C decreased their specific surface area to 20 m$^2$/g, and decreased crystallite size to 20–25 nm as well as caused formation of monocline ZrO$_2$ phase.

The prepared samples were densified by using spark plasma sintering (SPE-825-CE, SPS Syntex Inc.). densificatin of CSZ samples started at 860–900 $^\circ$C and dense materials with fine-grained microstructure (0.5–1.0 µm) were obtained at 1500 $^\circ$C during 3 min. Sintering process reduced the content of t-ZrO$_2$ phase, especially in the samples prepared by MS and SG synthesis.

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Applications of deep UV photodetecting and spintronic devices require semiconductors with bandgap values in the range of 4-6 eV. Zinc oxide (ZnO) has a wurtzite (wz) crystal structure with a coordination number of four at ambient conditions. Bandgap engineering by substitution of MgO up to 40% can extend the bandgap value of wz-ZnO from 3.3 eV to approximately 4.0 eV. A further extension of the bandgap is limited by the low thermodynamic solubility (<5%) of MgO even at high temperatures. An alternative approach is to add ZnO in six-coordinate rocksalt (rs) MgO, resulting in a pseudobinary Zn$_{1-x}$Mg$_x$O solid solution with a bandgap energy of 4.0-7.8 eV. In this work, we demonstrate that more than 80% of MgO can be substituted by ZnO in rs epilayers grown on MgO (100) substrate by molecular beam epitaxy. The optical properties of the Zn$_{1-x}$Mg$_x$O epilayers has been studied by means of cathodoluminescence (CL), photoluminescence (PL), excitation (PLE), and spectroscopic ellipsometry (SE).

Figure 1a shows the X-ray diffraction patterns obtained in an α/θ configuration of the Zn$_{0.50}$Mg$_{0.50}$O, Zn$_{0.83}$Mg$_{0.17}$O, Zn$_{0.88}$Mg$_{0.12}$O and Zn$_{0.96}$Mg$_{0.04}$O samples. It clearly demonstrates that the Zn$_{0.50}$Mg$_{0.50}$O and Zn$_{0.88}$Mg$_{0.12}$O samples have an rs structure with a strong (200) peak at 42.44° and 42.21°, respectively. With reducing the MgO content to 12% or lower, the samples show a wz structure with two diffraction peaks of (10 20) and (0002). Accordingly, the threshold content of MgO in rs-Zn$_{1-x}$Mg$_x$O is approximately 15%, coinciding well with the value (13%) suggested by Sans and Segura [1]. We argue that the stability of the rs epilayer relies indeed on the lattice strain provided from the substrate. Therefore the rs-Zn$_{1-x}$Mg$_x$O epilayer with x=0.13 may be obtained when it is grown in a pseudomorphic state. The high-resolution transmission electron microscopy results showed that rs-ZnO was indeed observed to grow epitaxially on MgO at a thickness of 5 nm.

Figure 1 (a) X-ray diffraction patterns of four Zn$_{1-x}$Mg$_x$O epilayers, (b) optical absorption spectra of the Zn$_{0.50}$Mg$_{0.50}$O and Zn$_{0.83}$Mg$_{0.17}$O samples, and (c) low-temperature CL spectra of the Zn$_{0.50}$Mg$_{0.50}$O and Zn$_{0.83}$Mg$_{0.17}$O samples.

The optical absorption spectra of the Zn$_{0.50}$Mg$_{0.50}$O and Zn$_{0.83}$Mg$_{0.17}$O samples are shown in Fig. 1b, indicating that the bandgap energy of the Zn$_{0.50}$Mg$_{0.50}$O sample is 5.33 eV. The high ZnO content sample (Zn$_{0.83}$Mg$_{0.17}$O) has a lower bandgap value of 4.73 eV. An rs-ZnO film grown on mica was reported to undergo a direct transition at 4.5 eV under a pressure of 9.5 GPa. Therefore, the bandgap energy of the rs-Zn$_{1-x}$Mg$_x$O epilayer increases in a rate of approximately 20 meV/at% with the addition of MgO. Both the CL spectra of the Zn$_{0.50}$Mg$_{0.50}$O and Zn$_{0.83}$Mg$_{0.17}$O samples acquired at 10 K (see Fig. 1c) contain a sharp, high-energy peak and a broad peak at lower energies. The high-energy peak is 1 eV lower than the corresponding absorption edge. The optical properties of the rs epilayers will be discussed in detail.

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Nonpolar m-plane ZnO epitaxial films have successfully grown on surface treated (100) $\beta$-LiGaO$_2$ (LGO) substrates by plasma assisted molecular beam epitaxy (PAMBE). As a promising substrate, LGO has small lattice mismatch with ZnO (1.9-3.9%). However, C. J. et al. indicated that LGO will decompose to LiGa$_5$O$_8$ and Ga$_2$O$_3$ at high temperature $^{[1]}$. In order to prevent decomposition of LGO substrate, we modified the pretreatment in Load Lock chamber of MBE. The LGO substrates were treated under activated hydrogen from $1 \times 10^{-6}$ to $3 \times 10^{-6}$ mbar and further investigated the influence of surface treatment. The surface morphologies of surface treated LGO substrates were characterized by atomic force microscopy (AFM). The optimum surface treated LGO substrate were then applied for epitaxial growth of m-plane ZnO. The structural and crystalline properties were characterized by high resolution X-ray diffraction (HRXRD) indicated that the ZnO epilayers were grown along the nonpolar [1 1 00] ZnO direction and the FWHM of X-ray rocking curves has improved from 0.5$^\circ$ to 0.05$^\circ$ (Fig. 1). The surface morphologies of ZnO films were investigated by scanning electron microscopy (SEM) (Fig. 2). Detailed structural characterization and defect analysis of nonpolar ZnO epilayer LiGaO$_2$ substrate was studied by transmission electron microscope (TEM). Optical properties of m-plane ZnO films were investigated by photoluminescence (PL).

**Fig. 1** (a) X-ray diffraction pattern of m-plane ZnO grown on LiGaO$_2$ substrate and (b) X-ray rocking curves before and after hydrogen flow.

**Fig. 2** SEM images of m-plane ZnO grown on surface treated LGO substrate at 600$^\circ$C.

Investigation of charge transport in Lead Oxide with photo-CELIV

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There is a great interest in utilization of non-crystalline materials as X-ray-to-charge transducer in direct conversion X-ray medical imaging detectors \cite{1}. Polycrystalline Lead Oxide (PbO) is one of the most promising candidates for this purpose since it possesses high theoretical conversion gain and high X-ray stopping power. Also, in contrast to other non-crystalline high-Z materials (like polycrystalline layers of HgI\textsubscript{2}, PbI\textsubscript{2}, poly-CZT), PbO inherently offers the higher spatial resolution.

Photo generated charge carrier extraction with linearly increasing voltage (photo-CELIV) method was used to investigate transport properties of polycrystalline PbO \cite{2}. The measurements were performed at various temperatures and wide range of applied electric fields. The hole mobility was found to be \(\mu_h\approx0.15\) cm\textsuperscript{2}/Vs, while the mobility of electrons is lower \(\mu_e\approx10^{-4}\) cm\textsuperscript{2}/Vs.

In addition, we found that bimolecular recombination is responsible for incomplete charge collection in PbO. The photogenerated charge carriers undergoes a Langevin-type recombination. This makes PbO even an attractive candidate to replace a-Se on the market of direct conversion X-ray medical imaging detectors.

\begin{thebibliography}{99}
\end{thebibliography}
Thin film bulk acoustic resonators (FBARs) using aluminum nitride (AlN) and zinc oxide (ZnO) have found wide spread use in mobile phones as duplexer and filters because of their small size, low insertion loss, high power handling capability and possibility of integrating with silicon very large scale integration technology. Recently, FBARs with Barium Strontium Titanate (BST) are attracting the attention of many researchers because of their tunable characteristics. Most of the results published in this area of research are on single composition BST. Recently, it has been reported that graded composition BaxSr1-xTiO3 (x=0 to 1) gives the opportunity to fabricate temperature independent dielectric constant components with improved piezoelectric constant over single composition BST. In this paper, we are presenting the tunable and switchable graded composition BaxSr1-xTiO3 (x=0.6 to 0.90) film bulk resonators (FBARs) based on Silicon dioxide/Tantalum oxide Bragg reflectors. The Bragg reflectors can withstand high temperatures of about 800 °C during annealing of BST film. BST films as well as Bragg reflectors were all deposited by spin on technique. The DC bias-dependent series resonance due to electrostriction of the graded BST film, decreases with increasing bias field and the tunability is about 2.6% for an applied bias voltage of 10V. The parallel resonance frequency is weakly dependent on applied bias and increases with applied bias. The calculated electromechanical coefficient for these resonators increases with applied bias and the maximum value of 12.5% is reached for a bias voltage of 10V. The maximum quality factor ‘Q’ for these devices was 80 at a bias voltage of 13V.
The lanthanum-gallium silicate group crystals as functional materials for optical and piezoelectrical application

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Lanthanum – gallium tantalate \( \text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14} \) (langatate) and lanthanum – gallium silicate \( \text{La}_3\text{Ga}_5\text{SiO}_{14} \) (langasite) are the crystals with the structure of the Ca-gallogermanate. The space group of symmetry is P3\(2\)1. High values of piezoelectric coefficient and thermostable cuts allowed to apply the langasite for creating filters and resonators on surface and bulk acoustic waves. The drift of the piezoelectric coefficients is not observed in langatate in contrast to langasite and other piezomaterials therefore it is used for high-temperature sensors of different physical values.

Currently, the electrophysical properties of langatate crystals and their dependence on the growth atmosphere have not been discussed much in the literature. Accordingly, here we present the results of our studies of the optical, luminescent and electrophysical characteristics of LGT and LGS crystals depending on their composition, orientation and growth conditions.

For this study the langatate and langasite crystals were grown from iridium crucibles by the Czochralski process at Fomos-Materials, in the atmospheres of argon (Ar), argon with oxygen (Ar+O\(_2\)). Oxygen concentrations in the growth atmosphere were about 2% for langasite and <1, <2, and ~2% for langatate.

Optical transmission spectra were measured using UV-Vis-Nir spectrophotometer «Cary-5000» (Agilent Technologies). The luminescence was excited at \( T=300 \text{ K} \) by third harmonic of YAG:Nd\(^{3+}\) (\( \lambda_{\text{ex}}=355 \text{ nm} \)) or by Xe lamp.

In a crystal point defects and their complexes influence its color and its electrical behavior, acting as color centers. Optical spectroscopy therefore represents a very sensitive tool to examine point defects. The influence of different growth atmospheres on optic transmission spectra of the crystals showed that decreasing of oxygen concentration in growth atmosphere of crystal lead to the considerable improvement of their optical characteristics [1].

In transmission spectra of LGS and LGT in visible and UV spectral regions we observed three absorption bands in the colored crystals (290, 380 and 490 nm) and only one band in the colorless crystals (290 nm). Also in transmission spectra of all investigated samples there are two bands in near infra-red region - 1850 and 2920 nm. We observed anisotropy of transmission spectra of samples – this effect in crystals with Ca-gallogermanate crystals is well-known [2]. However for the samples, which were cut in the direction parallel to axis Z we also observed dichroism. This effect occurs in some crystals with specific structure when naturally polarized light pass along directions perpendicular to the optical axis, and may be caused by the symmetry of the crystals’ structure or by the anisotropy of color centers. First studies of luminescence in LGT and LGS crystals demonstrated influence of growth conditions on the luminescent characteristics of these crystals. Therefore the method of luminescence spectroscopy was applied to determine existing emission centers in the studied crystals and their relation to the crystal's structure defects.

Langatate measuring sensors designed to operate at high temperatures often suffer from surface degradation beneath the current carrying coating, which is applied to a polar cut. The thermal and thermal-frequency dependences of langatate electrophysical parameters in constant and alternating electric fields in the temperature range 20-500 °C were investigated. The frequency dependences of relative dielectric constant (\( \varepsilon_1/\varepsilon_0 \)), admittance, \( \tan \delta \) depend on the growth atmosphere.

The langatate electrophysical properties in alternating electric field were analyzed by means of impedance spectroscopy method. The equivalent circuits were constructed by using the method with allowance for the electrochemical processes of a cell “electrode-crystal-electrode”. The parameters of this electrochemical cell were determined; the input of different near-electrode processes into electrophysical properties of LGT was estimated.

Excellence Centre of Advanced Material Research and Technology Transfer – stairway to excellence – Latvia Case

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Horizon 2020 Teaming project ‘The Excellence Centre of Advanced MAterial Research and Technology Transfer — CAMART²’ a key enabling tool for enhancement of the innovation and technology transfer power at the Institute of Solid State Physics, University of Latvia.

The development of CAMART² is in line with European Commission recommendations for development of a long-term cooperation platform for enterprises and scientists that can serve as a framework for efficient cooperation between scientists and entrepreneurs in order to improve the research infrastructure, to support joint research and to foster technology transfer.

Mission of CAMART² is to use the knowledge and infrastructure of Institute of Solid State Physics University of Latvia, KTH Royal Institute of Technology and Acreo Swedish ICT to address the European Union program “Horizon 2020” pillar “Societal Challenges”, by conducting research collaboration and competence transfer according to pillars “Excellent Science” and “Leadership in Enabling and Industrial Technologies”.

The aim of this project is to create CAMART² as a Baltic Sea region material science Centre of Excellence with high innovation and technology transfer capacity that will help to increase the level of commercialization, to develop a long term cooperation platform for businesses and academics, to support joint research.

The focus of CAMART² is in line with Latvian Research and Innovation Strategy for Smart Specialization (RIS3) ‘Smart materials, technology and engineering’ and the research areas at KTH ICT School, Acreo and Electrum Laboratory and covers:

1. Thin films and coating technologies
2. Functional materials for electronics and photonics
3. Nanotechnology, nanocomposites and ceramics
4. Computational material science by atomic scale modelling of technologically important materials and devices.

During the 1st project implementation phase a business plan must be elaborated for upgrading the existing infrastructure at ISSP UL to a new significantly stronger on European level Centre of Excellence for Education, R&D, Innovation and Technology Transfer by synergic employment of the EC-defined “Key Enabling Technologies” - Advanced Materials, Photonics, Nanotechnology and Micro- and Nanoelectronics.

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Sm-doped praseodymium nickelates-cobaltites and their nanocomposites as promising cathode materials

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State-of-the-art SOFC cathode materials based upon LS(F)C are deteriorated in the intermediate temperature (IT) range due to formation of carbonates blocking surface sites [1]. Stable to carbonation PrNi₁₋ₓCoₓO₃₋δ – doped ceria composites demonstrated a high performance in the IT range [2]. This work aims at elucidating effects of composition and microstructure of such materials on PrNi₁₋ₓSmₓNiₓCoₓO₃₋δ oxygen mobility and reactivity.

For PSNC samples sintered at 700 – 1000 °C the main phase is orthorhombic perovskite (P) Pr₁₋ₓSmₓNiₓCoₓO₃₋δ (PSNC) and fluorite (F) Ce₀.₉Y₀.₁O₂ (YDC) oxides were synthesized by Pechini route. PSNC–YDC composites were prepared by ultrasonic dispersion of powders mixture in isopropanol, then drying, pressing pellets and sintering at 800 – 1300 °C. Samples were characterized by XRD and TEM with EDX. Oxygen mobility was estimated by O₂ TPD and oxygen isotope heteroexchange with ¹⁵O₂ and ¹⁸O₂.

Figure 1. XRD patterns for Pr₀.₉Sm₀.₁Ni₀.₉Co₀.₁O₃₋δ samples sintered at different temperatures. # - Pr₀.₉Sm₀.₁Ni₀.₉Co₀.₁O₃₋δ perovskite, * - cubic Pr₀.₉Sm₀.₁Ni₀.₉Co₀.₁O₃₋δ, ▲ - Pr₁₋ₓSmₓNiₓCoₓO₃₋δ RP homologue, # - NiO, ▲ - plasticine.

For PSNC samples sintered at 700 – 1000 °C the main phase is orthorhombic perovskite with parameter ~ 5.450 Å. Admixture of cubic Fm-3m phase with composition Pr₀.₉Sm₀.₁Ni₀.₉Co₀.₁O₃₋δ according to EDX data is present, its amount decreasing with sintering temperature. For PSNC samples sintered at 1100 °C besides P phase only small amount of A₂B₂O₇ Ruddlesden – Popper (RP) homologue is found. For samples sintered at 1200 – 1300 °C RP Pr₁₋ₓSmₓNi₁₋ₓCoₓO₃₋δ is the main phase with some traces of P and Ni(II)O (Fig. 1). For PSNC – YDC composites strong cations redistribution is observed. For samples sintered at ≥1000 °C the main phase is F with P amount decreasing with sintering temperature. At 700 °C oxygen tracer diffusion coefficient Dₒ and surface exchange constant kₑ are ~10⁻⁸ cm²/s and ~10⁻⁷ cm/s, respectively, for PSNC sintered at 1100 °C. For PSNC – YDC composites these values are by about one order of magnitude higher. Such high oxygen mobility can be explained by disordering domains and P-F interface. Also Pr, Sm and Y-doped ceria itself shows a high oxygen mobility (Dₒ ~10⁻⁶ cm²/s at 700 °C) [3].

Sol-gel combustion synthesis and characterization of nanocrystalline gadolinium doped ceria

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Solid oxide fuel cells (SOFC) are currently attracting tremendous interest because of their huge potential for power generation in stationary, portable and transport applications and our increasing need for sustainable energy resources [1]. In recent years significant efforts have been made to reduce SOFCs operating temperature. The reduction in operating temperature leads to higher chemical stability of SOFCs and allows using cheaper materials [2]. Owing to its properties like high ionic conductivity and thermal stability at intermediate temperature (500-700 °C) gadolinium oxide doped ceria (GDC) is one of the most attractive material for the use as an electrolyte in SOFC [3]. It is known that ionic conductivity strongly depends on the quality of the ceramics, which is in turn, depends on the properties of the initial powder, such as sinterability, purity, homogeneity, and particle size. The nanocrystalline powders promote the sintering at low temperature and give dense material and also enhance the ionic conductivity, compared to their microcrystalline counterparts [4].

In this study we report on the sol-gel combustion synthesis of nanocrystalline GDC powders with gadolinium content of 10 and 20 mol% via three different combustion processes. Cerium (III) and gadolinium (III) nitrates were used as metal precursors and oxidants while ethylene glycol (EG), glycerol (GL) and tartaric acid (TA) were used as complexing agents and fuels. The amount of fuel was estimated according to the principle of propellant chemistry [5]. The stoichiometric fuel to oxidant ratio was chosen and calculated EG, GL and TA to metal nitrates ratios were 1.5:1, 1.07:1 and 1.5:1, respectively.

A range of techniques including thermal analysis (TG-DSC), X-ray powder diffraction (XRD) analysis, specific surface area determination (BET) and scanning electron microscopy (SEM) were employed to characterize the GDC precursor gels, final powders and ceramics. The obtained powders were sintered into pellets and afterwards electrochemical properties were measured by means of impedance spectroscopy (IS).

Supercapacitors with electrodes from wood-based nanoporous carbon

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Nowadays researches devoted to nanotechnologies are aimed at synthesis and characterization of activated carbons. These materials have highly developed nanoporous structure, with high specific surface, micropores volume and uniform distribution of pore sizes, and also are highly electrically conductive. New generations of activated carbons apart of chemical sorption processes are used in modern power-engineering, e.g. fuel cells, transmission and storage of electrical energy with supercapacitors.

There are two directions devoted to the increasing of power capacity of supercapacitors: one deals with the increasing of working potential by the application of organic and ionic liquids based electrolytes. Another one is aimed at increase of electronic structures capacity, in the first place by enhancing of electric double layer capacity of carbon electrodes.

The aim of this work was to synthesize nanoporous carbon materials on the base of charcoal precursor for application as electrode materials in supercapacitors with solution of tetraethylammonium tetrafluoroborate in acetonitrile as electrolyte.

Sodium and potassium hydroxides are the effective agents for coal and biomass treatment and were used in this study to form a nanoporous structure. Alkali activation consists of four main stages: 1) impregnation or mixing of precursor with alkali (proportion 1-5 g/g); 2) heating up to activation temperature (600-800°C); 3) isothermal treatment (1-3 h); 4) cooling and demineralization with consequent washing up to neutral pH. To decrease ash content in activated carbon the demineralization process was studied with different acids, their concentrations and time of treatment.

It was shown that when sodium hydroxide was used as activator carbon specific surface and total pore volume were higher than in the case of potassium hydroxide. Structure of activated carbons was tested by sorption methods, EPR and Raman spectroscopy. Correlation between porous structure and electrochemical electrodes properties was studied.

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Pt supported TiO$_2$-nanoparticles and TiO$_2$-nanofibers as catalysts for glycerol oxidation

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Supported Pt catalysts have been found to be very active in the glycerol oxidation processes. Up to now several Pt supports are used, of which the most popular are metal oxides and activated carbon [1]. Mostly the catalysts are selective to glycric acid, but in some cases also glycolic acid, lactic acid or glyceraldehyde depending on oxidation conditions obtained. It is well known that support can play a significant role on the whole catalyst characteristics, as well as influences catalyst’s selectivity and activity. Until now only carbon nanofibers [2] and multiwall carbon nanotubes [3] were known as Pt support.

In this work new Pt containing composition in glycerol oxidation is studied – Pt supported TiO$_2$ nanofibers (Pt/NF-TiO$_2$). TiO$_2$ nanofibers were prepared by a microwave method similar to hydrothermal method. Then TiO$_2$ nanofibers were modified with platinum and calcinated in air at 500 °C. In this work also investigation of activity of fine-disperse platinum catalyst, supported on TiO$_2$ nanopowder (Pt/NP-TiO$_2$), will be continued. Platinum catalyst supported on TiO$_2$ nanopowder synthesis by extractive-pyrolytic method was described in [1].

![Figure 1 TEM microphotograph at magnification 200 000x of the Pt/NF-TiO$_2$ (a) and Pt/NP-TiO$_2$ (b) catalyst.](image)

Characterisation of morphology, crystallization, chemical content and surface areas was done by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and BET surface area analysis method. TEM images for nanocomposites with 4.8% Pt content are presented in Figure 1. The prepared nanocomposites were tested in glycerol oxidation processes by molecular oxygen. The oxidation of aqueous glycerol solutions in the presence of Pt/TiO$_2$nanocomposites was performed in an autoclave or in a thermostatted slurry bubble column reactor operated in batch mode. It was found that Pt/NF-TiO$_2$ and Pt/NP-TiO$_2$ composites are catalytically active in alkaline glycerol water solutions. In all cases the main product of glycerol catalytic oxidation was glycric acid, by-products were – tartronic, lactic, glycolic, oxalic, acetic and formic acids. It was shown that Pt/NF-TiO$_2$ and Pt/NP-TiO$_2$ catalysts activity and selectivity depends on oxygen pressure and NaOH initial concentration. The best results were achieved at the following oxidation parameters: $c_{\text{glycerol}}$ = 0.3 M, $c_{\text{NaOH}}$ = 1.5 M, $n(\text{glycerol})/n(\text{Pt}) = 300 \text{ mol/mol}$, $P(\text{O}_2) = 6 \text{ atm}$, 60 °C: selectivity by glycric acid 63%, with glycerol conversion 100% using Pt/NF-TiO$_2$ catalyst; selectivity by glycric acid 68%, with glycerol conversion 95% using Pt/NP-TiO$_2$ catalyst.

Production of CeO$_2$/NiO and CeO$_2$/NiO-Pt nanocomposites by EPM

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Due to its redox properties and high oxygen storage capacity, cerium oxide is widely used as catalyst support and promoter in oxidation and hydrogenation reactions [1]. Platinum supported on ceria is the promising catalyst for application in the water-gas shift (WGS) reaction [2]. The activity of ceria-supported platinum catalysts can be enhanced significantly by addition of oxide promoters [3].

In this work, we present the synthesis and characterization of CeO$_2$/NiO and CeO$_2$/NiO-Pt nanocomposites. Nickel oxide and platinum were deposited on the support surface (a commercial CeO$_2$ nanopowder) by the extractive-pyrolytic method (EPM).

An organic extract (a solution of nickel hexanoate Ni(C$_5$H$_{11}$COO)$_2$ in hehanoic acid) produced preliminary by solvent extraction was used as a precursor for the production of nickel oxide.

The XRD analysis of the pyrolysis products of the nickel-containing extract ($T_{pyr} = 400^\circ$ C) revealed a nickel crystalline phase along with nickel oxide (the mean crystallite size $d_{NiO} = 20$ nm) that is also confirmed by magnetic measurements. The sample exhibits ferromagnetic properties: the coercivity $H_c = 189$ Oe and the magnetization $\sigma = 10.6$ emu/g that corresponds to the 19 wt.% nickel content.

At the production of the CeO$_2$/5 wt.% NiO composite, the thermal treatment of the nickel-containing extract on the support at $T_{pyr} = 300^\circ$ C results in X-ray amorphous decomposition products. The pyrolysis temperature increase allows to produce the nickel oxide crystalline phase with $d_{NiO} = 10$ nm at $T_{pyr} = 500^\circ$ C and with $d_{NiO} = 18$ nm at $T_{pyr} = 700^\circ$ C. With reference to the data of magnetic measurements, the nickel content in the produced materials does not exceed 0.002 wt.%.

A series of CeO$_2$/Pt and CeO$_2$/5 wt.% NiO-Pt composites with different Pt loading have been produced. The process of CeO$_2$/NiO-Pt composite production involves the stepwise decomposition of a nickel-containing precursor first and then a platinum-containing one on the carrier. The procedure of platinum-containing precursor production is described in detail in [2]. Referring to the XRD data, the platinum particles are amorphous in the composites with a platinum content from 0.3 wt.% to 2.4 wt.%, both with nickel oxide and without it. With the higher metal content (4.8 wt.%) in the CeO$_2$/NiO-Pt composites, the mean size of metal crystallites is 4 nm that is twice less if compared with CeO$_2$/Pt.

The prepared nanocomposites were tested in glycerol oxidation processes by molecular oxygen. It has been found that CeO$_2$ and CeO$_2$/NiO composites are catalytically inactive in alkaline glycerol water solutions. But the platinum modified CeO$_2$ and CeO$_2$/NiO composites are catalytically active. It was shown that the Pt weight loading (0.3 – 1.25 %) on the composites significantly affected the glycerol conversion (12 – 63 %). The main product of oxidation was glycric acid.


Correlation between magneto-resistive and magneto-optical properties of sputter-deposited Co/Cu multilayers in visible

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Physical properties of nanofilms, which have composition of “ferromagnetic-normal” (FM-NM) metal, can considerably differ from ones of bulk FM and NM metals. These distinctions are caused by appearance of new electronic states due to space modulation of electron density in ultrathin metal layers and by changes of interface structure at changes of conductivity electron density on layers boundaries. Opportunities to influence on the film parameters by the way of variation of layers components and variations of technological conditions stimulate practical interest for comprehensive studying of FM-NM structures.

It is reported about revealing of correlation between behavior electroresistivity at magnetic field and longitudinal magneto-optical Kerr effect (LMOKE) of multilayer \[\text{[Co(0.8 nm)/Cu(\text{d}_\text{Cu})] \times 20}\] nanofilms. From approximations of magnetic field strength dependencies of magnetoresistivity and LMOKE by the Langevin functions it was found that sizes of superparamagnetic (SPM) cluster formations in the films are depended on copper layer thicknesses. The SPM clusters are considerably smaller in the films with the copper spacer layer thicknesses, for which exchange coupling between Co layers through Cu conduction electrons is expectedly extreme (Figure 1 (a)).

Decreasing of SPM clusters is accompanied with considerable enhancement of LMOKE (Figure 1 (b)). In the work an analysis of possible origins of this enhancement was carried out. It was concluded, that enhancement of magneto-optical Kerr rotation in the films with smaller SPM clusters is connected with additional LMOKE from Co/Cu interfaces. Decreasing of SPM cluster sizes is likely connected with change conditions for condensation of Co atoms on the Cu layer, in which there is the space quantization of conductivity electrons.

![Figure 1](image-url)

Figure 1 (a) The averaged sizes of SPM clusters in units of the Bohr magneton vs thickness of copper spacer layer in the [Co/Cu(111)]×20 films. The sizes of SPM clusters were derived from approximation of magnetic field strength dependencies of the Kerr rotation angle and magnetoresistance by the Langevin functions. The thicknesses of copper layer \(\text{d}(\text{Cu}) = 0.9, 1.35 \text{ to } 1.8 \text{ nm}\) are pointed by the arrows to indicate maximum values of antiferromagnetic (AFM) and ferromagnetic (FM) exchange coupling for [Co/Cu(111)/Co] films. (b) The LMOKE rotation angle in [Co/Cu(111)]×20 films at their magnetic saturation (wavelength of light equal to 632.8 nm) The dashed line is calculated for multilayer model with sharp layer boundaries using the bulk optical constants of Co and Cu.
Multifunctional structured coatings via sol-gel phase separation method

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We present our results in nano- and microstructural design of silica materials by synthesis strategies based on phase separation in sol-gel system. While this method allows to prepare relatively complex architectures and multifunctional materials, the preparation method is essentially simple, inexpensive and adaptable to large-scale production.

We have used the sol-gel phase separation principles and spraying technique in a novel method for patterning substrates with round silica features [1]. Silica domes are formed through silica-rich phase nucleation in continuous solvent-rich phase and further growing as polymerization proceeds and solvent is evaporating. It is possible to vary the diameter of domes (Fig.1) with size distribution from about 200 nanometers to few micrometers by modifying precursor solution and spraying parameters. Also, different morphology can be achieved.

Structured coatings resemble the surfaces of lotus leaf and moth-eye, which are known for their non-wetting and anti-reflective properties [2]. According to this, prepared coatings show hydrophobic characteristics and optical functionality is also achieved as surface features act as lens. These patterned surfaces can thus be used as structured diffusive, light trapping or anti-glare coatings.

Production of semiconductor CdS nanoparticles by plant hairy root culture

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QDs are fluorescent semiconductor nanocrystals, composed of materials from the elements in the periodic groups of II VI, III V or IV VI, e.g. cadmium sulfide or indium phosphamide. These nanoparticles show unique optical and electronic properties, including size-tunable light emission, simultaneous excitation of multiple fluorescence colors, high signal brightness and long-term photostability [1]. To now, several methods have been reported for the synthesis of nanoparticles including an organic or a microwave-assisted method. However, biological synthesis is preferred due to chemical methods that are complicated, toxic and have low productivity [2]. Preparation of nanoparticles using plants has drawn a great attention because of its rapid, economical, eco-friendly protocol of the biosynthesis process. The present investigation suggests a novel approach to the biosynthesis of cadmium sulfide nanoparticles using hairy root culture of flowering plant Linaria maroccana L.

In this study hairy root culture was grown in a liquid medium which consists of MS basal salt mixture, vitamins and sucrose during 7 days under 28°C. Subsequently root material was thoroughly washed in sterile distilled water and cut into fine pieces. These pieces were heated and filtered through filter paper in order to remove root residues. 0.025 M solution of CdSO₄ was added in the resulting extracellular liquid and cultured during 4 days. After that 0.5M Na₂S was added to the solution. After 3 days culturing 6 ml of liquid culture was sampled and centrifuged (10 min, 5000 rpm). Selected samples were used for physical analysis.

It was found that the maxima in absorption spectrum corresponded to 362 nm, 398 nm and 464 nm. For samples containing CdS nanoparticles in luminescence spectrum were observed several distinct peaks at 425, 462 and 500 nm (excitation by a wavelength λ = 340 nm). By the method of transmission electron microscopy it was revealed that obtained semiconductor nanoparticles have spherical shape and size predominantly from 5 to 7 nm. Our work demonstrated that hairy root culture can be effective for biotransformation of the inorganic compounds into luminescent semiconductor nanoparticles.

Elastic and dielectric properties of aged polyethylene based composites with functionalized multi-walled carbon nanotubes

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Polymer nanocomposites are in the focus of global academic research of recent years due to enormous possibilities to obtain unique original materials with substantially improved exploitation properties, necessary for applications in energetics, electrotechnics, electronics, structural engineering and other relevant fields of national economy [1-5]. Unique properties of the nanocomposites are generally imparted by modifying the matrix polymer by addition of nanostructured fillers of various geometries.

Carbon allotropes, among them fullerenes, nanotubes and graphene, represent the most versatile class of nanostructured fillers. Introduction of carbon allotropes within polymer matrix is burdened due to the absence of functional groups on the surface of the nanofiller. Consequently, successful introduction of carbon nanofillers within polymer matrix requires some surface modification of the nanofiller, in spite of the fact that this can lead to certain impairment of it unique electrical, thermal and mechanical properties. Functionalization of carbon nanotubes with carboxyl, hydroxyl, acyl, amine and amide functional groups are most widely known [6-8].

The current research considers modification of thermoplastic polyolefines and polyolefine copolymers by means of functionalized multi-walled carbon nanotubes (MW-CNTs). Covalent and non-covalent functionalization routes (including carboxylation and treatment with ionic liquids) of MW-CNTs have been considered. The amount of neat and functionalized MW-CNTs in a polymer matrix has been changed in a rather broad range from 0,5 to 10,0 wt.%. The effectiveness of direct melting and masterbatch approaches has been compared for obtaining the nanocomposites with desirable dispersion of the nanofillers within the thermoplastic polyolefine matrix. MWCNTs dispersion patterns within the polymer matrix have been studied by means electron microscopy. Electric and mechanical performance of the nanocomposites has been characterized by means broadband dielectric spectroscopy as well as dynamic mechanical thermal analysis. The factors of external environment (UV irradiation, temperature, moisture content) on the electrical and mechanical properties of the aforementioned polymer nanocomposites have been also evaluated. Especial attention has been paid to evaluation of reinforcing efficiency of MW-CNTs on the accelerated weathering impaired polymer nanocomposites, the aspect investigated relatively scarcely in the scientific literature.

Results of the investigation testify that proper choice of the manufacturing technology allows considerably improve distribution of the nanofiller within the thermoplastic polymer matrix. Besides it has been observed that by increasing the nanofiller content within the polymer matrix elastic and dielectric properties of the investigated nanocomposites can be considerably increased. Especially remarkable is protective role of MW-CNTs on the properties of UV impaired polymer nanocomposites.

Thermal and Thermo-Mechanical Properties of Polyurethane Modified With Graphite Oxide and Carbon Nanotube Nanoparticles

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Research and development in novel functional composites remained to be a hot topic for last decades. Exploitation properties of polymers are not sufficient for all needs and have to be enhanced. Various nanoscale fillers are generally added to improve the polymer material performance properties. The proposed paper deals with the new formulations of polyurethane (PU) containing carbon nanoparticles of different shape. The aim of this investigation is synthesis of the Graphite oxide (GO) by the use of the method [1]. Then, we aimed to fabricate the PU/GO nanocomposites with very small content of nanoparticles (0.05, 0.1, 0.3 wt.%.) and analyze their properties. As reference, for comparison reason, we have used as-prepared PU nanocomposite filled with commercially available multi wall carbon nanotubes (CNT, Nanocyl 7000). The mixtures of the CNT and GO (1:1) nanocomposites were also used. The fabrication of the PU nanocomposite is following: nanoparticles are dispersed in laboratory prepared rapeseed oil based polyol with the use of ultrasonic treatment [2]. The polyol-nanoparticle mixture is cured with the disiocyanate at room temperature. As a whole 9 different PU/CNT, PU/GO and PU/CNT/GO nanocomposite formulations containing different nanoparticles content are fabricated.

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) Storage modulus versus temperature and (b) Damping coefficient versus temperature of PU/GO nanocomposites.

Thermal and thermo-mechanical properties of the prepared specimens were investigated. Thermo-Mechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA) and Light Flash Analysis (LFA) measurements were performed. Linear thermal expansion coefficient was calculated from the curve slopes in TMA experiments. Storage, loss moduli, damping coefficient were calculated from DMA tests. Figure 1(a) and (b) showed the experimental data for PU/GO nanocomposite as an example. Thermo-mechanical characteristics for the nanocomposites in comparison with ones of PU were improved. Thermal diffusivity, thermal conductivity and specific heat of the materials were calculated according to the Cape-Lehman model. Those significantly enhanced after incorporation of carbon nanoparticles. The processed novel polyurethane formulations are proposed as adhesives, coatings and composites matrix with enhanced thermal and thermo-mechanical properties.


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Transmission optical spectra of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ thin films deposited by magnetron sputtering

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Ecological reasons and high piezoelectric parameters stimulate growing interest to lead-free ferroelectric Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) and solid solutions based on it. During the last decade it has been reported that NBT thin films were prepared by chemical solution decomposition, pulse laser deposition and radio field magnetron sputtering [1]. It was mentioned that obtained polycrystalline thin films were probably multiphase and characterized by high coercive field and conductance. In the abstract we report the technology of NBT thin films magnetron sputtering and results of optical transmission spectra measurements.

The NBT ceramic target shaped as a tablet of 40 mm diameter was sintered from stoichiometric oxides mixture. To clear up the role of the substrate, two types of materials were used: fused quartz and silicon single crystal. Thin films were deposited by magnetron sputtering in Ar atmosphere with pressure of about ~10 mTorr. The polycrystalline NBT films with thickness from 40 to 290 nm were obtained. The conditions of thermal annealing were optimized. The deposited thin films were crystallized at the temperatures from 500°C to 800°C in air.

XRD phase analysis of the prepared thin films shows presence of the reflexes from (100), (110) and other lattice planes of NBT structure. The reflex from (111) plane [1] is not detected, presumably due to formation of the textures with mainly oriented crystallites. In the XRD patterns there are some additional weak peaks from unidentified phase.

 Optical transmission spectra measured in a wavelength range 280–500 nm are given in Fig.1 for NBT films and for bulk single crystal ($d = 110 \mu$m). It is evident, that self-absorption edge sufficiently depends on films width d and shifts to short wave length side as d decreases. The Fig.1 shows that increasing of the films thickness from 40 nm to 290 nm leads to shift of absorption edge to long wavelength region. To calculate an optical band gap $E_g$ from the experimental spectra, one has to know direct or indirect electronic transitions determine self- absorption edge [2]. Our results show, that $E_g$ decreases monotonically as width $d$ increases from 3.76 eV (40 nm) to 3.41 eV (290 nm). For the film with $d = 290$ nm optical band gap approaches $E_g$ value of bulk crystal (3.19 eV). Presumably such behavior could be attributed to dependence of unit cell on films width just as it was observed for NBT films in [3].

![Figure 1](image_url)

Figure 1 The optical transmission spectra of NBT films deposited on fused quartz substrate (curves 1-5) and bulk single crystal (curve 6)


Effect of Iridium Ions on the Optical Spectra of Zinc-Iridium Oxide Thin Films

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Although the transparent conducting oxides (TCOs) have broad range of application, minimal work has been done on the active device fabrication using TCOs. This is because most of the aforementioned TCOs are n-type semiconductors [1, 2]. Corresponding p-TCOs, which are essential for junctional devices, were surprisingly missing in thin film form for a long time, until in 1997 Kawazoe et. al. [3] reported the p-type conductivity in a highly transparent thin film of cupper aluminium oxide. Since this initial publication of p-TCO a variety of p-TCOs have been investigated. Despite these recent advances limitations on transparency and low conductivity continue to restrict the technological applications of p-TCOs [4]. Several precious metal based transparent oxides have also shown p-type conduction including crystalline ZnM2O4(M= Ir, Rh, Co)[5-7]. This paper presents results of the absorption spectra investigation of zinc-iridium oxide thin films. Zinc-iridium oxide thin films were deposited by reactive DC magnetron sputtering on various substrates. Iridium concentration was controlled by iridium amount on the zinc target erosion zone and oxygen to argon ratio.

Zinc-iridium oxide thin films are transparent in the visible region. Iridium concentration increase leads to attenuation film transparency. The absorption spectra in the visible range contain broad bands with maxima at 446 and 710 nm. Iridium concentration growth shifts the absorption edge toward to the shorter wavelength compared to the crystalline ZnO and leads to higher absorption coefficient in the visible range. In the near infrared and infrared regions the absorption spectra of zinc-iridium oxide thin films with different iridium ions concentration demonstrate two broad bands with maxima at about 1100 nm and 3330 nm. The 1100 nm band intensity in the zinc-iridium oxide thin films increases with the iridium concentration growth, reaching a maximum at iridium concentration of 29 %. The further enhance of iridium concentration up to 41% intensifies the band of 3330 nm. At the iridium concentration from 47 to 56 % the ratio of the intensities of the 1100 and 3330 nm bands does not change.

Iridium has the ability to form compounds in many different oxidation states. The most stable ones are+3 and +4. The mixed-valence nature of the Ir ions (Ir3+ and Ir4+) has been established observed in the previous study [8, 9]. It is shown that the observed absorption bands of zinc-iridium oxide thin films obtained by reactive DC magnetron sputtering are associated with iridium ions in different valence states. In the visible range the absorption spectra are observed band due to the presence of Ir4+ ions. The excess charge of Ir4+ is compensated by cation vacancies. Recently, an oxide composed of zinc and iridium with the same spinel structure has been produced in thin films [6, 10]. In crystal structure of ZnIr2O4 of normal spinel, the Zn+2 ions occupy octahedral positions Disordering leads to a transition of the Ir+3 ions in a tetrahedral environment. At low concentrations of iridium in the ions occupy octahedral positions. Iridium concentration growth leads to a partial transfer of Ir+3 ions in tetrahedral positions. At iridium concentration more then 47% further transition of Ir+3 in tetrasite does not occurs. Iridium concentration increase leads to the formation of the inverse spinel structure.

Effects of oxygen deficiency in epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ films

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Perovskite-type oxide La$_{0.7}$Sr$_{0.3}$MnO$_3$ belongs to a family of manganites with strongly correlated electron systems that exhibit colossal magnetoresistance. It is known that Sr doping induces holes in La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) that leads to a complex phase diagram with a number of transitions between antiferromagnetic metal, paramagnetic metal, paramagnetic insulator, ferromagnetic metal, ferromagnetic insulator, and spin-canted insulator states. Recently, electrostatic doping with holes has been realized in epitaxial heterostructures of LSMO and ferroelectric thin films. The metal-insulator phase transition controlled by hole doping can enable novel applications. Acquiring more knowledge and understanding of this transition is thus of both fundamental and practical importance. On the other side, it is well known that properties of perovskite oxides are very sensitive to oxygen stoichiometry. In particular, oxygen deficiency in epitaxial (La,Sr)CoO$_3$ and (La,Sr)MnO$_3$ films can result in ordering of oxygen vacancies and formation of brownmillerite crystal phases. Phase diagrams, electronic structure, and properties of such films are practically unstudied.

Here we report on experimental studies of the effects produced by oxygen deficiency on electronic properties in the epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ films. The films were grown on single-crystal SrTiO$_3$ and LSAT substrates by pulsed laser deposition. Proper oxygen stoichiometry in the films was achieved by using high oxygen pressure during deposition and post-deposition cooling. Oxygen deficiency was created by high-temperature annealing (400 – 700°C) in atmosphere of hydrogen, argon, or nitrogen. Re-oxidation was performed by annealing in oxygen atmosphere. The electronic structure and excitations were inspected by studies of optical constants in a wide spectral region from infra-red (photon energy 0.03 eV) to vacuum ultra-violet (9 eV). The measurements were performed using variable angle spectroscopic ellipsometry. The results are discussed in terms of structural and electronic phase transitions.
Young’s Modulus for TiO$_2$-based Nanotubes

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Theory of elasticity [1] proves that the Helmholtz free energy determines the Young’s modulus of any elastic material at the isothermal deformation. However, usually, to obtain the Young’s modulus from the results of computer simulations the change in the total energy of the nanosystems is computed, thus neglecting the thermal contributions. Consequently, the correct way to compute the Young’s modulus $Y(T)$ is to use the following definition:

$$Y(T) = \frac{1}{V_0(T)} \frac{\partial^2 F(T)}{\partial \varepsilon^2},$$

where $F(T)$ is the Helmholtz free energy, $\varepsilon$ is the strain and $V_0(T)$ is the equilibrium volume.

In this work the temperature dependence of Young’s modulus for the hexagonal TiO$_2$-based nanotubes with the different chirality was calculated using Equation (1). The strain- and temperature-dependent Helmholtz free energy was computed in quasiharmonic approximation. The calculations of phonon frequencies and the Helmholtz free energy in the temperature interval $T = 0$ - 600 K have been performed using molecular mechanics and lattice dynamics simulations with the help of GULP computer code [2]. The force field model of Matsui & Akaogi [3] was applied in these computations.

Figure 1a demonstrates $Y(T)$ functions of four zigzag single-wall (SW) nanotubes (NTs) and the consolidated single-wall (CSW) (16, 0)$@$(24, 0) nanotube. The CSW nanotubes are produced through merging together the cylindrical SW constituents of the multi-wall nanotubes [4]. The results of present investigation demonstrate that the reduction of the nanotubes stiffness value achieves 6-7% of Young’s modulus value and the unit cell vector increase on heating is approximately 0.3-0.4% in the considered temperature interval, see Figure 1b.

![Figure 1a](image1.png)

![Figure 1b](image2.png)

Figure 1 Temperature dependence of SW (10, 0); (20, 0); (30, 0); (40, 0) NTs properties: (a) the Young’s modulus; (b) the length of NT unit cell vector.

The Young’s modulus values of the zigzag ($n$, 0) SW nanotubes are higher than those of the armchair ($n$, $n$) ones. The stiffness of some CSW nanotubes is lower than that of corresponding SW constituents, for example in (16, 0)$@$(24, 0) and (12, 12)$@$(18, 18) cases. The Young’s modulus value of the CSW (12, 12)$@$(16, 16) nanotube increases significantly in comparison with the ones of the (12, 12) and (16, 16) nanotubes. However the Young’s modulus value of the CSW (8, 8)$@$(12, 12)$@$(16, 16) nanotube exceeds the $Y$ value of the (16, 16) nanotube only by several GPa units. This difference can be explained by the different structural reconstructions taking place during the merging process. At the same time, the temperature dependence of the Young’s moduli of all considered CSW and their SW constituents is similar.

Enhancement of superconducting critical temperature in In-opal nanocomposites with large granules

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Recent experiments on single isolated hemispherical Sn grains [1] have reported large oscillations in the size dependence of the energy gap in the region around 10 nm, which is in full agreement with the theoretical prediction [2]. However some puzzles are still present. For instance, a substantial (~20%) monotonic enhancement of the superconducting gap has been observed in the largest grains up to 30 nm [1, 2] that cannot be explained by shell effects or surface phonons. It has been suggested that this enhancement is caused by spatial inhomogeneities of the Cooper pairs' density of probability [3]. A similar improvement of superconductivity is predicted for other weakly coupled superconductors. Motivated by these experimental and theoretical investigations we explore the possible shell-like and inhomogeneous pairing effects in Indium-opal nanocomposites with large grains. Strictly speaking, phase coherence cannot exist in a single isolated grain since the number of particles is fixed. Therefore, the phase of the order parameter is delocalized inside the grain. The situation is different in a Josephson array composed of such nanogranules. In principle, this engineered granular material could maintain phase coherence and have a higher critical temperature $T_c$Array than a bulk non-granular sample $T_c$ due to size effects [4]. Indeed, the studied samples show size dependent critical temperature higher than bulk $T_c = 3.41$ K. The highest $T_c$Array = 3.61 K among In-opal samples with rather large nanogranules (up to 90 nm) has been observed. We ascribe the enhancement of superconductivity in nanocomposites with large granules to the model of inhomogeneous pairing [4]. The superconducting transition in the magnetic field has been also investigated. It is found that the critical field of the nanocomposites is considerably increased relative to that of homogeneous bulk indium sample. This is consistent with transition from type-I to type-II superconductivity in mesoscopic structures.

High tunable BaSnTiO$_3$ and BaZrTiO$_3$ thin films for microwave applications


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Ferroelectric thin film materials are employed in a wide range of technological applications. Among these materials the barium titanate (BaTiO$_3$), one of the most studied perovskite ABO$_3$ ferroelectrics, is used in a large variety of applications like capacitors, thermistors, transducers, and nonvolatile memories in the microelectronic industry. Due to a rapid development of electronics in the last decade requirements to material parameters are increased. One of the ways to improve dielectric properties of BaTiO$_3$ is the doping of it with different elements such as Zr, Sr, Sn, Hf, Ce, and Y. In particular the use of Zr and Sn as doping materials leads to the decrease of microwave losses, dielectric constant and leakage currents, improvement of pyroelectric properties, etc. [1-4]. Note, that properties of BaTiO$_3$ with Zr and Sn doping are studied mainly for use in dynamic random access memories (DRAMs), while their properties in a paraelectric state at high frequencies for microwave applications are not considered. This work aims to fill this gap.

Sandwich ferroelectric varactors on the base of Cu/BaSnTiO$_3$/Pt and Cu/BaZrTiO$_3$/Pt structures were investigated. To form these structures, BaSn$_{0.5}$Ti$_{0.5}$O$_3$ (BSnT) and BaZr$_{0.5}$Ti$_{0.5}$O$_3$ (BZT) thin films of thickness 0.4 μm were deposited on prepatterned platinumized 0.5 mm thick single crystal r-cut Al$_2$O$_3$ substrate by magnetron sputtering. The top copper electrodes were formed by thermal evaporation in a vacuum at T–250°C, followed by photolithography and Ar ion milling.

The dependencies of the capacitance of the BSnT and BZT capacitor structures on the bias voltage are presented in Figure 1. Parameters were measured at 2 GHz frequency. The presented curves show that tunability value for both structures correspond to K > 3 (K=C(0)/C(U$_{max}$)) at the electric field strength E = 60 V/μm. The level of dielectric losses is admissible for the application in microwave devices for both materials. The tunability of the capacitor structures based on BSnT and BZT films is comparable to the best published results of microwave structures based on barium-strontium titanate thin films.

![Figure 1 Dependencies of the capacitance and dielectric losses on voltage for ferroelectric capacitors based on a) BSnT and b) BZT.](image)

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[4] D.Y. Wang, P. Yun, Y. Wang, H.L. W. Chan, C.L. Choy, Influence of oxygen partial pressure on the structural and dielectric properties of Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ thin films grown on (LaAlO$_3$)$_{0.6}$(Sr$_2$AlTaO$_6$)$_{0.4}$ (001) using pulsed laser deposition, Thin Solid Films, 517, p.2092-2098 (2009).
Ferroelectric BaSrTiO$_3$ films structured by an intermediate annealing during the deposition

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In recent years, there is stable interest in ferroelectric (FE) thin films that is related to the possibility of creating new electrically controlled microwave devices. In this case the crystal structure of FE films has to possess the minimum of lattice defects in order to maximize the tunability and to minimize the dielectric losses [1]. In this work the method of multicomponent oxide films structuring by an intermediate annealing during the ion-plasma deposition process is proposed for the first time. The point of the method is the successive deposition of ferroelectric layers with intermediate annealing in oxygen ambient. The intermediate annealing allows to form dense, homogeneous crystal structure, which is free from defects in the anionic and cationic subsystems. Absence of sputtered atoms flux from plasma to substrate during the intermediate annealing allows the embedding of the diffusing adatoms into the growing crystal lattice without the secondary nucleus formation on the film surface [2]. Sandwich capacitors based on the Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ films with bottom platinum and top copper plates were fabricated by method mentioned above. In figure 1 relative capacitance vs. voltage curves for intermediate annealed capacitors (var) are presented in comparison with the best samples of the capacitors based on the same composition film deposited at the continuous process with constant conditions (const). The tunability of BSTO ferroelectric thin film varactors of about 5 times has not been reported before this work.

Dielectric losses in ferroelectric films investigated were estimated at (1-2) GHz by the resonance measurements of the ferroelectric film based planar capacitors [3]. Ferroelectric films fabricated with intermediate annealing demonstrated the decreasing of the average dielectric losses from tan$\delta$ = 0.017 (const) to tan$\delta$ = 0.01 (var).

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Highly oriented BaSrTiO$_3$ films on sapphire graded by an substrate temperature variation during the growth


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In recent years, there is stable interest in ferroelectric materials, in particular (Ba,Sr)TiO$_3$ (BST), that is related to the possibility of creating new electrically controlled microwave devices [1]. Ferroelectric materials are attractive for microwave devices due to two factors: the strong electric-field-dependent dielectric permittivity and the relatively low dielectric loss at microwave frequency.

Today, rapidly developing field of physics of ferroelectric materials is the creation and study of structures with a gradient composition: gradient ferroelectrics. Typically, such structures are prepared layer by layer from several sources. It is assumed that graded ferroelectric structures can be free from drawbacks of homogeneous systems and reveal novel properties [2].

Commonly, a mismatch in lattice parameters and thermal coefficients between the growing film and the substrate would cause difficulty in realizing excellent crystallinity of heteroepitaxial layers, due to appearance of dead layer on the interface. Insertion of a graded buffer layer between the film and the substrate seems to be effective in improving the crystallinity of growing films. Such a buffer layer could have a composition different from the main part of the film, hence a different lattice parameter. Recently [3] we have shown that the composition (and lattice parameter) of the polycrystalline BSTO films grown by magnetron deposition on sapphire substrate is strongly correlated with the deposition temperature. Therefore, by changing the deposition temperature during the film growth we can change the Ba/Sr ratio and, hence, adjust the lattice parameters of the film and the substrate and improve the crystallinity of the BSTO layer.

Therefore, in this work the method of structuring multicomponent films by the deposition temperature variation during their growth is suggested. This approach allowed for the first time to grow predominantly oriented BST films on sapphire without orienting underlayers and to achieve enhanced microwave characteristics of the related varactors.

In figure 1(a) X-ray diffraction pattern for the structured BSTO film on a pure sapphire (var) is presented in comparison with the same composition film deposited at the process with constant temperature conditions (const). Relative capacitance vs. voltage curves of capacitors based on these films are presented in figure 1(b).

Thus we have demonstrated that this approach improves the crystallinity of a graded BSTO film on sapphire, opening up the new practical application of BSTO films with physical properties modified by structuring the crystal lattice during the film growth.

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Properties of thin film ferroelectric multilayered structures “diamond/SiC/BaSrTiO$_3$/Cr/Cu”


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Ferroelectric (FE) films have received much attention as promising materials for the creation of microwave tunable devices. The most extensively studied ferroelectric materials for the use at microwaves are solid solutions of barium strontium titanate (BSTOP) in the paraelectric state. Voltage controlled passive tunable filters, continuously variable phase shifters, active frequency converters, parametric amplifiers can be realized on the basis of FE BSTOP films [1]. However, capacitance tuning under high power can lead to the nonlinear distortion of the operating signal, due to the overheating of the FE material and, as a consequence, undesirable changes in the capacitance [2]. The planar construction of microwave devices based on the ferroelectric film deposited on a high heat conducting substrate should radically increase the power handling capability as compared to semiconductor elements. In this case one of the most suitable substrate materials is a diamond. The devices based on diamond are expected to be operated under extreme conditions such as high temperatures and high power environments. The combination of ferroelectric oxides and diamond would find a lot of high power microwave applications. So far, however, there has been no successful work on the direct growth of BSTOP films on diamond because of the extremely high difference in thermal expansion coefficients of these materials.

In this paper, we report the first successful attempt of the growth of BSTOP films on polycrystalline diamond with the silicon carbide (SiC) sublayer, which compensates the thermal expansion difference between the FE film and the diamond substrate, and the characterization of the electrical properties of metal/BSTOP/SiC/diamond structure. It should be noted, that electrically tunable BSTOP FE structure on diamond substrate is realized for the first time.

Deposition of silicon carbide SiC buffer layers on diamond substrate was performed by high-frequency magnetron sputtering of the ceramic target in pure Ar at a pressure of 2 Pa. The temperature of film deposition was 800°C. Ferroelectric film Ba$_2$Sr$_{0.5}$TiO$_3$ was deposited by high-frequency magnetron sputtering of the ceramic target in pure oxygen atmosphere at a pressure of 2 Pa onto the SiC/diamond heated to 700°C. A copper film with Cr sublayer was deposited onto the BSTOP film to form electrodes. A capacitor structure was produced by standard lithographic processing. Measured dependencies of diamond/SiC/BSTOP/Cr/Cu capacitance on bias voltage are presented in Figure 1(a). Capacitance dependence on temperature is presented in Figure 1(b). This work was partly supported by RFBR, research project No. 13-02-12096 ofi-m, by the Ministry of Science and Education of the Russian Federation and by Act 220 of the Russian Government (Agreement No.14B25.31.0021 with the host organization IAPRAS).

Electrospinning of nano threads

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Thin polymer fibers are widely used in filters, absorbent materials, water-repellent fabrics, desalination, etc. [1-4]. These threads are obtained by placing the electrospinning polymer solution or melt into a strong electric field. Solution forms Taylor cones, from which large amounts of nano threads are created. As they move towards the substrate, they become thinner. Under these conditions, it is possible to experimentally measure single filament formation and its movement to the substrate using high-speed video cameras. However, it is also important to know the underlying phenomena governing the electrospinning process. Then it is possible to determine the properties of the solution that maximize the spinning performance and provide the desired thread diameter and structure. In this work, Newton's equations are solved at closed current supply (current here consists of ions that are on the surface of the thread and move together with the thread, as well as of the additional ions that flow into the thread from the source). The thread motion kinetics are calculated in this work, along with kinetics of thread speed variation in space, its diameter kinetics, surface charge density kinetics, spinning performance dependencies. In addition, this work determines the conditions under which a stable thread is formed (i.e., the thread reaches a certain stable length).

In this model, a thread is considered a constant-volume cylinder with one of its bases constant, while the diameter of the other base decreases with increasing thread length. The thread has a surface charge, and this charge in the external electric field makes the cylinder to increase in length until it reaches the opposite electrode. The model does not take into account the viscosity of the solution, but takes into account the surface tension (it is assumed that there is no solution mass injection, but this can be taken into account in the future).

After performing the calculations according to conditions presented in Figure 1, it is obtained that the total surface charge of the thread increases by 11% during the time needed for the thread to reach the other electrode – this additional charge is injected from the source. The results of calculations for the other cases indicate that the smaller the initial surface charge density, the larger the additional charge injected during the spinning process and consequently the lower the productivity of spinning. It is shown that the thread can be stable (neither lengthen nor shorten), if its length is less than half of the distance between the electrodes. Otherwise, the thread must increase in length until it reaches the opposite electrode.

Properties of Al$_2$O$_3$ and TiO$_2$ films atomic-layer-deposited using hydrogen-free precursors

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Studies performed in last few decades have demonstrated that TiO$_2$ and Al$_2$O$_3$ thin films prepared by atomic layer deposition (ALD) can be applied in micro- and nanoelectronic devices and in optical as well as in different kinds of protective coatings. In order to ensure sufficient quality of the films the low impurity content is frequently needed. Hydrogen is one of the impurities, which remains in the films due to incomplete deposition reactions and is frequently present in the films prepared by ALD. Unfortunately in some applications, e.g. in anticorrosion coatings or dynamic random access memory capacitors, the possible hydrogen contamination of films may markedly reduce the material quality. For this reason, methods for deposition of TiO$_2$ and Al$_2$O$_3$ from chlorides and ozone were developed in order to avoid application of precursors that could leave hydrogen in the films [1, 2].

The goal of this study is to reveal how the change of the oxygen precursor from H$_2$O to O$_3$ influences the phase composition, morphology and other parameters of TiO$_2$ and Al$_2$O$_3$ binary thin films as well as ternary films based on these oxides.

For that purpose X-ray reflection method was applied to determine the thickness, density and surface roughness of the films. To characterize the crystal structure the X-ray diffraction and the Raman spectroscopy methods were applied. The mass thicknesses and impurity contents of the films were measured by X-ray fluorescence spectroscopy. In order to determine the refractive indices and obtain supporting information on the thicknesses of the films, we employed spectroscopic ellipsometer. Electrical properties of the films were studied in metal-oxide-metal structures.

According to the results obtained, the replacement of H$_2$O for O$_3$ caused considerable changes in the properties of films. For instance, TiO$_2$ films deposited from hydrogen-free precursors showed lower surface roughness values and lower leakage current densities compared to the films deposited in H$_2$O-based ALD process. In addition, high-pressure high-density TiO$_2$-II phase was more preferentially formed in epitaxial films deposited on $\alpha$-Al$_2$O$_3$(001) substrates from hydrogen-free precursors than in similar films deposited in H$_2$O-based process. Characterization of ternary films revealed superior dielectric properties of those deposited in hydrogen-free process.

Carbon nanotube reinforced ceramic matrix composite based on magnesium aluminate spinel

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Insertion of carbon nanotubes (CNT) into ceramics gives significant improvement of characteristics of composite constructional material due to their specific microstructure, chemical inertness and excellent mechanical properties. The significant increase of fracture toughness and flexure strength after CNT insertion was demonstrated for alumina matrix using hot-pressing, spark plasma sintering and pressureless vacuum sintering techniques [1-3]. Magnesium aluminate spinel possesses the comparable with alumina thermo-mechanical characteristics but has lower density, better chemical stability, which is important for particular applications. Recently, carbon nanotube (up to 16.7 vol.% CNT) –magnesium aluminate spinel nanocomposites were obtained by hot-pressing method [4].

In the present study a composite material based on magnesium aluminate spinel reinforced with a large amounts of nanotubes (by 30 vol. %) was fabricated using hot-pressing technique. For reinforcing of ceramics we used multiwall CNT of 20–40 layers, obtained by pyrolysis of methane (500 °C with Ni as a catalyst). The synthesized magnesium aluminate spinel powder was bimodal and contained two kinds of agglomerates with average size 1.2–1.3 microns and about 200 nm, which, in their turn, consisted from particles around 1 nm. The sintered ceramic samples demonstrated uniform bulk distribution of CNT.

![Fig. 1a](image1.png) ![Fig. 1b](image2.png)

Fig. 1. Microstructure of CNT- magnesium aluminate spinel composite

The microstructure of composite samples was investigated by SEM — scanning electron microscopy (Jeol JSM-5910LV) and their fracture toughness and microhardness were evaluated according to the indentation results by Vickers hardnesstest. The microstructure of the composite at a magnification of 40,000 times shows that carbon nanotubes forming the frame structure binding the neighbor grains in the matrix of composite (Fig. 1a). In addition, the nanotubes are agglomerated in the places of crystal defects and prevent from forming the closed pores in the magnesium spinel matrix (Fig. 1b).

Relationships between Experimental Studies and Quantum Chemical Calculations of Hydrogen Sorption by Mg-based Nanostructured Composites and Clusters

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The aim of this study is to find relationships between the experimental data on H sorption and desorption behavior of nanostructured alloys and composites based on light metals such as Mg and Ti and precise quantum chemical calculations that are focused on studies of the interaction of hydrogen with light clusters of the mentioned metals, including those doped with other atoms. Such a combined approach will enable optimizing search of the novel materials based on light metals with improved hydrogen storage performance.

By using PCT measurements, programmed thermodesorption, in-situ high temperature X-ray diffraction, stepwise hydrogenation of the surface of compact specimens and metallographic examination, it was shown that modified microstructure of the eutectic alloys of Mg with RE metals and nickel improves the h/d behavior, and that the microstructure can be favorably modified by varying the parameters of the intensive plastic deformation that enables to decrease the crystallite sizes of the Mg phase down to 100–200 nm. Enhanced h/d kinetics was observed for the modified alloys which exhibit highly disperse microstructure, developed network of interphase boundaries, submicro- and nanosized crystallites of the Mg phase as well as the phases REHx and Mg-Ni, catalyzing the dissociation of H2 molecules and thereby favor the fast hydrogen diffusion. Thus, an amount of hydrogen of about 5.0 mass.% absorbed by a pristine alloy at 20 bar of H2 and 350°C within 12 min, substantially decreases to about 2 min in the case of the ECAP-ed Mg-Ni alloy. Metal hydride composites with nano-carbon additives have an improved hydrogen sorption performance. It was shown how the carbon additives alter the mechanism of H release from the MgH2 phase in the composites at temperatures lower than 300°C.

On the other hand, precise quantum chemical calculations with the use of density functional theory were performed in order to determine the potential energy surface of the elementary dehydrogenation reactions of Mg-based molecular clusters, both binary Mg23H40 and doped ones LMg22H40 (L = Ti and Ni). The effect of the dopant nature and the electronic state multiplicity of the clusters on the energies and activation barriers of the reactions of Mg-based clusters are considered. The energy barriers of hydrogen migration on the surface of the clusters are estimated. It is shown that the ground state of the system H2 + NiAl12 is the singlet state, and that this state determines the interactions between the reagents.

For both doped clusters TiMg22H40 and NiMg22H40 the most favorable is an isomer in which the dopant is located on the surface of the cluster and surrounded by four hydrogen atoms. An isomer in which the dopant is located in the center of the cage Mg22H40, has energy higher by about 40–60 kkal/mol, with the Ti atom being surrounded octahedrally, and Ni being surrounded by four neighboring atoms. Doping with Ti and Ni lowers the energy barrier of the dehydrogenation reaction by about 20 kkal/mol, as compared with the binary hydride Mg23H40. Also, Ni decreases the energy of the reaction by about 7–8 kkal/mol as compared with Mg23H40. In the case of Ti this decrease is weaker. The separation of H2 molecule from the clusters studied is accompanied by a considerable deformation of the structure of products Mg23H18 and LMg22H38, which is due to multiaxial intermolecular rearrangements.

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Phosphorized zirconium oxide nanoparticles / ionic liquid/ SPEEEK composite membranes for medium temperature fuel cells

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In alternative energy devices the medium temperature polymer electrolyte membrane (PEM) fuel cells are of growing importance due to higher efficiency and better choice of catalysts. It resulted in rising interest in field of ionic liquids as components for polymer membranes due to higher temperature (100-200 °C) and electrochemical stability [1].

The sulfonated polyetheretherketone (SPEEK) polymer was used for composite formation [2]. Ionic liquids (IL) synthesized and examined in this paper include: 1-butyl-2,3-dimethyl-imidazolium dimethylphosphate, 1,2,3-trimethylimidazolium dimethylphosphate, 1,3-dimethylimidazolium dimethylphosphate [2]. The mechanical stability test was done for selection of IL (20-200°C). At IL content higher than 15-20 wt.% typically the temperature range is limited to 140-150 °C. Phosphorized zirconium oxide nanoparticles prepared according following synthesis procedure [3]. SPEEK and appropriate amount of IL was dissolved in dimethylformamide by stirring the solution for 2h and following by dispersion of phosphorized zirconium oxide nanoparticles. Solution was poured in Petri dish which then was left in oven for 24h at 70°C evaporating the solvent. Structures of ionic liquids obtained in this work have been determined by 1H NMR and IR spectroscopy, but water content by Karl Fischer method. Thermal stability of ionic liquids and membranes was controlled by thermogravimetry analysis. Conductivity was obtained from impedance measurements using Autolab set-up in temperature range 20-200°C. For measuring stress-strain curves at room temperature, the Tinius Olsen H1K-S universal testing machine was used.

Mechanical properties of sulfonated polyetheretherketone composite membranes with ionic liquids and inorganic nanoparticles at elevated temperatures

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A fuel cell is an excellent alternative to an internal combustion engine, particularly because of its eco-friendly nature and high energy utilization efficiency. Typically, the water content limits the technological applications (high water partial pressure, limited choice of the fuel, etc.). Hence, the best strategy should be to minimize the existence of liquid water. It might be achieved in composite polymer membranes and ionic liquids (ILs) are suitable for composite formation because of their low vapor pressure, wide electrochemical windows, high chemical and thermal stability, and good ion conductivity. Therefore, IL-based electrolytes were widely studied for high-temperature anhydrous fuel cells [1-2]. A pressurized gas is typically used as a fuel (hydrogen, oxygen, chlorine) and mechanical strength of membranes is crucial. However, by adding the ILs the mechanical strength strongly depends on temperature due to the plasticizer effect [2-5]. In this work, mechanical properties of composite sulfonated polyetheretherketone (SPEEK) membranes with different ionic liquids: derivatives of methyl-imidazolium phosphates and chlorides have been investigated.

For measuring stress-strain curves at room temperature, Tinius Olsen H1K-S universal testing machine was used. For measurements, membranes were cut in bone shaped pieces with width of about 5 mm in narrowest point. Measurements then were taken with deformation speed 1 mm/min (for determining Young's modulus) and 10 mm/min for the determination of tensile characteristics up to the sample rupture (until sample breaks).

Testing at elevated temperatures was done using in-house equipment consisting of tension testing stand with controllable motor and heating camera, autotransformer for maintaining heating mode, Pico ADC-24 data logger, and thermocouple interface for controlling temperature [5]. Deformation speed was set to 50 mm/min. Measuring was done in a range from a room temperature to 200 °C.

Figure 1 Strain-stress curves at increased temperature for SPEEK. 1, 3-dimethylimidazolium dimethylphosphate composite membrane.

Surface wettability properties of ZnO nanorod layers

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In this paper we investigated the effect of aging on the surface wettability properties of the zinc oxide nanorod layers prepared by simple and low cost chemical spray pyrolysis (CSP) method. Possibility of controlling wetting behavior might be important for potential applications of ZnO nanorod layers as photocatalytic and self-cleaning surfaces, antireflection coatings, substrates to anchor biofunctional agents [1] and in fabrication of ZnO nanorod solar cells by solution techniques [2].

ZnO nanorod layers were grown onto indium tin oxide (ITO) covered glass substrate by CSP method from ZnCl2 aqueous solutions (c=0.1 mol/L). ZnO nanorod layers were characterized using optical spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), water contact angle (CA) measurement and X-ray photoelectron spectroscopy (XPS).

According to XRD studies, ZnO nanorods show c-axis oriented hexagonal crystalline structure. The SEM images show that ZnO nanorods with different dimension (l=450-1200nm, d=200-300 nm, where l – length, d – diameter) and uniform coverage can be prepared by CSP method. Figures 1a and 2a present SEM images of ZnO nanorod layers with the ZnO crystal aspect ratios (l/d) of 6 and 1.5, respectively.

The surface wettability of the sprayed ZnO nanorod layers was evaluated by water CA measurements. It was found that fresh ZnO nanorod layers showed water CA of 25° (Fig.1b and 2b), irrespective of their aspect ratio. However, after two weeks of storage, ZnO nanorods layers with higher aspect ratio still show the CA of ca 25° (Fig.1c) but ZnO nanorod layer with lower aspect ratio practically lost its hydrophilic nature as CA increases up to 80° (Fig.2c). Annealing of ZnO nanorod layers at 400 °C for 30 min in air transforms the ZnO nanorod layer surface to more hydrophilic (CA=6°), irrespective of the aspect ratio of the ZnO nanorod layers (Fig.1d and 2d). Further storage of the annealed samples for two weeks in plastic boxes increases water CA from 6° up to ca 100° (Fig.1e and 2e), which is also characteristic of one year old sample stored in a plastic box. XPS study to investigate the surface chemical composition is in progress. The effect of ZnO nanorod layer morphology and surface composition on layer wettability is discussed.

Figure 1. (a) SEM image of ZnO rods. Water contact angle of ZnO rods (b) after deposition; (c) after two weeks of storage; (d) after annealing at 400 °C; (d) after two weeks of storage after annealing.

Figure 2. (a) SEM image of ZnO rods. Water contact angle of ZnO rods (b) after deposition; (c) after two weeks of storage; (d) after annealing at 400 °C; (d) after two weeks of storage after annealing.


Theoretical modelling of nanodevices using embedded molecular cluster method

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One of the approaches for theoretical description of nanodevices is based on quantum transport theory. It is proposed by Gross with co-workers [1] and is combination of time-dependent density functional theory (TDDFT) with cluster model. When we theoretically describe nanodevice we have to treat the whole quantum system as two subsystems: small fragment of the system containing nanodevice (cluster) and the rest of the system containing electrodes. Problem "cluster in the field of the rest of system" is successfully solved in the frameworks of embedded molecular cluster (EMC) model with orthogonal wave functions. We have modified EMC model treating cluster embedding problem in the frameworks of one-electron approximation with non-orthogonal wave functions. We have proposed new cluster embedding scheme based on our approach and have demonstrated that our cluster embedding method radically reduce boundary effects in EMC model [2].

Our present aim is application of our cluster embedding method for quantum-chemical modelling of processes in nanosystems and calculation of electrical properties of nanodevices. We study possibility to combine our cluster embedding scheme with quantum transport theory approach of Gross et al. [1] based on time-dependent DFT. We demonstrate [3] that our cluster embedding method based on Hartree-Fock calculation scheme is compatible with DFT Kohn-Sham calculation scheme. Cluster embedding equations remain the same if instead of Fock operator we use Kohn-Sham Hamiltonian. Therefore, our embedding scheme may be combined with TDDFT. Our cluster embedding method is compatible with electric current calculation method based on TDDFT [1] if electron transitions are described correctly: occupied and vacant cluster states are localized in the cluster region in the same manner. We get occupied and vacant states of the same localization degree if instead of our initial cluster embedding equations [2] we use modified equations [4].

Method of Gross implies that wave functions of nanodevice central part are orthogonal to the wave functions of the electrodes. We show that approach for electric current calculation developed for orthogonal wave functions may be applied for non-orthogonal wave functions if we transform initial equations assuming that overlaps between wave functions are small [3]. We propose approach for calculation of electric parameters of nanodevices combining our cluster embedding method and TDDFT quantum transport theory of Gross et al. It gives us possibility for theoretical modelling of nanodevices from the first principles.

Quantum transport theory methods for electric current calculation may be applied if we use one-electron approaches. In this case we can easily construct one-electron density and get continuity equation for electric current. Treating processes in nanosystems it is possible to overcome limitations of one-electron approaches using configurations interaction (CI) and perturbation theory (PT) methods. Our cluster embedding scheme is compatible with both PT and CI methods, because solutions of modified cluster embedding equations [4] correctly describe electron transitions. One-electron density may be constructed for CI or PT many-electron wave function, too. But possibility to get continuity equation and expression for electric current when we use CI or PT methods requires further study.

Structural investigation of graphenic carbon materials obtained on nickel particles

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For graphenic carbon material (GCM) production a special nickel-carbon powders mixture was heated in inert atmosphere to a temperature of 1000°C and cooled to RT. As a result, a significant portion of the carbon material was transformed into GCM. The carbon material was extracted from the mixture and studied using scanning electron microscopy (SEM) Fig. 1, X-ray diffraction (XRD), and Raman spectroscopy.

Fig. 1 – Representative HRTEM images of different regions of GCM sample (a, b) – GCM sheets with some particles on the surface indicated with arrows, (c, d, e) – (002) fringe of some GCM sheets with the number of graphene layers from 7 to 14, (e, f, g) – onion-shaped particles on the surface GCM (indicated with arrows on a, b), (h, i) – amorphous particles detected on the GCM sheets.
New ion-exchanger nanocontainers with anti-corrosion effect

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New concepts of light design of materials used in aeronautical industry require new solutions for corrosion protection. Standard protective coatings which isolate materials surface from the environment and interlay different types of materials are effective only when no defect is presented. In the case of scratches and cut-edge corrosion they lose their properties. To avoid this drawback, coatings can be modified with corrosion inhibiting species. Corrosion inhibitors can be directly incorporated into coatings. However, the inhibitors could interact with the material which can result in deactivation of inhibiting properties, degradation of the polymer matrix, and delamination at metal/coating interface [1]. In order to diminish these negative effects, it is necessary to encapsulate the inhibitors. Some layered compounds are able to keep inhibitors in ionic form as a part of their own structure (interlayer). Since recently, nanocontainers based on layered double hydroxides (LDHs) are used for intercalation of anionic corrosion inhibitors [2-4]. Another family of layered compounds, bentonites, is promising as nanocontainers of cationic inhibitors [3,5]. LDHs and bentonites are available as nature minerals and can be easy prepared from relatively cheap reagents or even from wastes.

LDHs are known as ion-exchangers [5,6]. In LDH structure, positive charge of the layers of mixed metal M(II)-M(III) hydroxide is compensated by negatively charged layers (interlayers) of anions. The LDH nanocontainers are loaded with inhibitors and dispersed in the coating near the metal surface. They remain on standby until the corrosion conditions occur. Then the inhibitors are replaced by OH⁻ formed by the cathodic reaction of water reduction or by chloride anions from the aggressive environment. It results in a double active protection effect, namely the inhibitors release and trapping of the corrosion-active anions.

Bentonites are cation-exchangers. Bentonite consist of negatively charged alumosilicate sheets, between which inhibiting cations can be intercalated [5,7]. Release of the inhibitor is triggered by metal cations available in the environment. In the case of corrosion of coupled aluminium alloy and carbon fibre reinforced polymer the role of external cations can be played by Na⁺ available in the aggressive environment or Al³⁺ released from the material during its degradation.

In this work, the LDH nanocontainers were loaded with different types of inhibitors, organic (2-mercaptopbenzothiazol [3], 1,2,3-benzotriazole (BTA) [3], and inorganic (vanadate, molybdate and tungstate). In the case of bentonite nanocontainers, 1,10-phenantroline, 2,2-bipyridyl, 4,4-dipyridyl, BTA, 5% Cl–BTA, and 2-mercaptobenzothiazol were explored as organic inhibitors and Cerium(III) was used as inorganic one.

Chemical composition, crystal structure and microstructure of the obtained nanocontainers were characterized using x-ray diffraction and scanning electron microscopy. Preliminary results suggest the complete or partial intercalation of the inhibitors into the interlayers of the nanocontainers.

Structure analysis of rare earth activated glass-ceramics containing NaLaF$_4$ nanocrystals

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Lanthanide activated fluorides are promising materials for sensors, lasers, displays, solar cells, biomedical research and electroluminescent devices [1]. Glass samples with nominal composition 16Na$_2$O-9NaF-5LaF$_3$-7Al$_2$O$_3$-63SiO$_2$ (mol%) activated with 3 mol% one of following rare earth activator component: TbF$_3$, PrF$_3$, NdF$_3$ and DyF$_3$ were prepared by melting. Glass samples were converted to glass-ceramics by thermal treatment at 600°C, 700°C or 800°C temperature for 30 min.

NaLaF$_4$ crystalline phases have been observed in X-ray diffraction for all heat-treated at 600°C and 700°C samples. Samples were analyzed by scanning electron microscopy (fig.1) and dispersive X-ray spectroscopy techniques to characterize spatial location of the elements and rare earth activator precipitation into nanocrystals.

Studied rare earth activated glass ceramics-samples can detect electron beams (tested by cathodluminescence) and X-rays (tested by X-ray stimulated luminescence). Terbium activated heat treated at 700°C sample has a most intense luminescence. Praseodymium and neodymium activated samples have fastest decay times.


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Electrical and Thermo-physical Properties of Hybrid Materials Made from Multi-Walled Carbon Nanotubes with Polymerized Thiophene Derivatives

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Over the last decade, there has been attributed much attention to functionalize multi- and single walled carbon nanotubes (MWCNT, SWCNT) and graphene nanofillers by using none-covalent ionic liquid modifiers or by modifying surface of carbon nanofillers with carboxylic, amine, acyl, etc. functional groups in order to change the filler structure and improve the thermal, mechanical, electrical properties of polymer composites made from them [1-2]. Improvement of electrical and dielectric properties of polymers through the addition of such functionalized materials is essential for the development of novel conductive materials with an application in electrical devices. The recent researches have been attributed to use of the classical polymer systems of thermoplastic polymers and copolymers [3] as alternative matrices to conventional conductive polymer systems (polyaniline, polypyrrole, polythiophene, etc.) in combination with functionalized CNTs by developing conductive materials with sufficient electrical properties even at low filler contents, and gaining improved mechanical characteristics in comparison to pristine polymer matrices [4].

The presented contribution is dedicated to the development of suitable polymer nanofiller materials by polymerisation of thiophene derivatives with alkyl side chains attached to MWCNTs prior functionalized by thiophene groups. The content of MWCNTs in the developed materials is varied from 20 to 80 wt.% in order to evaluate the best composition of the functional content for the gain of potentially most suitable conductive filler material.

Structure of the developed materials is researched in details using the spectroscopic and, spectrometric methods (FTIR, XRD, etc. methods) as well as by research of thermo-physical properties, e.g. calorimetric properties, thermal stability. The mechanical properties are also estimated by using dynamic mechanical thermal analysis. The results obtained by research of dielectric properties and the measurements of conductivity show an improvement of polythiophene moieties containing hybrid material potential for use in thermoplastic matrices in comparison to less dispersible unmodified pristine MWCNT filler particles.

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Photothermoelectric effect in graphene-based room-temperature THz detectors

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Detection of terahertz (THz) radiation continues to be an important field of innovation in a variety of applications: spectroscopy, security imaging, biomedical imaging, RF tagging, etc. [1]. A long-neglected aspect is the ability to freely position detectors on a variety of substrates and surfaces. For this purpose, graphene-based devices offer unprecedented options because graphene can be transferred to many materials. A class of promising THz detectors which can be made from graphene are graphene field-effect transistors (G-FETs) [2]. Efficient detection of 0.6 THz radiation achieving an optical responsivity up to 14 V/W and an optical noise-equivalent power as low as 515 pW/√Hz at room-temperature has already been reported [3]. This work is devoted to the detailed study of the electrical response to electromagnetic radiation spanning from 100 GHz to 1 THz of G-FETs such as those presented in [3]. The upper graph of Figure 1 shows the dc drain-source resistance versus gate voltage. The lower graph compares calculated (dotted line) and measured (solid lines) responsivities for various frequencies. The calculated values for the nonlinear rectification signal are based on the relationship between voltage response and channel conductivity as given in [2]. For the purpose of clarity, the measured responses were rescaled to overlap at one specific point of the gate bias (Vgs = 0 V).

![Figure 1](image_url)

Figure 1. Upper graph: DC resistance versus gate voltage. Lower graph: Voltage responsivity normalized at Vgs = 0 V. Solid lines represent measured data, dotted lines represent calculated data. The dashed line marks the position of the Dirac point (CNP).

The measurements show an interesting asymmetry of the response relative to the Dirac point. The asymmetry is frequency-dependent, becoming more pronounced at higher frequencies. Such findings indicate that besides the nonlinear rectification of THz radiation, other effects play an important role, of which thermoelectric effects are the most probable ones [3]. For a quantitative analysis, we are currently developing a model, which accounts for the diffusive contribution of hot carriers (hot-carrier Seebeck effect).

In conclusion, we show that G-FETs are suitable for efficient broadband THz detection. The understanding of thermoelectric effects is likely to enable further improvements of these detectors.

Terahertz properties of graphene/polymer sandwich structures

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Due to its unique properties, graphene has been a subject of intensive interest since it was successfully isolated. Its material parameters including mechanical strength and elasticity, very high electrical and thermal conductivity, and others suggest that graphene could replace various materials in existing applications and could also enable development of new technologies [1]. In particular, the high electron mobility and unique energy band structure provide a great potential for development of high-speed electronic device operating in microwave[2] and terahertz (THz) frequency range [3]-[4]. This fact substantially increases research activities in this area.

In this communication, THz response of graphene/PMMA sandwich structure with different number of layers has been investigated experimentally and theoretically. The structures were produced as follows. The graphene sheet was synthesized by chemical vapor deposition (CVD) at 1000 °C in methane atmosphere on a copper foil and was covered by 600-800 nm thick PMMA layer. After desiccation of PMMA layer copper substrate was wet etched in ferric chloride. The obtained PMMA film coated with graphene sheet was washed in distilled water and placed on metallic frame. The same procedure was repeated several times and allowed us to fabricate free-standing multilayer sandwich containing several graphene sheets. The measurements of complex transmission in the frequency range from 100 GHz up to 1.4 THz were performed using the time domain terahertz spectrometer (EKSPLA, Vilnius Lithuania) based on femtosecond laser (wavelength 1 mkm, pulse duration less than 150 fs) and GaBiAs photoconductive switch as THz emitter and detector.

The theoretical analyses based on the solution of boundary problem for multilayer graphene/PMMA system allowed us obtain electromagnetic transmission/reflection/absorbance coefficients. In our calculations, we take into account that in the THz spectral range, the conductivity of graphene is dominantly determined by the intraband carrier transition [5]. Comparison of experimental data with theoretical predictions allows us to estimate the electron relaxation time (\( \tau = 0.4 \cdot 10^{-13} \) s) and value of the chemical potential (\( \mu = 0.28eV \)) of fabricated graphene. Our results are important for future development of THz and microwave devices.

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Porous anodic alumina formation in selenic acid electrolyte

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Porous anodic alumina (PAO) is shown to be a suitable matrix for nanomaterials formation for various applications, such as sensors, photonic crystals, plasmonic devices. Specific requirements to the alumina matrix properties exist for each of the applications. Therefore the development of new electrolytes, which afford expanding the range of porous alumina matrix properties, is essential.

This work presents a study of the fabrication and characterization of porous alumina films formed during the galvanostatic anodization in selenic acid electrolyte with concentrations ranging from 0.04 to 1 M.

Two different overshoot shapes are observed in the voltage-time curves. At high concentrated electrolytes (0.5 M – 1 M) the broad faint peak is formed. So that, the electric field oxide dissolution is considered to play the main role in pores initiation. In more dilute electrolytes (0.08 M – 0.3 M), an acute overshoot is seen. In this case, the tensile stress is suggested to increase in the growing barrier film, leading to the small cracks formation and its further evaluation into the porous structure. The local “burning” is observed for the low electrolyte concentrations (0.04 M – 0.15 M).

The aluminum dissolution and oxidation efficiency for different selenic acid concentrations was examined by gravimetric measurements during the first anodization stage. High oxidation efficiency is observed. The electrolyte affords to synthesize porous oxide films with a high rate (around 4 μm/h for 5 mA/cm² current density). Oxidation efficiency decreases with the concentration increasing caused by higher alumina etching speed at higher electrolyte acidity.

Morphology and ordering degree of the porous alumina formed in selenic acid electrolyte are studied by scanning electron spectroscopy. The best pore arrangement for the applied technological parameters is obtained in the samples formed in 0.3 M - 0.5 M H₂SeO₄.

Chemical composition and chemical bounds of the porous films was studied by X-ray photoelectron spectroscopy and Raman spectroscopy respectively. The kinetic energies of secondary, photoelectrons and Auger electrons for aluminum and selenium overlap. To differentiate selenium peaks from the aluminum, selenium species extracted from the selenic acid were measured as a reference sample. Amount of the selenium was counted on the top of the sample and depth profiles through all the oxide thickness are plotted. The highest amount of the selenate species was found at the surface of the samples. It varies from 3 to 5 at. % and it doesn’t change with the electrolyte concentration. The amount of the species inside the porous films is significantly lower (around 1%). The amount of the species embedded in the oxide is increasing with the electrolyte concentration.

For porous alumina films obtained in selenic acid, a clear Raman spectrum is observed. Two peaks are found: the medium band at 337 cm⁻¹ and the strong band at 899 cm⁻¹. The first peak corresponds exactly to the symmetric stretching mode of SeO₄²⁻ species. The second one usually associated with the (OH) band and SeO₄ asymmetric stretching mode. Matrices formed in selenic acid don’t exhibit noises in the Raman spectra, comparing to the samples synthesized in the oxalic acid and phosphoric acid electrolytes. This advantage is notably interesting for generating and studying nanostructures for optoelectronics, as well as for the investigation of other functional nanostructures by light scattering techniques.

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Temperature-dependent photoluminescence spectroscopy of nonpolar m-ZnO/ZnMgO quantum wells, grown on lattice-matched (100) LiGaO$_2$ substrate

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Temperature dependent (3–300 K) photoluminescence (PL) was used to study optical properties of five stacked ZnO/ZnMgO quantum wells (QWs), grown along nonpolar m-axis [10–10] on lattice-matched (100) LiGaO$_2$ substrate. Low temperature PL of different excitation intensity provided three distinct optical features (see Figure 1, a–c). Sharp peak at 3.3 eV, under high-excitation is related to near-band edge emission from ZnO buffer layer (Figure 1, a). On the left side of this peak, a far more intensive feature spanning the region 3.5–4.4 eV is associated with the ZnO/ZnMgO QWs, while, on the right side, a broad “green” band centered at 2.8 eV is due to the defects. It was found that the relative intensity of the established features varies dramatically with the excitation power (see Figure 1, a–c), owing to the saturation of defects. Also, a large degree of polarization (DOP) of QWs was estimated from m-plane through selective PL emission along polar [0001] and nonpolar [11–20] axes. Moreover, the consistency of DOP was observed in 3–300 K temperature (Figure 1, d).

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Figure 1 Low temperature PL spectra of m-ZnO/ZnMgO QW structure at high (a), moderate (b) and low (c) excitation power density. Significant polarization anisotropy of QWs was found investigating the in-(10–10)-plane optical response along polar [0001] and nonpolar [11–20] axes. High-excitation DOP values in QW are consistent in 3–300 K temperature (d).
Influence of chemical passivation on electric properties of individual GaAs nanowires studied by current-voltage measurements on AFM

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Semiconductor nanowires (NWs) find extended applications in nowadays technology from gas sensors and Solar cells to single-photon detectors and super high resolution monitors on electroluminescent imaging. Meanwhile, GaAs NWs are expected to be used widely as elements for Solar cells, but number of shortcomings decrease their potential efficiency. One of such drawbacks is existence of surface states which cause electric charges to be captured inside NW shell and photon energy scattered. Surface passivation can be used to reduce charge trapping, however no reliable study was done for single NWs.

Photoluminescence is general method to study efficiency of passivated NW arrays, while Scanning Probe Microscopy provide reliable characterization of individual nanosize structures [1, 2]. It was found in earlier studies that GaP and InP passivation of GaAs NWs can increase current up to few orders of magnitude comparing to unpassivated samples [3]. We demonstrate results of our study concerned with comparing main types of passivation done on individual nanowires with standard BRUKER Multimode 8 AFM in PeakForce mode. AFM imaging followed by taking the current-voltage characteristics of single NWs is supposed to be most convenient and fast method to characterize such 1D structures.

We compared NWs of 20 and 40 nm diameter grown at MBE chamber than covered by GaP or InP layers. Difficulty was in taking the proper image and reliable contact between AFM tip and golden cap on top of the NW. We found that passivation increased current flow inside the studied nanowires comparing with unpassivated structures. This data are in agreement with predictions and literature, but were firstly approved by AFM method.

We expect that such results can be used to further compare the conductive properties of GaAs nanowires to increase efficiency of Solar cells. Moreover, methodical value seems to be in improvement of method to take I-V curves on nano small objects with AFM.

Native defect-induced luminescence of aluminum nitride (AlN) was studied. AlN powder with macro-size grains (~ 4 µm) obtained from Aldrich Corp. and nanosize AlN powder (~60 nm) synthesized in Institute of Inorganic Chemistry, Riga Technical University, pressed in pellets were used for investigations. Photoluminescence (PL) spectra and its excitation (PLE) spectra of AlN powders were studied within the spectral ranges 350-500 nm and 200-360 nm, respectively, and temperature interval from 8 K to 300 K. Luminescence band at 420 nm was observed (see Fig. 1, a, and c), which can be excited either through exciton processes at 215 nm (see Fig. 1, b, d) or donor-acceptor recombination processes (excitation around 260 nm) together with direct excitation of luminescent defect at 315 nm. Features of this luminescence are different from those related to oxygen containing centers [1].

It was found that 420 nm luminescence is highly sensitive to oxygen gas surrounding the AlN sample reducing its intensity. It allows conclusion that the defects responsible for the 420 nm luminescence of AlN are the surface defects and material is prospective for developing of oxygen gas sensor.

CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cell grown by interdiffusion of stacking layers

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Organometallic halide perovskites in last two years have emerged as new class of light absorbers that have demonstrated exceptional progress in solar cell performance [1]. To overcome pinholes problem in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ we have been used modified interdiffusion method [2]: on patterned ITO coated glass after cleaning it in chloroform, deionized water, acetone and 2-propanol in an ultrasonic bath for a 15 min each; aqueous PEDOT:PSS layer was spin coated at 8000 rpm for 50 s. After heating this layer at 140°C for 30 min the mixture of PbI$_2$ and PbCl$_2$ (with molar ratio 3.4) dissolved in DMF and DMSO mixture with molar ratio 3 was spin coated at a rate 6000 rpm at 65°C using 65°C hot solution and was dried at 70°C in argon atmosphere for 45 minutes. On top of this layer CH$_3$NH$_3$I solution in 2-propanol (40 mg/mL) was spin coated at a rate 6000 rpm at 65°C. The obtained bilayer system was annealed in closed system at 107°C for 1 h and additionally 1 h in argon atmosphere. After cooling to room temperature system was covered with PCBM dissolved in DCB (30 mg/mL) at a rate 2000 rpm for 60 s and annealed in argon atmosphere at 105°C for 1 h, cooled down and put in vacuum chamber where 50 nm thick C$_60$ layer and 60 nm thick Ag electrode were thermally evaporated at pressure 10$^{-6}$ mbar.

All photoelectric measurements have been made in the same homemade vacuum cryostat where electrode was deposited at p~5·10$^{-7}$ mbar without breaking the vacuum and moving the cell. The spectral dependences of short circuit photocurrent external quantum efficiency (EQE), fill factor (FF) and open circuit voltage (V$_{OC}$) has been investigated in spectral range 370-900 nm, using synchro-detection technique and PC controlled data storage equipment.

Preparation of Au modified TiO$_2$ nanofibers and their photocatalytic activity

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TiO$_2$ is one of the most promising photocatalysts in solar energy harvesting and environmental pollution control due to its low cost, non-toxicity, and chemical and thermal stability. Pure anatase is active only in UV spectral part but modified with gold it becomes active also in visible light.

In the present work formation of active TiO$_2$ nanoparticles in microwave synthesis and their modification with gold were studied. TiO$_2$ P25 nanopowder and 10M KOH solution were used as raw materials. Microwave assisted synthesis method [1,2] permitted to obtain TiO$_2$ nanofibres with a diameter of 5nm and a specific surface area in the range of 70 - 150m$^2$/g. In order to modified TiO$_2$ nanofibers with gold HAuCl$_4$ (5g/L) water solution was added to suspended TiO$_2$ nanofiber solution at temperature 35°C and pH 7. The resulting suspension was kept at 40°C temperature and formaldehyde (3%) solution as reducing agent was added. The pH was adjusted to 6,5 by NH$_4$OH water solution (1:2). The obtained gold modified TiO$_2$ nanofiber powder was filtered, dried and calcinated at 500°C for 2h.

In SEM micrographs (Fig.1) show that TiO$_2$ fibers consist of large amount of individual TiO$_2$ nanowires before and after modification with gold. Gold content was determined by XRF analysis and it was 4.80wt%. Photocatalytic activity was determined by degradation of the methylene blue solution under UV and visible light irradiation. The gold modified nanofibers showed almost two times higher photocatalytic activity with respect to pure TiO$_2$ nanofibers.

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Pyrimidine and Pyrrolo[2,3-d]pyrimidine Core Based Derivatives for Fluorescence Sensing Applications

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Over recent years, organic molecules with a π-conjugated backbone have received much attention due to their applications in a wide range of electronic and optoelectronic devices. Introduction of heteroaryl moieties into the backbone of extended π-systems considerably influences molecular orbitals, stereochemical structure and linking topology of the substituents. Particularly azaheterocyclic compounds are widely used in organic electronic devices, such as organic light emitting devices (OLEDs), solar cells, sensors etc. Pyrimidines and pyrrolo[2,3-d]pyrimidines are functional groups often used in more complex donor-acceptor organic structures due to strong aromaticity, significant π-deficiency, n-π electronic states, pH sensitivity, and ability of their nitrogen atoms to take part in specific intermolecular bonding and interactions in the solid state. Moreover, pyrimidines and pyrrolo[2,3-d]pyrimidines are extensively studied due to their medical activity as some antiviral, antibacterial and even antitumorous agents. They share a similar chemical structure with four DNA nucleobases. All the above mentioned qualities could be promising in potential applications of pyrimidine and pyrrolo-pyrimidine compounds as materials for bio-sensing and bio-labelling.

In this work we report on the photophysical properties of novel donor-acceptor-type chromophores based on pyrimidine and pyrrolo[2,3-d]pyrimidine cores and carbazolylphenyl branches at the periphery. The impact of the polar and steric substituents on the photophysical properties of the synthesized donor-acceptor chromophores were assessed by investigating their optical and electrochemical properties in various surroundings. The results were supplemented with DFT modelling. Tuning of optical properties by polar substituents of pyrimidines and pyrrolo pyrimidines is discussed with special emphasis on intramolecular charge transfer and intersystem crossing processes. In addition, highly selective fluorescence sensing of Pb2+ and Fe2+ ions by acceptor-substituted pyrimidine and pyrrolo-pyrimidine derivatives was demonstrated.
Radiative and nonradiative recombination pathways of pyrrolo[2,3-d]pyrimidine derivatives

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The performance of the organic optoelectronic devices, such as OLEDs, solar cells and field transistors, strongly depends on molecular and photophysical properties of the organic materials. Pyrrolo-pyrimidine derivatives demonstrate antiviral, antibacterial and antitumorous properties. They also share similar structure with two of the four DNA nucleobases – adenine and guanine. Efficient blue fluorescence of pyrrolo-pyrimidine derivatives could lead to their successful applications as bio-sensors and labels. Thus, it is of great interest to elucidate and, eventually, control the photophysical properties of such compounds. Here we analyze the fluorescence and phosphorescence properties of two pyrrolo-pyrimidine derivatives with substituents of different polarity.

In this work the pyrrolo-pyrimidine derivatives with tert-butoxycarbonyl (1) and phenyl-methoxy (2) substituents were investigated. After a detailed analysis of the emission spectra dynamics in time, three emission channels were pointed out. Initially, the fluorescence is observed, which is thought to be prevailed by the emission of the charge transfer state. Regarding the 1 compound, the emission from singlet state peaks at 390 nm and shifts to 420 nm, lasting for 100 ns. As for the 2 compound the fluorescence is located at 415 nm and also shifts to 450 nm, while continuing for 120 ns. Afterwards, the slightly redshifted (due to reabsorption) delayed emission is registered from 120 ns to 400 µs. For both compounds the phosphorescence spectra express vibronic structure lasting several seconds. The maxima of 1 and 2 compounds are positioned at 500 nm with 1% mass ratio of compound to the host matrix and 544 nm with 5% mass ratio. The bathochromic effect of the fluorescence and phosphorescence in the samples with higher concentration is caused by the enhanced interactions between the molecules.

The emission decay time characteristics of the pyrrolo-pyrimidine derivatives with different substituents at pyrrolo-nitrogen position demonstrated one-exponential molecular fluorescence decay. The non-linear delayed fluorescence decay for both compounds implies to the triplet-triplet annihilation (TTA) [1] process. The TTA is known to be highly dependent on concentration, however, the pyrrolo-pyrimidine derivatives exhibited no such dependency. The most efficient emission from triplet states was registered in the samples with 1% mass ratio.

The photoluminescence emission is influenced only by the singlet energy states and polarity of the substituents. The compound with acceptor-like tert-butoxycarbonyl fragment demonstrates more rapid energy relaxation from the singlet states, increased intersystem crossing and more expressed phosphorescence in comparison to the compound bearing donor phenyl-methoxy functional group.

Figure 1. Emission spectra of Pyrrolo-pyrimidine with tert-butoxycarbonyl (1) and phenyl-methoxy (2) derivatives.

Facile strategy to influence the photoactive blend film characteristics utilizing pre-heated solvent exposure

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The performance of bulk heterojunction photovoltaic (PV) cells is strongly correlated with the nanoscale morphology of the active layer, where the photogenerated excitons dissociate, and the charge carriers move towards the respective electrodes via hole/electron transportation [1]. In order to optimize/modulate the active layer morphology, several approaches have been utilized: use of mono or co-solvent, thermal annealing, solvent vapor treatment, solvent soaking etc [2, 3]. However, spin-coating may be a convenient approach to overcome many other drawbacks.

In this investigation, we chose an inexpensive solvent (methyl alcohol, MA) to study the characteristic changes at the interface between organic active layer and metal electrode and to improve the performance of fabricated organic PV cells (OPV). We utilized a photoactive blend system composed of poly(3-hexylthiophene) (P3HT) and a [6,6]-phenyl-C71-butyric acid methyl ester (PCBM). Our results demonstrate that exposure of MA (at room temperature, or pre-heated at 65°C) atop the blend system, improves the performance of the fabricated OPV cells. After the solvent exposure, the P3HT:PCBM thin films/devices were evaluated for crystallinity, morphology, mobility, and photovoltaic characteristics. Our results revealed that use of the pre-heated solvent on the organic active layer significantly influences the micro/nano scale morphology and phase segregation of the P3HT:PCBM thin films, as well as the charge carrier mobility. Consequently, OPV cells modified with the MA pre-heated at 65°C exhibited a power conversion efficiency (PCE) of 3.36%, with open-circuit voltage of 0.59 V, short-circuit current density of 13.83 mA/cm², and fill-factor of 0.41. In contrast, the unmodified P3HT:PCBM (pristine) cell showed a PCE of only 2.13% (Figure 1). This facile pre-heated solvent exposure strategy could be applied to any photoactive blend system to realize improved PV performance by choosing appropriate solvent.

Figure 1. Current density – Voltage (V) characteristics for the pristine and MA (@RT or preheated @65°C) modified cells


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Influence of trench defects on photoluminescence properties in InGaN quantum wells

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InGaN is widely used in commercial blue and white light-emitting diodes (LEDs) and laser diodes (LDs). The emission of InGaN light-emitting diodes and laser diodes can be tuned over the entire visible light spectrum by varying the indium-to-gallium ratio, however, introduction of In above approximately 20% results in extended structural defects, mostly threading dislocations. The dislocations can also form closed loops, which are considerably less studied. This study is focused on the trench defects and their influence on photoluminescence (PL) efficiency and other properties.

The trench defects were studied in InGaN multiple quantum wells (MQWs) with different indium content ranging from 9 % to 25 %. The active layer of each sample consists of 5 InGaN quantum wells, 5 nm in width, separated by 20 nm thick GaN barriers. The samples were grown at AIXTRON-SE by metal organic chemical vapor deposition (MOCVD) on a sapphire substrate with a GaN buffer layer.

The samples were studied using confocal and atomic force microscopy modes of the WITec alpha300 S microscopic system coupled with a spectrometer. Mappings of PL parameters with the spatial resolution of ~250 nm were obtained using a laser diode emitting at 405 nm for excitation and a high numerical aperture objective (NA = 0.9). Surface morphology was measured with 10 nm resolution. The quantum well width was measured using transmission electron microscopy and the composition was estimated from X-ray diffraction measurements.

The atomic force microscopy revealed the presence of pits, close-loop and partially enclosed trench defects (Fig. 1a). The densities of all types of defects as well as the surface roughness increase with increasing indium content. Use of a multi-microscope system allowed matching of surface morphology and photoluminescence parameter mappings. The matching revealed that the emission from areas enclosed by trench defects is more intense (Fig. 1b) and blueshifted (Fig. 1c) when compared to the emission from the surrounding area.

Figure 1. Surface topography image of InGaN MQW sample (a), corresponding spatial distribution of spectrally-integrated photoluminescence intensity (b), and spatially-integrated spectra (c) from two areas indicated in (b). Horizontal scale bar is 400 nm.

The luminescence properties were interpreted by model calculations of the influence of strain relaxation induced effects (reduction of the quantum confined Stark effect, band gap shift, and compositional pulling) and the variation in quantum confinement due to the increase of well width within the trench defect. The calculations demonstrated a strong dependence of the competing influences on the well width. It is shown that the blueshift of the PL band observed within the trench defect loops in the InGaN structures with wide quantum wells is mainly caused by the reduction in efficiency of the quantum-confined Stark effect due to strain relaxation.
Structural, optical and photo-electrochemical research of anodised TiO\(_2\) nanotube arrays

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Studies on titania (TiO\(_2\)) nanostructures and their photoactivity have grown rapidly since 1972 after publication of Fujishima and Honda [1]; however, titania has been widely used in various applications for more than a century. Some of the recent developments are usage of titania nanostructures in dye sensitized solar cells and photo-splitting of water for hydrogen production.

There are several techniques to obtain TiO\(_2\) nanotube arrays, such as hydrothermal chemical vapour deposition, sol–gel synthesis, and electrochemical anodization. Electrochemical anodization is a method with highly controllable parameters to grow ordered self-oriented nanotube arrays. Investigations of initial anodization parameter influence on growth, morphology of TiO\(_2\) nanotube arrays and photocatalytic parameters are described in this work.

TiO\(_2\) nanotube arrays were grown on titanium foils using electrochemical anodization. Before experiments, substrate foils were mechanically and chemically cleaned. Arrays were grown in fluoride-based electrolyte applying constant voltage. Structural analysis of gained nanostructures were performed using X-ray diffraction, EPR and Raman spectroscopy methods. Morphological differences were observed and compared by SEM. Photocatalytic activity was determined in three-electrode reactor measuring open circuit potential.

In these experiments was found that with simple experimental set-up self-ordered TiO\(_2\) nanotube arrays can be obtained. By controlling initial parameters, such as electrolyte properties and voltage, it is possible to control geometry and properties of grown structures.

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Properties investigation of plasmonic-enhanced photovoltaic structures based on CZTS

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In recent years, copper-based chalcopyrite materials have gained a great deal of interest as a photo-absorbing layer for low-cost thin film solar cell (SC) applications. In particular, Cu2ZnSnS4 (CZTS) semiconductor compound possesses promising optical properties: near-optimum direct band-gap energy for solar cells of 1.5 eV and large absorption coefficient (>105 cm−1) [1]. Despite that, solar cells based on ultrathin layers absorbers over time degrades the solar light absorption, which as a result leads to lower conversion efficiency in comparison with conventional thick film solar cells. The plasmonic solar cell concept suggests the implantation of metallic nanoparticle arrays into a solar cell structure, to increase light absorption capacity and thereby increase different solar cell types conversion efficiency [2]. Also worth noting that the addition of metal nanoparticles in the PV structure can offer new absorber physical thickness reduction method [3]. Plasmonic-enhanced light absorption increase the photocurrent, and demonstrate conversion efficiency at the level of SC with ultra light absorbing material [4].

In this study, the Au nanocluster arrays were formed by vacuum thermal evaporation of gold portions from molybdenum evaporator at a distance of 20 cm from evaporator to the substrate [5]. The size of the gold particles was varied in the range of 10-100 nm, which is determined by the weight of evaporated portion. The absorber multi-component metal sulfide layers (CZTS) were deposited by SILAR technique [6]. The composite samples that consisted of Au-NPs and the CZTS were prepared in two configurations (Figure 1).

The bottom SC configuration (Figure 1a), the Au-NP layer was deposited firstly onto a soda-lime glass with FTO followed by the deposition of the CZTS thin film. For the top SC configuration (Figure 1b), the CZTS thin film was deposited firstly followed by the deposition of Au nanoparticles.

![Figure 1 - Sketches of Au nanoparticles and CZTS nanocomposite film configurations. (a) Glass/FTO/Au-NP/CZTS and (b) glass/FTO/CZTS/Au-NP.](image)

The Au-NP arrays, the CZTS layers, the Au-NP layer covered with CZTS layer (Au-NP/ CZTS), and the CZTS films covered with Au-NP layer (CZTS/Au-NP), were characterized using optical transmittance and reflectance spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) methods. Also CVC measurements of test solar cell structures were performed.

Glucose oxidase (GOx) enzyme activity was first reported by Muller in 1928 and growing interest in this protein doesn’t come to a stand. Usually free enzymes are not stable. Different immobilization procedures have confirmed that immobilized enzymes exhibit better stability, sensitivity, specificity and durability than free enzymes in solution. Combined systems with polymer immobilized enzymes draw great interest in biosensors. GOx is composed of two subunits harbouring non-covalently bound flavin adenine dinucleotides complexes (FAD) as redox-active prosthetic group. FAD’s primary role is being a cofactor necessary for the activity of flavoproteins. Polypyrrole (Ppy) is one of the most widely investigated conducting polymer because of its stability, biocompatibility, and catalytic activity, relatively minor and inexpensive synthesis. Hydrogen peroxide produced during catalytic reaction of GOx initiated the polymerisation of polypyrrole.

Among the optical methods, fluorescence is a promising kind of spectroscopy because of the sensitivity, broad array of possible parameters to measure, real-time data acquisition, distant monitoring opportunity. Changes in intrinsic fluorescence can be applied to monitor configuration of a molecule and structural changes in a protein. Before embedment of GOx enzyme to the polymeric matrix of Ppy, time-induced unfolding process of the GOx was studied by fluorescence measurements (Fig.1.).

![Figure 1](image-url)

Figure 1. Fluorescence spectra of (a) GOx in Na-acetate buffer and polymerization solution recorded at first (solid line) and 17 days (dashed line) after preparation of solution; (b) Fluorescence average decay time dynamic after preparation of solution.

While redox enzyme, GOx, initiated synthesis of polypyrrole and GOx self-encapsulation within this polymer has been the subject of our previous investigations [1, 2], the present investigation is aimed for a deeper understanding of internal interactions in such system. Changes of fluorescence properties were evaluated over time. Fluorescence decay time, spectra intensity and shape changes during the monitoring time are presented.

Influence of apparatus-technological contamination caused by electron beam melting process on content of impurities in FZ silicon single crystals

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Replacement of chloride (Siemens) process to the alternative, which is less energy-intensive and does not contain potentially harmful substances process is an urgent task we implemented in the project “Development of energy-efficient technology for polycrystalline silicon production No.2 / EZZLV02 / 14AK / 010”.

The resulting polycrystalline silicon rods are to be used to obtain single crystals of silicon for solar energetics and power microelectronics (power rectifier devices). Efficiency of the solar cell is dependent on the concentration of impurities in silicon from which it is made. The purity of silicon also determines the parameters of power devices. Therefore, the developed technology is to provide high purity material and it shall not introduce additional contaminants during the process of growing the silicon rod. The technology being developed involves a two-step process - growing polycrystalline rods using the electron beam melting, and then use the standard FZ process for growing the silicon single crystals.

In frames of a new original technology for producing the silicon rods using electron-beam melting, investigations of the apparatus-technological contamination of the process were carried out. Initial silicon was analyzed with electrophysical methods. The content of carbon and oxygen was determined by FTIR-spectroscopy methods. The content of impurities was analyzed by GDMS and SIMS. Silicon samples with approximately the same level of impurities were selected for loading into the electron-beam furnace

The resulting polycrystalline silicon rods obtained using electron-beam method were remelted into a dislocation free single crystals using FZ method. Both polycrystalline and monocrystalline silicon were analyzed by GDMS and SIMS. The content of impurities in silicon single crystals was determined by low-temperature FTIR-spectroscopy. Stresses in silicon crystals were studied by micro-Raman spectroscopy.

The combined analysis of the obtained results leads to the conclusion that the very process of electron beam melting (so-called apparatus-technological contamination) does not introduce significant contamination to the final product - the silicon, which will be used in solar energetics.

The investigation results show that the developed original technology based on the use of electron-beam melting allows you to produce high-purity silicon rods for subsequent production of solar cells, which have an efficiency of 30% higher than the commercial solar cells, while improving the price / quality ratio.

The results for the control of the impurity composition in silicon and the limits of applicability of the analytical procedures are discussed. The factors affecting the purity of the desired product are analyzed.
Quantum Chemical Study of Excited States of Phthalocyanine-Carotenoid Light Harvesting Antennae

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Carotenoids play a crucial role in the energy dissipation process by quenching chlorophyll (Chl) singlet excited states in photosynthetic antennae. Additionally they are also involved in the photoprotection process in green plants as quenchers of Chl triplets and, thus, responsible for protection of the system from the singlet oxygen generation [1]. Artificial light-harvesting antennae are used for better understanding the details of carotenoids involved in light harvesting, energy transfer, electron transfer, and photoprotective processes [2]. These artificial structures are capable of performing the specific functions carried out by their natural counterparts. The experimental and theoretical investigation allows one to determine photophysical and photochemical mechanisms underlying the behavior of the natural systems [3].

Here we present the quantum chemical study for the phthalocyanine-carotenoid dyads in which a phenylamino group links phthalocyanine moiety to carotenoids having from 8 to 11 backbone double bonds (Fig. 1). Theoretical investigation of systems with polyene chains are known as a difficult problem itself because of the dark electronic states of carotenoids, which cannot be determined by means of the TDDFT method. The density functional method (DFT and TDDFT) with CAM-B3LYP functional and 6-31G(d,p) basis set was used for computations. Geometries of all structures were optimized for the ground and the several lowest excited electronic states. This allows determining the changes in electronic spectra during relaxation of the excited states. Nonempirical multiconfigurational methods were used for the comparison purposes with TDDFT results and for the determining the possible role of the optical dark electronic states in the dyades.

Figure 1 Phthalocyanine-carotenoid dyads. Phenylamino group links phthalocyanine moiety to carotenoids having from 8 to 11 backbone double bonds (d-8, d-9, d-10, d-11).

Energy Harvesting from mechanical vibrations using different kind of pendulums.

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Together with the continuing miniaturization of electronic devices, their demand for energy supply is also diminishing. To use the energy-saving electronic circuits in portable devices means their longer operation time when using the same batteries or allows using smaller rechargeable batteries. Nevertheless batteries have some unavoidable drawbacks, the most important one is that the energy is inherently limited. That is why people started to search for alternative energy sources for such electronic devices. Among them are the gadgetry converting energy of mechanical vibrations to the electric energy (energy harvesting devices) [1]. This is very promising approach for industrial applications, since in case of success, it allows power supply for the small-power devices without any additional source of energy such as battery. Above all, it resolves the problem when the electronic devices are in the places inaccessible or with the limited access, since it makes the system in a sense maintenance-free.

The energy sources can be found almost everywhere: mechanical energy of different machines, living organisms, the elemental forces or the energy of electrostatic or magnetic interactions. Frequently the temperature or pressure difference are used, as well as gas and liquid flows. For example, every machine with rotary parts is forced to vibrate due to imperfection in balancing and in most of the cases it is the drawback. But sometimes it can be an advantage and introduced intentionally by the constructors. One can get the energy due to such vibrations, however one needs to have corresponding transducers for such purpose. Among them one can distinguish three types of converting the energy of mechanical vibrations: electromagnetic, the one employs smart materials (piezoelectric, magnetostrictive) and electrostatic. A considerable amount of publications were devoted up to now to the field of research related to different possibilities of energy harvesting from the mechanical vibrations. It is worthwhile to mention especially those devoted to the applications for micro-systems [2-7].

In this work we focus on the problems related to the energy harvesting from small mechanical vibrations by means of piezoelectric transducers, among others with spiral piezoelectric and torsion pendulum, with piezoelectric pendulum and corresponding micro-magnets.

The main goal was to study the relations between different electrical-mechanical parameters of the proposed systems of energy harvesting and their efficiency as well as to search for such piezoelectric materials and corresponding geometry in order to get the maximum generated output power.

The influence of nonlinearity on power generation in electromagnetic energy harvesting system

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We examine the power generation in electromagnetic energy harvesting device consisted of small magnet moving in isolating tube surrounded by the coil attached to the electrical circuit. The device can work both in the linear and nonlinear regime. In the nonlinear case the magnet vibrates in between two fixed magnets attached to the both ends of the tube. Additionally two springs are added to limit the movement of the small magnet. The linear case is when the moving magnet is attached to the repelling springs, and the static magnets have been replaced by the non-magnetic material. We calculate the potentials and forces using both the analytical expressions and the finite elements method. The numerical results show that the power efficiency in the nonlinear case exceeds the corresponding efficiency in the linear case at relatively high values of base accelerations greater than 5g. The generated output power in the linear case reaches the peak value 80mW near the resonance frequency $\omega_0$ for maximum base acceleration considered by us, whereas in the nonlinear case the corresponding output power has the peak value 95mW and additionally relatively high values in the excitation frequencies range up to $\omega = 1.2\omega_0$.

The results additionally show the increase of harvested energy in the relatively broad band of excitation frequencies in the nonlinear case.
Light conversion remains an extremely interesting topic for the decades. For example, converting higher energy photons to the lower energy ones (down-conversion) is employed in white light generation for general lighting applications. Conversely, generation of more energetic light out of the lower energy source (up-conversion) is less conventional and traditionally is used, e.g., for second-harmonic generation. While the two-photon absorption requires high power densities of coherent excitation, for the up-conversion via triplet-triplet annihilation (TTA) incoherent excitation with much lower power densities, in the range of several mW/cm², suffices. The low power up-conversion is considered to be very promising for enhancing performance of photovoltaic cells, since the power density of the sun light is sufficient to accomplish the conversion of otherwise unusable IR radiation to electron-hole pairs. Despite the fact that up-conversion efficiency achieved in a solution exceeds 30%, [1] in a solid state it drops down by more than one order of magnitude. Although all the factors contributing to the efficiency drop are still unclear, most of them are mainly associated with the self-quenching of an emitter serving also as an annihilator in the TTA process. Reduced concentration of an emitter may prevent quenching, however, it will lower exciton hopping probability thereby decreasing possibility for them to encounter, thus finally causing reduction of TTA efficiency. Obviously, this implies trade-off between emitter self-quenching due to its aggregation and the triplet exciton diffusivity. Therefore, to maximize the up-conversion efficiency, the overall influence of each process needs to be evaluated as a function of emitter concentration. Although the evaluation of concentration quenching of an emitter is possible via utilization of integrating sphere method, quantification of the triplet exciton diffusion length (Lₐ) implies much more sophisticated experiments. Essentially, evaluation of Lₐ value is crucial for fabrication and further development of high-performance light up-converting films.

To this end, the singlet and triplet exciton diffusion in the poly(methyl methacrylate) (PMMA) films containing 9,10-diphenylanthracene (DPA) as an emitter and platinum octaethylporphyrin (PtOEP) as a triplet exciton sensitizer was investigated. The films were prepared by melt-processing technique [2] for suppressing emitter aggregation at high concentrations. The determination of exciton diffusion was based on the evaluation of emission quenching efficiency in the DPA-PtOEP-PMMA films with randomly distributed quenchers. Monte Carlo simulations and Stern-Volmer formalism were applied to quantitatively model excited state relaxation dynamics in DPA-PtOEP-PMMA quencher blends with increasing quencher concentration (0 – 2 wt%) for the evaluation of Lₐ. [3,4] Quantum efficiency measurements for the up-conversion performed as a function of emitter concentration revealed optimal DPA concentration (25%), which is necessary to achieve maximal up-conversion efficiency (~1%) in the solid DPA-PtOEP-PMMA films. Exciton diffusion length for both singlet and triplet excitons was found to be similar ~50 nm in these films. Regardless of efficient singlet and triplet exciton diffusion in the films, relatively low up-conversion efficiency indicates various intermediate quenching processes adversely affecting up-conversion efficiency.

Research of advanced solid state hydrogen storage nanomaterials for sustainable energy applications

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To implement hydrogen as energy carrier in transport and stationary cogeneration (heat + electricity) it is important to solve hydrogen storage. Two types of storage are developed from middle 20th century – compressed gas storage in tanks (industrial applications) and liquid hydrogen in low-temperature Dewar (space technologies). Both of them have its advantages and disadvantages; at the last to be added the need for high-pressure compressor, and/or high energy consumption to reach and maintain very low temperature. It is studied also the third type of storage – hydrogen adsorbed or absorbed in solid state materials. In our work natural and synthetic zeolite, as well as graphene, both without and with modification (insertion of ions or cations) are studied as potential materials for room-temperature reversible hydrogen storage. Few layer graphene (FLG) is obtained from raw graphite material using alternative current exfoliation method and next ultra-sound crushing; natural clinoptilolite is washed in little acidic environment, but synthetic amorphous aluminosilicates grown by thermo-compression method. SEM and TEM analysis were applied to identify characteristic morphology of both types of materials (Figure 1). In SEM picture of FLG material the monolith piece is shown with some semi-transparent FLG sheets (Figure 1, left). Synthetic zeolite was obtained in amorphous state with closed pores and glass-like structure (Figure 1, right).

Simple reactor was constructed for observations of hydrogen absorption/desorption in synthesized materials, using Sievert (volumetric) method for analysis. From temperature-time and pressure-time data collected during measurements the temperature-pressure curve is plotted and characteristic sorption/desorption temperatures as well as amounts of bound/released hydrogen calculated. It has been found that for un-modified materials the highest hydrogen sorption exhibit natural zeolite with stored 0.84 wt% at -157 °C. From synthesized FLG powders – the highest values showed non-reduced few layer graphene – obtained from ultrapure magnetron graphite crucible) - 0.41 wt% at -175 °C. Modification with insertion of ions or cations is done with aim to increase adsorption temperature and amount of bound hydrogen. The most effective application for automotive industry of or researched materials would be solid state hydrogen storage cartridges for cars or refuelling stations.

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Research of Three-Component Proton Conductive Membranes for Fuel Cell Application

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Environmentally friendly production of electricity is vital for civilization since humankind is highly dependent on it nearly in every area. Fuel cells can be used for miniature, portable, medium-sized and large scale applications, and are between technologies that could lead to improving situation with energetics dependence from fossil fuels and nuclear plants. Polymer fuel cell has the advantage in portable and medium-sized applications due to its comparably low working temperature (typically below 100 °C), compact size and appropriate power range from several watts to kilowatts.

Proton conductivity in commercially produced membranes is based on water, and evaporation makes proton transport at higher temperatures complicated due to losing associated water molecules. Creating good proton conductor that is able to withstand high temperatures without noticeable decrease of proton conductivity is an important task to make technology successful. One of the ways to achieve this goal is to modify existing polymer proton conductors with organic and inorganic compounds.

In our work sulfonated poly(ether-ether-ketone) (SPEEK) was modified with another organic proton conductor (Nafion) to improve proton conductivity and inorganic compound to retain water at higher temperatures and low relative humidity. Nafion is well-known commercially available polymer with good proton conductivity. SPEEK is non-fluorinated compound that is an alternative to Nafion due to its price, processability, stability in fuel cell working conditions and possibility to be modified [1]. Hygroscopic oxides do not improve proton conductivity as such, but adding these compounds to polymer allows modified material to better work in drier and hotter conditions due to losing less water [2]. Using inorganic compounds to modify polymer material is well-known, but in this work we investigate combination between two polymers and third component – inorganic oxide compound, with aim to find best composition: higher proton conductivity in dry environment at an elevated temperatures.

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LiFePO$_4$/C/reduced graphene oxide composite cathode for lithium ion batteries

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A good electronic conductivity is a prerequisite of lithium ion battery electrode materials [1]. As many lithium ion battery electrode materials suffer from low electronic conductivity, electron-conducting additives are usually added to the active material. In this study carbon coating in combination with reduced graphene oxide (rGO) have been used to improve the electrochemical properties of LiFePO$_4$. Having a low electronic conductivity of $10^{-7}$ S/cm [2], LiFePO$_4$ is an ideal material to study the effects of such electronically conducting additives. Graphene is suitable as an electron-conducting additive because of the remarkably high electric conductivity [3]. rGO contains oxygen and hydrogen atoms and can be considered to be graphene with additional defects. rGO has excellent hydrophilic properties, therefore allowing to prepare a well-mixed composite of LiFePO$_4$ powder particles and rGO with some of the LiFePO$_4$ grains adhering to the rGO sheets. A rGO percolation network significantly improves the general electrochemical characteristics of the electrode. In this work we have studied the effect that the preparation technique and obtained grain structure have on the electrochemical properties of LiFePO$_4$/C/rGO composite.

LiFePO$_4$/C/rGO nanocomposite has been prepared via two step solution route by adding graphene oxide (GO) at different synthesis steps and then thermally reducing it. The structure and composition have been studied with X-ray diffraction and Raman spectroscopy. Morphology and grain structure have been analysed with SEM. These results have been analysed in context with the general electrochemical characteristics – charge capacity, rate capability and charge transfer resistance.

The X-ray diffraction analysis reveals peaks corresponding to the olivine-type LiFePO$_4$ with no apparent maxima corresponding to graphite. rGO content in the obtained LiFePO$_4$/C/rGO composite is 3 wt. %. LiFePO$_4$ particles seem to have been anchored on top of rGO sheets (see Figure 1 a). Electrochemical properties of LiFePO$_4$/C/rGO indicate that it is most beneficial that the GO is added to the synthesis precursor at the earliest possible stage (see Figure 1 b). This benefits the overall quality of mixing and helps to anchor LiFePO$_4$ particles on top of rGO layers. Results suggest illustrate clearly that the stage at which GO is added to the synthesis is of great importance. It was shown that it is best to add GO to the synthesis precursor at the earliest possible stage.

![Figure 1](a)

**Figure 1** (a) SEM image of LiFePO$_4$/C/rGO composite. (b) Electrochemical data – discharge capacity vs. C rate (1 C = 170 mA/g).

Effect of Ceria Addition on Electrical Properties of Scandia-Stabilized Zirconia

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Scandia-stabilized zirconia (ScSZ) electrolytes exhibit the highest ionic conductivity among all zirconia-based materials. However, for certain dopant concentrations (9–13 mol% Sc₂O₃), the highly conductive cubic phase undergoes a phase transition to rhombohedral phase below 800–900 K, which results in an abrupt decrease of ionic conductivity [1]. Thermal cycling of such material eventually leads to reduced conductivity and material degradation, which limits its applications.

It is known that the stabilisation of the cubic phase in ScSZ at lower temperatures can be achieved by co-doping with small amounts of other oxides [2]. 10 mol% Sc₂O₃ stabilized zirconia (10ScSZ), which exhibits the highest conductivity among ScSZ compounds, has been comprehensively studied in our recent work [3]. In the current work we present the investigation of 10 mol% Sc₂O₃ and 1 mol% CeO₂ stabilized zirconia (10Sc1CeSZ) electrical properties.

Measurements were carried out by means of impedance spectroscopy in the broad frequency range of 1 Hz to around 10 GHz and temperatures ranging from 300 to 900 K. Temperature dependency of the bulk conductivity $\sigma_b$ of ceramics was derived from complex specific impedance $\mathbf{\rho}$ plots at different temperatures. As indicated in Fig. 1(a), for all temperatures below 820 K (the range wherein the phase of 10ScSZ is rhombohedral), the bulk ionic conductivity of 10Sc1CeSZ is ten or more times higher than that of 10ScSZ. It was also found that 10Sc1CeSZ exhibits non-Debye relaxation behaviour, which rather would be represented by a continuous distribution of relaxation times (DRT). Due to the presence of charge carrier relaxation time distribution, the semicircles in the complex specific impedance plane $\mathbf{\rho}$ are depressed. The extent of DRT may be illustrated by the normalized imaginary impedance frequency peak value $\alpha = \frac{z_{\text{max}}}{z_b}$ (where $z_b = 1/\sigma_b$). This parameter directly indicates the extent of the DRT: lower value corresponds to more widely distributed relaxation times and vice versa [3]. The temperature dependency of $\alpha$ for 10ScSZ, presented in Fig. 1(b), has a clear minimum, located in the temperature region corresponding to the phase transition, which indicates a broadening of the relaxation time distribution. However, temperature dependency of $\alpha$ for 10Sc1CeSZ shows a monotonic increase of peak value with increasing temperature, which indicates the narrowing of the DRT function (Fig. 1(b)). The figure implies that the addition of 1 mol% CeO₂ to 10ScSZ significantly increases bulk conductivity and stabilises the cubic phase down to room temperature.

Li-ion dynamics in Li$_{0.5-x}$Na$_x$La$_{0.5}$Nb$_2$O$_6$ solid electrolyte system: Impedance spectroscopy study

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Li$_{0.5-x}$Na$_x$La$_{0.5}$Nb$_2$O$_6$ compounds crystallize into perovskite structure. Lithium ions are mobile in this system and the aim of partial Li$^+$ → Na$^+$ substitution is to investigate lithium conduction mechanism in such perovskites. The single phase compounds with $x$ changing from 0.1 to 0.5 were synthesized and dense ceramic samples of the compounds were sintered.

The electrical properties of ceramics were investigated in the broad frequency range from 10 Hz to 10 GHz and temperatures up to 800 K [1, 2]. Equivalent circuit technique was used to analyse impedance, complex conductivity, complex dielectric permittivity and complex electrical modulus spectra. Three dispersion regions of electrical parameters have been found in the investigated ceramics. The processes are thermally activated and correspond to lithium ion migration in the bulk and grain boundaries of the ceramics and then to ion blocking at the electrode-electrolyte interface. The latter dispersion was suppressed by measuring electrical parameters by four-electrode method [3]. Unlike in other perovskite system Li$_{0.5-x}$Na$_x$La$_{0.5}$TiO$_3$ [4], the percolation theory could not be applied in this study.

Electrical property investigation of La$_{2-x}$Ba$_x$Mo$_2$O$_9$-$\delta$ (x = 0 to 0.25) system of ionic conductors

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Solid ion conductors are of considerable interest as functional materials in fuel cells, high energy density batteries and chemical reactors. La$_2$Mo$_2$O$_9$ based conductors represent an interesting subset of oxygen ion conductors because of their high ionic conductivity, exceeding that of conventional zirconia-based materials. Moreover, their conduction mechanism, involving intrinsic oxygen vacancies, and temperature behaviour, exhibiting a phase transition at around 850 K from the low temperature monoclinic $\alpha$ phase to the high temperature cubic $\beta$ phase [1], are interesting from a fundamental perspective.

It is well known that the phase transition in La$_2$Mo$_2$O$_9$ can be suppressed by substituting some of the La ions with divalent cations (Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$ etc.) [2], thus stabilizing the highly conductive $\beta$ phase at low temperatures. In this work, the electrical property investigation of Ba-doped La$_2$Mo$_2$O$_9$ system over wide frequency (10 Hz - 10 GHz) and temperature (300 K - 1000 K) ranges, utilizing the unique impedance spectroscopy equipment built at the Faculty of Physics, Vilnius University.

Phase transition, as observed in the case of the undoped material, was found to be suppressed with the addition of as little as 1 at. % of Ba. However, the temperature dependence of doped compounds’ grain conductivity exhibits a broad kink in the Arrhenius plots around 600 K - 700 K. This was observed previously in the case of similar Bi doped compounds and explained as the transition from a static to a dynamic oxygen disorder [3].

Intra-crystallite ion relaxation frequency ($f_{\text{r}} \sim \sigma_0$) was chosen as an indicator of the bulk conductivity $\sigma_0$, which is less sensitive to the quality of the sintered ceramics and errors in determining the samples’ geometry. The relaxation frequency, determined by the position of the complex grain impedance imaginary part’s maxima (fig. 1a, arrow), in all doped compounds, was found to be lower than pure La$_2$Mo$_2$O$_9$. Consistently with the literature [2, 4], the relaxation frequency dependence on doping amount (fig. 1b) exhibits a maximum at 5 at. % Ba concentration. It is worth noting, that Ba concentrations exceeding 20 at. % are likely above the solid solubility limit of the system [4].

The influence of impurities boron nonmetal - to form the metal structure with optimum degree of imperfection prone to hydrogen absorption, due to emerging structural and impurity traps

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The interaction of hydrogen with metals is determined by the process for the two directions of research. One of directions of research carried out by us is the development of systems that can adsorb and desorb hydrogen convertible in acceptable external conditions (pressure, temperature). Diffusive migration of atoms of hydrogen in the volume of metal with subsequent formation of admixture segregations and hydride phases depends on the presence of structural and admixture traps. The second direction of researches consists in development of effective coverings for keeping atoms of hydrogen in a superficial layer of elements of designs of various purposes. In this case admixture and structural traps for atoms of hydrogen prolong a resource of operation of products and change their physic mechanical properties, both in a positive side, and in negative. Conclusions:

- The formation of the structure of metal and alloy in the form of small crystals with an optimal degree of deficiency carried out by electrochemical method using the Boron forming nickel alloy nanostructure.
- At introduction from 2 to 10 at. % of the boron in nickel occur transition from crystal structure (to 5 at. %) to implicitly expressed crystal structure (6-9 at. %) with transition to amorphous that is followed by increase in the extracted hydrogen from a sample (Fig.)
- Increase of concentration of the boron in Ni-B system causes increase in the content of hydrogen, in comparison with nickel.
- The number of defects in Ni-B system surpasses their quantity in pure nickel samples. The Boron is replacement impurity with a small nuclear radius in nickel.
- Electrochemical Ni-B, systems, where x = 0 … 0, 5 and the having about 3% weight of hydrogen are received without doping their by hydrogen.
- Increase in hardness, wear resistance, thermal stability, corrosion stability in salt environments and some other characteristics of electrochemical Ni-B-H systems in comparison with pure nickel and comparability to chrome.

Are various options for combinations of elements in chemical composition, which expands the range of materials, used for hydrogen storage. The impurity traps are substituent impurities of small atomic radius as compared with the base metal, such as boron impurity in nickel (r_B = 0.124 nm, r_B = 0.091 nm, r_H = 0.046 nm).

Impurity traps carried out the seizure of hydrogen atoms for a while due to the formation of complexes. With increasing temperature, the impurity atmosphere disintegrates, and hydrogen atoms are again transformed into a solid solution.


Structural traps (defects in the crystal structure of the electrochemical systems: dislocations, declinations, grain boundaries and others) to capture the hydrogen for a long time by forming a hydrogen segregation or hydride phase, which depends on the binding energy with field tension of structure and the thermal energy of hydrogen.

Captured hydrogen atoms are eliminated from the acting and did not take part in the diffusion processes. Boron as an impurity trap hydrogen atoms causes structural changes in nickel and creates conditions for the formation of structural traps for hydrogen atoms. As a result of structural and impurity traps reduce the hydrogen permeability of the metal.
Alloys on the basis of magnesium are perspective from the point of view modern requirements to systems hydrogen storage of with the low cost price. However their usages it is accompanied by the difficulties one of which is the hydrogen desorption temperature of alloys which is in limits 500-600 K.

One of ways of reception of materials in nanocrystalline state is introduction of chemical elements which have low solubility or do not co-interacti on at all with components. According to the phase state diagrams of systems Mg-Ti, Mg-V and Mg-Zr of interaction of these components do not exist.

To manufacture Mg-based composites the plasma evaporation-sputtering method was used enabling the atom-by-atom component growth. Thus, the composites with a wide range of the ratios of insoluble components were obtained [1]. Deuterium introduction into the samples was performed by the ion implantation method. The deuterium desorption temperature ranges and the deuterium storage levels were determined by the thermo-desorption spectroscopy.

It has been established that the introduction of Zr, Ti or V impurity to magnesium leads to the significant decrease of the deuterium desorption temperature (~400 K) as compared to the release from Mg samples (fig. 1).

A step-like form of the curve of the deuterium desorption temperature testifies to presence of two various structural conditions at composites Mg-V, Mg-Zr and Mg-Ti depending on the relation of components. The hydrogen desorption data obtained using Mg-based composites can be used for the further investigations into the hydrogen storage materials containing chemical elements with a low solubility in the alloy components.

The deuterium temperature drop can be caused by filamentary inclusions composed of Ti, V or Zr atoms in magnesium (insoluble component in magnesium) produced in the process of composites formation and providing the deuterium release from the sample at lower temperature (channels for deuterium diffusion and desorption through the surface barrier).

First principles calculations of hydrogen diffusion in ZnO crystals

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Knowledge of the atomic and electronic structure of defective/doped ZnO is of great importance for improving performance of electrodes in optoelectronic devices based on transparent conducting oxides, e.g. LED displays etc. A particular interest is understanding of a role of hydrogen impurities penetrating into ZnO thin films from plasma. It is known that interstitial hydrogen (Hᵢ), which acts as a shallow donor, is thought to be thermally unstable due to its small migration energy [1]. On the other hand, as a substitutional H (Hₒ) at an O lattice site, which is also a shallow donor, has a higher migration energy, the thermal stability of Hₒ was suggested to be much enhanced [2].

We report results of the ab initio modeling of atomic hydrogen in interstitial and oxygen vacancy positions (Hᵢ and Hₒ) of the ZnO structure based on hybrid DFT method (PBE0 exchange-correlation functional) as incorporated into the CRYSTAL-2009 computer code [3] using the supercell model and linear combination of atomic orbitals (LCAO) basis set. This approach allows us to obtain very accurate calculations of the energetic barriers of impurity migration in different paths. We compare properties of the hydrogen in the bulk with that on ZnO (10-10) surface. Also, we are calculated the defect-induced electronic charge redistribution, lattice distortion, defect formation energy for the bulk and on the surface, as well as density of electronic states (DOS). It is confirmed that Hᵢ in the bulk is a shallow donor with a considerable contribution into the conduction band bottom. At the surfaces hydrogen shows a strong binding to oxygen ions. Hydrogen can be adsorbed in the interstitial position, which, as we believe, is the starting point for migration into the crystal. Despite the charge redistribution the OH bond length in the bulk and on the surface are similar, surface hydrogen contribution into the electronic states of the conduction band is much larger than that in the bulk.

ZnO blocking layers by spray on transparent conductive electrodes

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It has been proven theoretically and practically that introduction of a compact layer at the FTO/porous TiO$_2$ interface effectively blocks the carrier recombination in dye sensitized solar cell (DSSC). TiO$_2$ compact layer is commonly deposited by spray or sol gel technique [1]. Application of ZnO compact layer between FTO and mesoporous TiO$_2$ has also been found to create an energy barrier at the interface which effectively reduces recombination and increases electron density in TiO$_2$, resulting in increased Voc and FF in DSSC [2]. ZnO has also been used as an effective hole blocking layer in an inverted organic solar cell [3]. ZnO blocking layer is rarely made by spray method, although spray technique is extensively used to deposit ZnO thin films.

In this study we report on deposition of ZnO compact layer on FTO/glass substrate. ZnO films were obtained by spray of 0.2 M Zn(CH$_3$COO)$_2$ solution onto the preheated FTO/glass substrates at temperatures in the interval of 350-450 °C. Films were characterized with the help of XRD, UV-Vis-NIR spectroscopy and SEM, current-voltage characteristics of TCO/ZnO/ P3HT, Au structure were recorded to evaluate the film electrical properties.

It appears that orientation of crystallites in FTO layer influences the orientation of crystallites in ZnO film. The (200) preferred orientation of SnO$_2$ crystallites in FTO layer promotes the growth of highly c-axis oriented ZnO films, while c-axis growth is less pronounced using FTO with the (211) orientated SnO$_2$. Both increase in film deposition temperature and reduction of the solution spraying rate increase undesirable c-axis orientation and formation of less dense structure composed of needle-like crystallites. Figure 1 illustrates the effect of the ZnO deposition temperature on the ZnO film microstructure. The smoothest ZnO films with dense structure were obtained when grown at around 350 °C using moderate solution spray rates of 2.0-3.0 ml/min, or using low amount of additives in the spray solution. ZnO compact layer is tested as a seed layer to grow ZnO nanorods, and as a blocking layer in an inorganic absorber sensitized nanostructured solar cell.

Preparation and characterization of transparent conductive films based on tin dioxide for dye-sensitized solar cells

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Dye-sensitized solar cells (DSSC) developed by Grätzel and O'Regan in 1991 [1], based on the principle of photosynthesis, changed the perception of the possibility of converting solar energy into electricity. Despite the fact that the efficiency η of DSSC is less than that of other thin-film solar cells (currently the maximum value of η is 15 % [2]), they are capable of detecting not only bright light and scattered radiation, have a high performance/price ratio, low toxicity of production of elements and components, etc. Due to these advantages DSSC is considered to be a cheap and clean energy source with wide application.

However in some manufacturing steps DSSC still uses complex and expensive manufacturing processes, for example deposition of transparent conductive films (TCF) on glass substrates, which acts as an electrode. A layer of tin-doped indium oxide (ITO) is most commonly used as TCF. However, due to the scarcity of indium on the planet and it is necessary to use expensive alternative materials [3]. Tin dioxide seems to be more suitable for this purpose because it is stable enough in different weather conditions, chemically inert, mechanically stable and can withstand high temperatures, but its conductivity has not yet reached the level that ITO has [4].

SnO₂ thin film can be produced by many methods such as chemical vapor deposition, magnetron sputtering, sol-gel, a reactive evaporation, pulsed laser deposition and spray pyrolysis. The spray pyrolysis method is the most promising due to the simplicity, low cost, the possibility of varying the properties of films by changing the mode of deposition, large surface coverage and capacity for mass production. Thus the use of technology which is based on the method of spray pyrolysis may allow to produce cheaper and more effective DSSC.

The purpose of this research is to obtain a thin film of tin dioxide doped with antimony by spray pyrolysis with different doping levels Sb ([Sb] / [Sn] = 0.0 to 1.5 wt. %) and to study morphological and optical properties. Deposition of films on soda-lime glass substrates was carried out by using a solution prepared from tin tetrachloride pentahydrate (SnCl₄·5H₂O) and C₂H₅OH. To implement doping of the films the precursor admixture – antimony trichloride (SbCl₃) – was added to this solution. Spraying of the fluids on a heated substrate was produced by means of compressed air supplied at a pressure of 2 bar. The deposition temperature was 450 ºC.

Figure 1 shows the example of the surface morphology of a thin film of pure SnO₂. Images taken with a scanning electron microscope VEGA3 SB TESCAN, shows the uniformity of the film deposition. The optical properties of the films were also studied. In particular, their transparency was measured in the wavelength range from 300 to 1000 nm (Figure 2). Studies demonstrated that the transmittance of the films initially increases with increasing of dopant concentration (0.5 wt. %), and then decreases at higher levels of doping by Sb (1.0 and 1.5 wt. %).

Figure 1. SEM image of pure SnO₂ thin film.

Figure 2. Transmittance spectra of SnO₂: Sb ([Sb] / [Sn] = 0.0, 0.5, 1.0, 1.5 wt. %) thin films as a function of wavelength.

High magnetic field induced electric polarization of antiferromagnet LiCoPO$_4$

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LiCoPO$_4$ is a well known magnetoelectric belongs to the olivine family of orthorhombic antiferromagnets LiMPO$_4$ (where M = Ni, Mn, Co, Fe). The LiCoPO$_4$ crystal is strong anisotropic antiferromagnet. Transition to the ordered antiferromagnetic state ($T_N = 21.6$ K) is accompanied by loss of the symmetry center. It reveal a variety of magnetic and magnetoelectric properties which are not fully explained yet and require additional studies, e.g. a large linear magnetoelectric effect [1], an ultra weak longitudinal (parallel to AFM vector) ferromagnetic moment [2] and a multistep magnetization process [3]. Attracts attention a region on the M(H) curve (fig.1a) with linear change of magnetic moment [3], such behaviour is not typical for strongly anisotropic antiferromagnets. In addition, a large Li-ion conductivity [4] of this compound makes it attractive for applied studies.

It was expected that study of magnetoelectric effect in strong magnetic field will give important additional information about exchange constants and symmetry of magnetic structures forming during field-induced spin reorientations.

The electric polarization of the sample was measured along the crystallographic axis $a$. Pulsed magnetic field up to 280 kOe was applied along the crystallographic axes $a$$||x$, $b$$||y$ and $c$$||z$ alternately. Experiments were carried out at the temperature $T = 4.2$ K.

It was found that magnetically induced electric polarization disappeared at the first transition field $H_1 = 121$ kOe and reappeared in the vicinity of the second one ($H_2 = 226$ kOe). Transition to the saturated paramagnetic state ($H_3 \sim 276$ kOe) lead to finally disappearance of polarisation. Obtained transition fields are rather in good agreement with the data from magnetization measurements in pulsed magnetic field. The possible magnetic structures formed in magnetic field during the spin reorientation and their symmetries were proposed.

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![Figure 1](image1.png)

**Figure 1.** Field dependences of (a) – magnetization [3] and (b) – electric polarization for LiCoPO$_4$ single crystal sample in pulsed magnetic field.

Photoluminescence of GaAs and Ga$_{1-x}$Al$_x$As (0≤x≤0.3) layers obtained by organometallic vapor phase epitaxy

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The atomic ratio between $A^{III}$ and $B^{V}$ has a significant influence on the properties of AB semiconductor. In particular, photoluminescence and other physical properties of doped GaAs layers is not enough studied. Recently, the GaAs and Ga$_{1-x}$Al$_x$As layers were obtained by organometallic vapor phase epitaxy (MOCVD) on GaAs (111)A substrate at pressure ~70 Torr and relatively low crystallization temperature ~570-670 °C [1]. In practice, the layer deposition with a good morphology was possible at the certain conditions and only with a high $B^{V}/A^{III}$ relationship.

Present research work is the study of photoluminescence and galvanomagnetic properties of the Si-doped GaAs and Ga$_{1-x}$Al$_x$As layers obtained by MOCVD on GaAs substrate with crystallographic orientation of (111)A/B and (100). The layer deposition were carried out in a various ratio between partial pressure of gaseous arsine, $\text{AsH}_3$, and trimethyl gallium, $\text{Ga(CH}_3)_3$, meaning the different $B^{V}/A^{III}$ relationship. The process of the nonstoichiometric defect formation was discussed in details. Impact of the defects on the appearance of the doped layers with a different type of conductivity and sharp interfaces was considered in practice. All experimental results might be used for the formation of GaAs and Ga$_{1-x}$Al$_x$As layers with excellent crystal and interfacial quality and special physical properties.

Properties of the electrochemically synthesized composites based on polyaniline and modified MWCNT

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Among the many types of composites, great attention is focused on the electroconductive materials based on conjugated polymers [1]. The unique physical properties of MWCNT make them suitable components for the composite based on polyaniline that was the first polymer with application in power sources [2].

Electrochemical synthesis of polyaniline composites with 0-20 wt% of MWCNT is proposed in the present work. Their characterization is the main goal of the study. During synthesis, electrode surface becomes covered by polyaniline with the typical fibril structure, while addition of MWCNT results in its aggregation. SEM observation confirms high-dense morphology of the aggregates with higher thickness of the polymer fibrils at the gradual increase of MWCNT content. Beginning from 1 wt% of MWCNT in the composites a clear separation and increase in the intensity of the bands responsible for vibrations of chinone- and benzo- fragments is identified by FTIR. The highest value of density is found for the composite with 2 wt% of MWCNT that is in good agreement with maximum in capacitance and corresponds to a steep increase of electrical conductivity.

Surface morphology of Si doped GaAs(111)A epitaxial layer

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Formation of a mirror-like surface of GaAs (111)A epitaxial layers by organometallic vapor phase epitaxy was successfully solved by optimization of the process conditions and B⁵/V⁵ relationship [1]. This can be achieved at low temperature through modulation flow of trimethyl gallium, Ga(CH₃)₃, and a high value of B⁵/V⁵ relationship.

Spectroscopic study of structural defects in Si doped GaAs(111)A epitaxial layer is the main subject of the present work. Based on photoluminescence performed at 27 and ~196 ºC it was found that in the epitaxial layers, grown at B⁵/V⁵ relationship of 80-200 and temperature region of 610-680 ºC, appearance of bands in spectrum is due to the nonstoichiometric structural defects. At low value of B⁵/V⁵ relationship V₃As vacancies and pair of V₃As-SiAs are formed while higher B⁵/V⁵ relationship (180-200) promotes anti-structural defects of As₃Ga that finally can form pairs of As₃Ga-SiAs at 630 ºC. Detailed analysis confirmed different nature of the defects in the Si doped GaAs epitaxial layer with crystallographic orientation of (111)A and (100).

INVESTIGATION OF MECHANICAL AND ELECTRICAL PROPERTIES OF Li DOPED SODIUM NIOBATE CERAMIC SYSTEM

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The perovskite niobates constitute a very interesting group of functional materials, because of their extreme physical parameters sensitive to external factors. Some solid solutions based on a sodium niobate have i.e. a very good piezoelectric properties, moreover, they contain no lead and so they fulfil a very important demand of high technology industry concerning a reduction of the environmental pollution. One of the most interesting and extensively studied system is a lithium niobate -sodium niobate solid solution (LiNbO₃-NaNbO₃).

Pure and 4 mol% Li-added sodium niobate ceramics were prepared by a two-stage hot-pressing technology in the Institute of Solid State Physics at the University of Latvia. The preliminary structural studies were carried out by X-ray diffraction technique showed the formation of single perovskite phase in the investigated compositions. The effect of Li doping on a microstructure and mechanical properties of the Li₀.₉₆Na₀.₀₄NbO₃ solid solution was investigated at room temperature. The microstructure and EDS measurements were performed by means of scanning electron microscope with field emission Hitachi S4700 and microanalyses system Noran-Vantage. To determine the elastic constants (the Young's modulus E, the shear modulus G, bulk modulus K and the Poisson's ratio v) of Li₀.₀₄Na₀.₉₆NbO₃ a method of measurement of the longitudinal (V_L) and transverse (V_T) ultrasonic wave velocities for this type of material was developed. The electric properties of NaNbO₃ and Li₀.₀₄Na₀.₉₆NbO₃ ceramics were investigated in the frequency range from 100 Hz to 200 kHz and from room temperature to 750 K, in the heating and cooling process. Both electric permittivity and conductivity exhibit an anomaly as a function of the temperature and frequency. The a.c. electric conductivity as a function of angular frequency \(\sigma(\omega)\) follows the relation \(\sigma(\omega) = A\omega^{s}\). The local minima of electrical conductivity \(\sigma\) were observed, which are probably associated with a polaronic transport mechanism.
The vibronic-proton mechanism of the ferroelectric phase transition in the KH$_2$PO$_4$-type systems

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We present a vibronic-proton model of the KH$_2$PO$_4$ (KDP)-type ferroelectrics. In [1-5] the importance of the proton subsystem and the proton-phonon coupling was stressed in these systems. In this report it is shown that the electron-phonon (vibronic) interaction in the PO$_4$ groups (including also the K$^+$ ions) between the conduction electronic states and the valence states mixing these bands by the [K-PO$_4$] dynamic displacements of the potential soft optic vibrations (the covalent hybridization) takes place. This interaction is the driving force in the mechanism of the KH$_2$PO$_4$ ferroelectric phase transition. The results of the ab initio calculations of the electronic band structure in KDP [6] are used. Acoustic electron-lattice interaction sufficiently contributes to the ferroelectric ferroelastic phase transitions in the KH$_2$PO$_4$-type systems. The tunneling of protons between the two equivalent positions in KH$_2$PO$_4$ (the neutron Compton scattering measurements support the large value for the tunnel splitting [7]) interacts with the optic phonons corresponding to the dynamic displacements of the [K-PO$_4$] cluster along the z direction. This coupling contributes also to the dynamic instability of the KDP-type crystals. The actual vibronic anharmonicity is produced by the electron-phonon couplings and the phonon-phonon anharmonicities are taken into account. The spontaneous polarization in the ferroelectric phase and the dielectric constants (including the anisotropy) in the paraelectric and ferroelectric phases are calculated. The spontaneous shear strain $u_{0i}$ ($e_{0i}$) is caused by the deformation potentials (the electron-phonon interactions with the acoustic vibrations) and it contributes essentially to the change of the symmetry of KDP systems at the ferroelectric transition which is also ferroelastic one. The influence of the isotope effects (H→D and $^{16}$O→$^{18}$O) on the ferroelectric properties of the KDP systems are estimated.

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Doping of BaTiO$_3$ polycrystalline leads to important modifications of its physical properties. In order to improve the properties of BaTiO$_3$ to realize multi-functionality, various dopants have been introduced into bulk of the BaTiO$_3$ to substitute the Ba$^{2+}$ or Ti$^{4+}$ ions. For example, an effective method for the stabilisation of the high temperature hexagonal phase of BaTiO$_3$ at room temperature is by the substitution of Ti ions with Mn, Fe, Zr or Hf. The studies of influence of additive are mainly focused on improving electrical properties of these ceramics, whereas studies on mechanical properties are scarce. Therefore, the improvement of the elastic properties of BaTiO$_3$-based ceramics by the addition of metal ions with variable valence has been studied. The effect of doping on mechanical properties of the BaTiO$_3$ solid solution was investigated at room temperature. For this purpose, elastic modulus: Young's modules E, shear modules G and Poisson ratio $\nu$ were measured. The shear modulus, G, related to strain response of a body to shear or tensional stress. It involves change of shape without change of volume. To determine the elastic constants a method of measurement of the longitudinal ($v_L$) and transverse ($v_T$) ultrasonic wave velocities for this type of material was developed. Elastic behaviour of doped BaTiO$_3$ were compared to those of pure BaTiO$_3$ ceramics. The mechanical properties showed that the elastic modules are correlated to the lattice constants. Furthermore, for doped and pure ceramics the dielectric measurements were performed in cooling processes. The electric properties of ceramics were investigated in the frequency range from 0.1 Hz to 10 MHz and temperature between 150K and 550 K. It was found that doping influence on elastic and dielectric properties too.
Relaxor Strontium-Barium Niobate: A Lead-Free Anisotropic Electrocaloric Material

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Solid solutions of the strontium-barium niobate Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ where $0.25 < x < 0.8$ (SBN) are environmentally friendly (lead free) polar materials of oxygen octahedral family. This type of materials is recognized as very prolific due to its five different cationic crystallographic sites. Consequently, physical characteristics of SBN are strongly correlated to composition and chemical bonding. As a result of the compositional flexibility, SBN is recognized to exhibit diverse properties. Correspondingly, its potential applications are based on very attractive pyroelectric, electromechanical, electro-optic, photorefractive, and nonlinear optical and dielectric properties.

Structurally strontium-barium niobate is distinguished by its open tungsten bronze structure, i.e. the compound contains five AB$_2$O$_6$ formula units per tetragonal unit cell in which six A sites are occupied by five divalent metal ions A. As a result the empty sites give rise to quenched electric random fields even in the stoichiometric compound. Consequently, by changing the ratio between strontium and barium components one may tune the system from ferroelectric ($x < 0.5$) to a generic relaxor ($x > 0.6$) behavior while maintaining the structure unchanged [1].

Results reported in our contribution represent the first direct ECE study of strongly anisotropic non-perovskite materials. It is shown that both the absolute values of ECE and the width of the temperature range over which they are observed strongly depend on the direction of applied electric field [2]. These results are confirmed both by direct experimental measurements on single crystals cut in different directions, and theoretical predictions based on statistical mechanics. Our direct ECE measurements have also evidenced that, contrary to the polar nano-regions found in known perovskite relaxors, the PNRs are highly anisotropic in tetragonal tungsten bronze SBN75. This anisotropy highlights another promising feature of these tungsten bronzes; A solid state cooling device utilizing a highly textured form of these materials would allow for an optimized use of the ECE response, by making the most of the largest ECE directional component instead of just averaging the ECE values of randomly oriented polycrystalline systems.

Solid State NMR study of calcium hydroxyapatites: cut-off averaging of dipolar coupling, spin clusters, CP beating and relaxation effects

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Materials based on calcium phosphates especially calcium hydroxyapatite (Ca10(PO4)6(OH)2), further CaHA) have found many applications in implantology, orthopedic, and periodontal surgery due to close similarity to the mineral of hard tissues (bone, enamel, dentin, etc.) and therefore high biocompatibility with them. In this study three calcium hydroxyapatites which differ in their morphology were investigated: commercially available (CA-CaHA), CaHA with amorphous clustered phosphate phase (ACP-CaHA), nano-structured CaHA (Nano-CaHa).

High data point density 1H→31P cross-polarization kinetics measurements have been carried out for CA/ACP/nano CaHA. The chosen setting of the sampling frequency of 5·10^4 s⁻¹ allowed to reveal all spin interactions having the dipolar splitting b ≤ 25 kHz. In the case of 1H–31P interaction this means that the structures with the internuclear distances r ≥ 0.45 nm could be resolved. The novel processing of CP MAS data has been developed introducing the variable cut-off Gaussian distribution of the dipolar coupling. It was used in the averaging of CP kinetic curves and the fitting to the experimental results. This procedure allowed to describe the oscillatory kinetics and CP curves in nano-structured materials over a wide range of contact time and to determine the characteristic size profile and composition of the spin clusters (Fig 1).

It is interesting to note that in CA/nano-CaHA under sufficient fast MAS (7 kHz) another oscillatory process appears. The 31P spectrum consists of two overlapped spectral lines which probable corresponds to two crystallographically non-equivalent sites (tetragonal and hexagonal). The difference of the dipolar interactions is much smaller than the initial values and CP beating appears. To our knowledge such process have never been seen before and it is needed to investigate more. The 1H and 31P spin-lattice and spin-spin relaxation time measurements have revealed the fast spin motion takes place in ACP-CaHA. The corresponding correlation time τ ~ 7·10⁻⁷ s at ~ 300 K has been determined. The effect of MAS rate on the 31P signal shape also confirms that this motion runs in the time scale of microseonds or even nanoseconds. The magnitude of the anisotropic broadening 1220 ± 20 Hz determined for nano-CaHA is very close to the maximum of the dipolar 1H→31P coupling distribution profile estimated using CP MAS kinetics. The dynamics of 1H–31P spin interactions in nano-CaHA (τ ~ 3.3·10⁻⁵ s) is much slower than in ACP-CaHA.

Influence of alternating voltage on Compton effect caused by X-ray radiation in a quartz monocrystal

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The experiment was done using a monocrystalline quartz plate with dimensions 0.5 mm × 5 mm × 7 mm and with silver electrodes (the sample). The sample was exposed to non-monochromatized X-ray radiation of the DRON-3M diffractometer with a Cu X-ray tube at anode voltage \( U_a = 10 – 25 \) kV and anode current \( I_a = (2 – 25) \) mA. After applying alternating voltage \( U_s \) with frequency 13.47 MHz and magnitude (80 – 200) V to the sample surface, a significant decrease of diffraction intensity was observed (Fig. 1). Duration of one measurement was 2 s, the time interval between measurements was 1 s. The total time of a single experiment was 7 hours.

This change of intensity is proportional to amplitude of applied alternating voltage. The observed decrease of intensity can be explained by influence of alternating electric field and capture of Compton recoil electrons into defects, decreasing the rate of recombination of those electrons with remaining positive Si ions. The mass absorption coefficient of oxygen atoms is approximately 5 times less than that of Si atoms. Free electrons released during photoelectric absorption are captured by impurity ions, vacancies and intrinsic atoms. Inside the crystal, electrons are acted upon by electric fields of positive Si ions, vacancies created by the Auger effect, impurity ions, as well as by the external alternating electric field. This causes creation of deformations of the crystal structure and resonances, which persist while high-frequency external electric field acts upon metastable point defects.

At \( I_a = 2 \) mA, the root-mean-square deviations of the lattice atoms’ positions increase proportionally to the increasing voltage \( U_a \) applied to the sample (Fig. 2). At higher values of \( I_a \), influence of alternating voltage on peak intensity becomes less pronounced. The deformation of the crystal lattice is proportional to magnitude of applied voltage. This is due to oxygen and silicon atoms ionized during Compton scattering and due to Auger effect, which creates negative vacancies in Si tetrahedra, as well as due to resonant interaction of electrons with nuclei of neighboring Si atoms. Si atoms are connected to each other via pairs of oxygen atoms connected with each other by strong bonds. Those oxygen atoms are weakly affected by X-ray radiation.

As a result, the O-O bonds in the link Si-O-O-Si are not broken and influence of defects generated in Si tetrahedra on lattice deformation is less than in Si crystals. Consequently, the mean square displacement of the lattice \( \langle u^2 \rangle \) increases linearly with increasing \( U_s \). When \( I_a \) is increased, photoelectrons probably begin to compete for vacancies in Si1 K layer, thus limiting the increase of point defect concentration. With increasing \( U_s \), radiation penetrates deeper into the crystal, where influence of \( U_a \) acting on the surface is weaker (Fig. 3).

When \( U_s \) is increased to 200 V, the recorded angular position of the intensity peak decreases by 0.16°. This corresponds to an increase of the inter-plane distance by 0.04 Å and lattice deformation by 1.2%.

---

**Fig. 1**
Time dependence of peak (101) intensity when alternating voltage of (80 – 200) V is applied to the sample surface.

**Fig. 2**
Dependence of mean square displacements of quartz crystal lattice on magnitude of alternating voltage applied to the sample surface at different values of anode current \( I_a \) of the X-ray tube.

**Fig. 3**
Dependence of mean square displacements of quartz crystal lattice on anode voltage of the X-ray tube (\( I_a =2\)mA).
Impedance spectra of the intermediate state in Li$_2$O-7GeO$_2$ glass-ceramics

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Among dielectrics with high ionic conductivity, the crystals of lithium germanate family Li$_2$O-xGeO$_2$ are investigated actively and, in particular, a special attention is paid to lithium heptagermanate (x=7) [1]. Li$_2$O-7GeO$_2$ glass quenching and its stage-by-stage crystallization on heating were reported earlier in [2]. The electrical properties of Li$_2$O-7GeO$_2$ glass and phases, obtained during glass crystallization, were studied in [3]. It was shown that heat treating makes possible to obtain the samples in the intermediate metastable state with increased electrical conductivity $\sigma$. Conductivity of the samples in the intermediate state exceeds by three orders $\sigma$ of the polycrystalline samples and by one order higher than $\sigma$ of the initial glass [3]. In the abstract we report the impedance spectra measured for the intermediate state in Li$_2$O-7GeO$_2$ glass-ceramics. Preliminary DTA analysis showed that on heating crystallization of Li$_2$O-7GeO$_2$ glass was marked by two exothermic peaks at $T_1=840$ K and $T_2=915$ K [2]. The samples in the intermediate state were prepared by heating of the initial glass to the temperature between $T_1$ and $T_2$ and subsequent cooling to room temperature. More details on the samples preparation and measuring procedure can be found in [1].

An impedance spectrum of the sample in the intermediate state is shown in Fig.1 as diagram in ($\rho''$–$\rho'$) plane. One can see that the diagram consists of two well resolved arcs. It is known that such hodographs can be simulated by equivalent circuit containing two serially connected parallel $R$ and $C$ circuits. Visible shift of the semicircles centers downward from $\rho'$ axes is usually attributed to relaxation times $\tau=RC_j$ ($j=1,2$) distribution and is described by substituting in $R$C$_j$ circuits of $C_j$ by generalized frequency dependent capacitances $C_j^n=\Lambda((\omega\tau)^n)$, where $\omega$ – external field frequency, $0<\omega\tau\leq1$. For limiting cases $n=0$, $C_j^n$ reduces to usual resistor or capacitance correspondingly. The curve calculated by using of impedance of equivalent circuit, mentioned above, is shown in Fig.1 by solid line.

![Impedance spectrum of the Li$_2$O-7GeO$_2$ sample in the intermediate state at $T=600$ K](image)

Presence of a few arcs in ($\rho''$–$\rho'$) diagrams is typical for multiphase composite systems. Obviously that two arcs in Fig.1 reflect charge transfer in the regions with different structures. X-Ray phase analysis, performed in [4], makes it possible to propose that low frequency arc in Fig.1 corresponds to charge transfer in the intergrain regions whereas high frequency arc is contributed by carriers motion within nucleus with Li$_2$Ge$_2$O$_5$ and Li$_2$Ge$_5$O$_9$ structures. Accounting the previous data (see [1] and refs therein) one can assume that mobile Li ions determine hopping transport in Li$_2$O-7GeO$_2$ glass- ceramics. Comparing relaxation times values $\tau_1=3\times10^{-6}$ s, $\tau_2=6\times10^{-4}$ s one can conclude that increased conductivity of Li$_2$O-7GeO$_2$ intermediate state is determined by high mobility of Li ions moving within the nucleus of ordered phases.

Nanoscale magnetization of a single vortex in $d$-wave superconductors

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The finite-size scaling of the nanoscale magnetization $m$ on size averaging $R$ of a single vortex in $d$-wave superconductor is developed using quasiclassical Eilenberger equations. The nonlinear (Volovik and the order parameter effects) and the nonlocal corrections to the London equation in the vortex state are investigated in this framework. The ratio between the characteristic lengths in this scaling is $\xi < R << \lambda$, where $\xi$ and $\lambda$ are the coherence length and the London penetration depth, respectively. It is found that temperature dependence of magnetization shows flattening at low temperatures, in contrast to linear dependence of $\lambda(T)$ in Meissner state. The temperature dependences of the two-point $\chi(T, R_1, R_2) = m(T, R_2) / m(0, R_2) - m(T, R_1) / m(0, R_1)$ with $R_2 > R_1$ and the one-point $\chi_\infty(T, R_1 \to \infty, R_2)$ correlation functions are calculated. It is found that both functions are nonmonotonous of temperature and have opposite signs changing them at high temperatures. This nonmonotonous temperature dependence can be understood as a resulting from the competition between a) the Volovik effect and the nonlocal corrections to superconducting electron density which dominate at low temperatures and flatten $m(T, R) / m(0, R)$ dependence with respect to $\lambda^2(T)$, and b) current-induced suppression of the order parameter that dominates at high temperatures. Large-scale simulations ($R \leq \lambda$) are also done and screening effects are considered. In this case $\chi(T, R_1, R_2)$ is positive and the corrections to the London equation are small relative to screening effects. Our method of studying nanoscale effects can be considered as a first step to understanding of the vortex properties in high-$T_c$ nanoparticles [1] and nanocomposites [2].


Measuring of dielectric parameters of ferroelectrics depending on the temperature
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To develop the elements of functional electronics based on ferroelectrics it is required a study of the dielectric parameters dependences from the influencing factors that determine the physical effects. For example, in [1], the piezoelectric properties of SrTiO3-BiTiO3 ceramics are described.

As the phase state of the ferroelectrics depends on the temperature, the study of its influence on the dielectric parameters regarded in this paper, is an actual task. The authors proposed a method that allows to obtain dependences of the dielectric parameters of ferroelectrics (the inverse dielectric susceptibility \( \chi \) and known relations of the dielectric constant \( \varepsilon \), capacitance, polarizion associated with it) with the phase transition of the first and second kind with a minimum number of measurement procedures, the using of measuring instruments in a narrow measurement range, by the theoretical-empirical modeling. The temperature dependence of the inverse dielectric susceptibility of ferroelectrics with a phase transition of the second kind is a straight line, the slope of which is differed in 2 times in the ferroelectric and paraelectric phases, respectively, which formalized the phenomenological theory. For example, in the paraelectric phase the temperature dependence of the inverse dielectric susceptibility may be approximated by a straight line of the form \( \chi_p(T) = a_p + b_pT \), where \( a_p \), \( b_p \) – the parameters which are calculated by approximating the experimental data, such as the method of the least squares, it is considered in detail in [2].

In real conditions of the experiment a systematic error due to the fact that the dielectric constant on the alternating sinusoidal signal measured under adiabatic conditions takes place. This leads to the methodical error of the inverse dielectric susceptibility measuring \( \delta \chi \):

\[
\delta \chi = \frac{16\pi^2 T\varepsilon_0 C p^2}{\varepsilon^2 C^2 p^2},
\]

where \( C_p \) - heat capacity of volume unit at constant polarization \( P \); \( C \) – Curie constant.

Figure 1 shows the graphs of functions \( \varepsilon(T) \) and \( \chi(T) \) for ceramics based on barium titanate, which are characterized by the place with high steep (almost vertical portion 2 in Fig. 1, (б)). In the transition from the ferroelectric phase to the paraelectric one, the Curie temperature \( T'_C \) can be defined as the abscissa corresponding to the minimum value of the inverse dielectric susceptibility.

The methods for measuring the temperature dependences of the dielectric parameters of ferroelectrics of first, second kind and with a diffuse phase transition are proposed in this paper. Their use allows to reduce the costs of measurements and it is advisable to increase the measurement efficiency to control technological processes.


Electric properties of polycrystalline (Ba$_{1-x}$Sr$_x$)(Ti$_{1-x}$Zr$_x$)O$_3$ solid solution

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The results of the research on the influence of the substitution, in the both cationic sublattices (barium titanate), Sr$^{2+}$ and Zr$^{4+}$ ions on the electric properties and characteristics of phase transitions in the (Ba$_{1-x}$Sr$_x$)(Ti$_{1-x}$Zr$_x$)O$_3$ (BSTZx) solid solutions are presented. The aim of these studies was to obtain a functional material of appropriate microstructure and diffusion of ferroelectric – paraelectric (FE – PE) phase transition. The material with electrical parameters which would be stable over a wide temperature range.

Polycrystalline samples of (Ba$_{1-x}$Sr$_x$)(Ti$_{1-x}$Zr$_x$)O$_3$ solid solution were obtained by means of a conventional high temperature technology. The ions substitutions in the both cationic sublattices simultaneously generated the higher heterogeneity of structure which was confirmed by the X-ray measurements. The differences in the sizes of ionic radii of Ba$^{2+}$ and Sr$^{2+}$ as well as Ti$^{4+}$ and Zr$^{4+}$ ions cause the changes in the size of solid solution unit cell. The substitution of ions of different size leads to the mechanical deformation of crystallites. SEM images taken with an electron microscope show a well-formed structure with visible layers.

We observed that with increasing the concentration of substituted ions the temperature of phase transition FE – PE reduces and its diffusion increases. At temperature of 340 K and for Sr$^{2+}$ and Zr$^{4+}$ ions concentration of $x = 0.10$ in the BSTZx sample all three structural transitions turned into one R – C (rhombohedral – cubic) phase transition which is also a diffuse phase transition FE – PE.

From a.c measurements the relaxation times and activation energy were determined. The investigation confirmed the improvement of the electrical properties compared with polycrystalline barium titanate. Due to its high values of permittivity and low dielectric loses the BSTZx material becomes a very good candidate for applications as the elements of FRAM memory and tuning capacitors.
Influence of Sr substitution on the electric properties of PbTiO$_3$ ceramic

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The results of research concerning an influence of the strontium (Sr$^{+2}$) ions substitution in the cationic sublattice A on the electric properties and nature of phase transition in a [(Pb$_{0.4}$Sr$_{0.6}$)$_{0.9}$Bi$_{0.1}$]TiO$_3$ ceramic are presented. The investigated material was obtained with the use of a conventional method. Based material - PbTiO$_3$ ceramics finds widespread applications in optoelectronics and microelectronics because of their special ferroelectric and piezoelectric properties. PbTiO$_3$ is highly sensitive to the addition of certain ions. Considering the different behaviors of the solid solutions with various A-site substituted cations, is it important the study of influence of these substitutions on the electric properties. Isovalent substitution of Sr$^{+2}$ for Pb$^{+2}$ in PbTiO$_3$ lowers the Curie temperature, thus raising the value of dielectric permittivity in the room temperature. A-site substitution of Pb by Bi may also influence on ferroelectric properties of (Pb,Sr)TiO$_3$ system. Therefore the electrical behavior of [(Pb$_{0.4}$Sr$_{0.6}$)$_{0.9}$Bi$_{0.1}$]TiO$_3$ ceramic material were investigated by broadband dielectric spectroscopy. The investigations of the microstructure and chemical compositions of polycrystalline sample was performed by using the electron scanning microscope with field emission Hitachi S 4700 and the system Energy Dispersive X-ray Spectroscopy (EDS) Noran-Vantage. The obtained results confirm the high purity and the expected quantitative composition. The dielectric measurements were performed by means of cryogenic temperature control system – Quatro Cryosystem together with Alpha-AN High Performance Frequency Analyzer system WinDETA Novocontrol software. Measurements were performed in a wide range of temperatures from 140 K to 600 K and frequency between 0.1 Hz and 10 MHz. The impedance and modulus spectroscopic analyses were carried out. The grain and grain boundary relaxation times were evaluated and the activation energies were also calculated.
Physical and Chemical Properties of Highly Doped Optically Nonlinear LiNbO$_3$:Zn Single Crystals

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The LiNbO$_3$ crystal is of interest for experts in integral and nonlinear optics, acoustic and quantum electronics, and solid state physics. Single crystals LiNbO$_3$: Zn at “threshold” Zn concentration ($\sim 4.5\div5.0$ mol. %) are of special interest because of high resistance to optical damage and possible application in planar technologies of optical converters on the basis of periodically polarized structures [1 – 4].

The LiNbO$_3$:Zn melt-crystal system is studied by small steps of the admixture concentration over the range of 4 - 9 mol.% ZnO that has allowed finding the concentration thresholds in the melt more accurately to be $\sim 5.4$ and 6.8 mol. %. Three regions of concentrations are revealed where the melt properties change significantly. Thus, the characteristics of the LiNbO$_3$:Zn crystals grown from melt of a different concentration region are different. Optically and compositionally homogeneous LiNbO$_3$:Zn crystals without defects are grown from melt containing admixture within the concentration range 5.4 - 6.8 mol. % ZnO. The best characteristics were revealed for LiNbO$_3$:Zn single crystals grown from melt containing 6.12 mol. % ZnO. A significant change of the properties and the structure of the crystals occurs at $> 6.8$ mol. % ZnO in melt. Thermodynamic properties of the melt in the range of admixture concentration $> 6.8$ mol. % are such that single-phase LiNbO$_3$:Zn crystals without defects are obtained only under condition that less than 20 % of the melt mass is crystallized since the crystals exceeding more than 20 % of the melt mass contain two phases: Li$_6$ZnNb$_4$O$_{14}$ and LiNbO$_3$. Admixture distribution coefficient in the LiNbO$_3$:Zn ($> 6.8$ mol. % ZnO) crystals is much less than unity in this concentration range the admixture distribution being classical as the concentration grows toward the bottom of the bulb. Crystals grown from melt of this concentration range contain a large amount of defects and have a high tendency to crack due to compound inhomogeneity.

Due to significant change of the melt properties with changing concentration from one region to another it is quite possible to obtain LiNbO$_3$:Zn crystals with different intrinsic structures of the same admixture concentration. The LiNbO$_3$:Zn system is sensitive to zinc concentration in the melt, which makes it completely different from the LiNbO$_3$:Mg system. Proximity of the ionic radii of Zn$^{2+}$ and Mg$^{2+}$ cations is not significant enough to assume the two melt-crystal systems would behave alike.

Effects of High-Intensity Light on Structure and Mechanical Characteristics of Ceramic Nb₂O₅ and Nb₂(1–y)Ta₂yO₅ Pentaoxides

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In mixtures of niobium and tantalum oxides co-precipitated from hydroxides the presence of one pentoxide affects the polymorphic transformations of the other (transformation of the low-temperature phase of niobium oxide L-Nb₂O₅ into the high-temperature phase H-Nb₂O₅ is suppressed by tantalum pentoxide) and can be used to prepare mixed low-temperature polymorphs of niobium-tantalum pentoxides Nb₂(1–y)Ta₂yO₅ of low fluorine content.

The developed technological approaches to obtaining mixed Nb₂(1–y)Ta₂yO₅ oxides are shown to allow synthesis of LiTaₓNb₁₋ₓO₃, LiₓNa₁₋ₓTaₓNb₁₋ₓO₃ and NaTaₓNb₁₋ₓO₃ solid solutions at lower temperatures the properties of the obtained solid solutions being different (for example, a higher value of the high-frequency permittivity and ion conductivity). The results are of great practical interest to comparative studies of the ways the structure and properties are affected by conditions under which the mixed niobium and tantalum pentoxides are prepared.

Mixed Nb₂(1–y)Ta₂yO₅ (y = 0.068, y = 0.111, y = 0.363) oxides of fluorine concentration of less than 0.05 wt.% and concentration of basic cation impurities not exceeding ~ 5·10⁻⁴ wt.% have been obtained. The structure and mechanical properties of ceramic Nb₂O₅, Nb₂(1–y)Ta₂yO₅ ceramics co-precipitated from oxides, prepared by conventional techniques and by high-intensity light treatment are studied and compared.

Figure 1 Microstructure of the Nb₂(1–y)Ta₂yO₅ ceramic prepared by a conventional ceramic processing technique:

y = 0.068 (a) and y = 0.363 (b).

The changes of the polycrystalline structure in the Nb₂(1–y)Ta₂yO₅ ceramics series is shown depending on the tantalum concentration and the way of being prepared (Figure 1). Dependence of the modulus of elasticity and micro-hardness of Nb₂(1–y)Ta₂yO₅ ceramics on the particular features of microstructure are revealed. The treatment by high-intensity light significantly changes the structure of Nb₂O₅ and Nb₂(1–y)Ta₂yO₅ ceramics as manifested by changes somewhat improving mechanical characteristics of the materials, such as micro-hardness, strength, micro-fragility. High-intensity light treatment affects mostly the structure of Nb₂O₅ while the structure of Nb₂(1–y)Ta₂yO₅ at y = 0.363 is the least affected; perhaps because the structure of Nb₂(1–y)Ta₂yO₅ is “loosening” with rising the concentration of Ta₂O₅ having a higher melting point.
Structure and properties of niobium-tantalum pentaoxide ceramics prepared by high-intensity light technique

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A study by scanning probe microscopy and Raman spectroscopy of the effects of high-intensity light (HIL) flow treatment on ceramics of Nb₂(1-y)Ta₂yO₅ (y = 0, y = 0.068, y = 0.111, and y = 0.363) prepared from co-precipitated oxides is reported. The treatment is found to increase the proportion of finer grains changing mechanical properties of the materials. The modulus of elasticity of the Nb₂(1-y)Ta₂yO₅ ceramics decreases with increasing the Ta content. However, it is somewhat larger in ceramics prepared in optical furnace, as seen from Table 1.

Table 1. Micro-hardness (H) and modulus of elasticity (E) of Nb₂O₅ and Nb₂(1-y)Ta₂yO₅ ceramics prepared from co-precipitated oxides by conventional ceramic techniques (CCT) and by processing in optical furnace (HIL)

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>H, GPa</th>
<th>E, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCT</td>
<td>HIL</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>9.43±1.30</td>
<td>11.82±1.43</td>
</tr>
<tr>
<td>Nb₂(1-y)Ta₂yO₅, y = 0.068</td>
<td>6.37±0.65</td>
<td>6.34±0.94</td>
</tr>
<tr>
<td>Nb₂(1-y)Ta₂yO₅, y = 0.111</td>
<td>5.45±0.78</td>
<td>6.78±0.99</td>
</tr>
<tr>
<td>Nb₂(1-y)Ta₂yO₅, y = 0.363</td>
<td>5.57±0.5</td>
<td>5.06±1.04</td>
</tr>
</tbody>
</table>

Substantial changes are observed in Raman spectra of ceramic Nb₂(1-y)Ta₂O₅ samples prepared in optical furnace as compared with ceramics prepared by conventional technology (Figure 1).

The narrowing of Raman bands and vanishing of the 540 cm⁻¹ band is considered as evidence of structural ordering while broadening of the bands in the 150 – 300 cm⁻¹ range ascribed to cation vibrations inside the oxygen octahedrons – as evidence of disordering of the cation sub-lattice. Broadening of the 630 cm⁻¹ band assigned to symmetric stretching of the octahedrons – caused by increase of anharmonicity.

High-intensity light treatment affected the most structure and the least structure. Perhaps this is due to the “loosening” of Nb₂(1-y)Ta₂O₅ structure with rise of Ta₂O₅ concentration because Ta₂O₅ has higher melting point than Nb₂O₅.

The high-intensity light at preparing ceramics in optical oven has the strongest effect on the structure of Nb₂O₅ ceramics, the weakest – on the structure of the Nb₂(1-y)Ta₂O₅ ceramics at y = 0.363.
Studies of electrical properties of ferroelectric potassium-sodium niobate ceramics under long-lasting conditions of exposure to constant temperature, electric field and radiation are reported. The samples of \((K_{0.5}Na_{0.5})(Nb_{1-x}Sb_x)O_3\) (KNN-\(x\)) at \(x=0.05\) (KNN-5) have been synthesised by conventional solid state reactions with admixture of 0.5 mol \% MnO\(_3\).

The photocurrent excited by low-intensity (0.2 W/cm\(^2\)) UV (\(\lambda = 405\) nm) radiation has been measured in a shortcut circuit of unpolarised sample irradiated through perforated electrode. The Sawyer-Tower techniques are used to record polarisation loops at different duration under sinusoidal field of constant amplitude \(E\) to study the infralow-frequency dielectric response.

The characteristic behaviour of photocurrent in KNN-5 ceramics at 61 °C switching the light on and off is presented in Figure 1. The inset shows approximation of the decline of photocurrent after switching off the exciting radiation by equation \(I(t) = (I_{\text{max}} - I_{\text{end}}) \exp(t/\tau) + I_{\text{end}}\) where \(I_{\text{max}}\) is the maximum value of the photocurrent and \(I_{\text{end}}\) – the stationary current, \(\tau\) - the relaxation time constant.

Figure 1. Time dependence of photocurrent in KNN-5 ceramics at switching the UV radiation on and off. Inset: Experimental points and approximation curve of photocurrent after switching off the radiation.

The exponential decline of photocurrent points to relaxation of the space charge in KNN-5 emerging at irradiation as in other ferroelectrics. The current does not decrease to zero, which is an evidence of the photovoltaic effect known in light-sensitive ferroelectrics [1].

The decrease of photocurrent maximum being found after 50 min under infralow-frequency sinusoidal field is ascribed to destruction of the space charge.

Behaviour of polarisation loops at different numbers of cycles of the sinusoidal electric field \(E\) is presented. A considerable rise of the dispersion of dielectric permittivity is observed at increasing \(E\), after the samples are held at constant temperature and constant bias field.

Electrically and optically active defects in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ single crystal

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Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) crystal is considered as a basic compound to create new lead-free piezoelectric materials for electro-optic modulators, piezoelectric transducers, sensors and actuators [1]. In the abstract we report the effect of heat treating in air and in vacuum on the electrical and optical properties of NBT. The single crystals studied were grown from the melts by Czochralski method. Heat treating was performed in air ($T_{ann}=1070$ K for 1 h) and subsequently in vacuum ($p=8$ mTorr, $T_{ann}=1070$ K for 2 h). Electrical permittivity $\varepsilon$ was measured along [001] direction in AC field ($f=1$ kHz) by using of bridge P5083 in the interval 300-800 K. The optical transmission spectra were studied with the help of spectrophotometer SPECORD M-40 in the wavelength range 400–900 nm at room temperature.

![Image of temperature dependences of dielectric permittivity (a) and optical absorption spectra (b) for NBT single crystals: 1 – the sample annealed in air; 2 – the sample, annealed in vacuum. T$_{ann}$=1070 K](image-url)

Figure 1 Temperature dependences of dielectric permittivity (a) and optical absorption spectra (b) for NBT single crystals: 1 – the sample annealed in air; 2 – the sample, annealed in vacuum. $T_{ann}=1070$ K

Fig.1 shows $\varepsilon$($T$) dependences and optical absorption spectra for NBT samples, annealed in air (curves 1) and in vacuum (curves 2). One can see that after annealing in vacuum broad relaxation maximum of $\varepsilon$($T$) arises around 700 K and optical absorption noticeably increases in the range of self-absorption edge. It is expected that annealing in vacuum at $T_{ann}=1070$ K mainly increases concentration of oxygen vacancies $V_O$. The data in Fig.1 and the results given in [2, 3] show that in NBT structure $V_O$ form the complex defects with electric dipole moments and sufficiently effect optical absorption. Re-annealing in air decreases $V_O$ content and enables to measure the dependences similar to the curves 1 in Fig.1.

The Impact of Mn, Fe and Co Modifiers on the Dielectric Properties of (Ba, Pb)TiO$_3$ Ceramics

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The ABO$_3$ perovskite compounds are known for essential changes of properties of the material brought by 3d modifiers even at small concentrations the microscopic mechanisms of which are still being discussed. A study of the (Ba$_{1-x}$ Pb$_x$)$_3$O$_3$ (x=0; 0.05; 0.2 and 0.3) ceramics modified by Mn, Fe, Co (Me) at admixture concentrations of 0.001; 0.01; 0.1 % by mass is reported the dielectric properties being determined from measurements of the dependence of the complex dielectric permeability $\varepsilon^*=\varepsilon'-i\varepsilon''$ on temperature and frequency complemented by polarisation as function of the electric field intensity $P(E)$. SEM and XDR techniques have been used to find the changes in the structure.

The most important changes induced by modifiers include:
1) regardless to the amount of Pb in the lattice and the particular Me a broadening of the $\varepsilon(T)$ curve and decrease of the value of $\varepsilon_{\max}$ is observed with the growth of Me concentration;
2) at $x < 0.3$ (it is, at $x = 0.05$, 0.1 and 0.2) admixture of Mn always causes a shift of $T_{\varepsilon_{\max}}$ to a higher temperature, at $x = 0.3$ it causes a shift of $T_{\varepsilon_{\max}}$ to a lower temperature in the sequence Fe ≥ Co > Mn;
3) two different polarisation mechanisms are displayed by $\varepsilon''(f)$ curves: the high-frequency ($f>\sim19$kHz) mechanism dominates in unmodified samples while the low-frequency ($f<\sim19$kHz, Maxwell-Wagner) mechanism – in modified samples;
4) a decrease of remnant polarisation ($P_{\text{remn}}$) is displayed in polarisation loops $P(E)$ at room temperature without essential change of the coercive field $E_c$ value.
5) results of XDR (at room temperature) show that admixtures do not affect essentially the size and tetragonality of the unit cell while the ratio of the 210/211 diffraction maximums increases in the sequence Mn > Co > Fe.

As possible microscopic mechanisms are discussed:
1) the effects of oxygen vacancies (Vo) generated by Me$^{2+}$ and Me$^{3+}$ acceptors in the B sub-lattice: a) dipole pairs Me$_{Ti}^{2+}$-Vo and , b) Vo as a mobile charge carrier;
2) Jahn-Teller effect (electron configurations d$^4$(Mn$^{3+}$, Fe$^{4+}$) and d$^9$(Co$^{2+}$));
3) attributing the changes in the effect of 3d admixtures with the increase of Pb concentration in the A sub-lattice to interaction between the non-bonding Pb 6s$^2$ electrons with the 3d elements.
Germanium modified perovskite as a promising material for multifunctional devices

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In the technology of electronic ceramics the ferroelectric materials with perovskite-type ABO₃ structure play a key role in the group of advanced ceramic materials, in particular barium titanate BaTiO₃ (BT). It is a functional material of great importance, where the different effects and phenomena occurring therein are used. Barium titanate BaTiO₃ doped germanium (Ge) seemed to be a promising candidate to replace the lead-containing materials and due to its unique electric characteristics should affect the extension of the applications of the functional material of BT type in modern electronics.

The BaTiO₃ modified germanium polycrystalline samples were prepared by a solid state synthesis in the Institute of Solid State Physics of University of Latvia. The X-ray studies were performed on XPert PRO (PANalytical) diffractometer using the CuKα radiation (λ = 0.154178 nm) and a graphite monochromator. The micrographs of the polished cross sections after thermal treatment were determined using the high performance Hitachi S4700 scanning electron microscope (SEM), equipped with an Oxford Instruments Energy Dispersive X-ray Spectroscopy (EDS) stage. Dielectric measurements were carried out using an Alpha-AN modular measurement system together with cryogenic temperature control system - QuatroCryosystem and WinDETA Novocontrol software, at frequency varying from 0.1 Hz to 10 MHz and temperature range from 140 K to 600 K. The investigations shown, that the obtained ceramic materials characterized by the high density, the homogeneity of microstructure, the polyhedral shape of grains and the low porosity. EDS results confirmed the high purity and the expected quantitative composition (no significant impurities were detected in an EDS survey spectrum). The impedance answer of studied ceramic materials indicated the presence of two relaxation processes: one with a dominant resistive component and the other with a small capacitive component. This was confirmed in the curve of dielectric loss tangent. The observed dielectric relaxation process is temperature dependent and has a "non-Debye" character.
Quantum chemical modeling of atomic hydrogen migration in KDP

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Molecular models are widely used for electronic structure calculations in solid state physics. It is possible due to the fact that the calculations of the electronic structure of molecules as well as crystals consider the system of electrons and nuclei. Their interaction determines the properties of molecules and crystals. The application of quantum-chemical calculation methods for ionic crystals with complex cations and anions reveals new opportunities. Radiation defect formation in the crystals is largely determined by the decay processes of anionic or cationic complexes. Quantum chemical calculations allow us to understand the electronic and geometric structure of defects and get an entirely new insight into the mechanisms of their formation and transformation. To find out the mechanisms of radiation - stimulated processes analysis and comparison of the calculations and modeling, physical experimental results are rather essential. Thus, the modeling of processes that fail to be experimentally observable and moreover a directed experiment based on an analysis of calculations can create physically reasonable models of processes. In this paper, a modern semi-empirical method (MNDO) serves as the basic design scheme. The accumulated experience in application of the design scheme shows that the modern semi-empirical method, MNDO is the most efficient for calculating the energy parameters [1]. PC adapted software package have been used for calculations.

We have performed quantum chemical modeling of hydrogen migration of interstitial position. Some results with of earlier found experimental data have been compared to test the possibility of obtaining adequate results from calculations based on MNDO method for potassium dihydrogen phosphate. We have modeled a part of the cluster to calculate the geometry of the phosphate anion and the provisions of the bridging hydrogens. Baseline data: the lattice parameters of the crystal KDP - \( a = 1.046 \) nm, \( b = 1.054 \) nm and \( c = 0.692 \) nm; angles - \( \alpha = 29^\circ \), \( \beta = 54.6^\circ \), \( \gamma = 56^\circ \) [1, 2].

In the calculations we have considered only the position of hydrogen atoms near the \( \text{O}_2 \) and \( \text{O}_4 \). Other possible positions for the hydrogen atoms were left vacant. The selected design scheme gives results in good agreement with the literal. Charge of the hydrogen atoms is the same and equal to +0.86e, i.e electron density is significantly shifted to the oxygen atoms. Equal charge is due to hydrogen so that they are equivalent, but with different relative phosphate anions.

Thus, quantum-chemical calculations show the possibility of migration of atomic hydrogen, which is localized in the interstice. With this process it may be associated with recombination of \( \text{A}\)-radicals.

Recombination luminescence of potassium metaphosphate doped thallium ions

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This article presents results of the study of the recombination luminescence of potassium metaphosphate doped by Tl⁺ ions. To this the potassium nitrate addition to the initial solution in an amount of 0.1 mol%.

Figure 1 shows the spectrum of the thermally stimulated luminescence (TSL) of potassium metaphosphate doped ions NO₃⁻. We observed a new TSL peak at 175 K in the spectrum of KPO₃-No₃. It confirms the incorporation of the nitrate anions into the lattice of the potassium metaphosphate salts.

![Figure 1: TSL curves of (a) KPO₃-No₃ at 80 K (300 kGy) and (b) spectral composition of the TSL peaks.](image)

TSL peak at 175 K may be associated with changes of the level of thermal stability of radiation defects, localized near the impurity Tl⁺ ions. We observed that two peaks (at 175 K and at 260 K) have the same recombination luminescence. Hence, the peak at 260 K has an electronic mechanism of recombination.
Physicochemical processes in modified Li$_4$SiO$_4$ pebbles under action of accelerated electron irradiation

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The main role of lithium-containing ceramics in the fusion reactors is tritium breeding. Presently, lithium orthosilicate (Li$_4$SiO$_4$) pebbles with 10 mol% lithium metasilicate (Li$_2$SiO$_3$) are considered as reference tritium breeding ceramics [1]. However, the latest irradiation experiments showed that the reference Li$_4$SiO$_4$ pebbles may crack and form fragments under operation conditions as expected in fusion reactors [2]. Therefore, it has been suggested to change the chemical composition of the reference pebbles and to replace the Li$_2$SiO$_3$ with a mechanically more stable lithium metatitanate (Li$_2$TiO$_3$) phase [3]. The main aim of this research was to investigate the physicochemical processes in the modified Li$_4$SiO$_4$ pebbles with different contents of Li$_2$TiO$_3$ for the first time, in order to estimate and compare radiation stability.

The three types of the modified Li$_4$SiO$_4$ pebbles with 10-30 mol% Li$_2$TiO$_3$ (screened to 650-900 μm) were selected for investigation together with the reference pebbles. The reference and modified Li$_4$SiO$_4$ pebbles were irradiated with accelerated electron flux ($E = 5$ MeV) up to 5000 MGy absorbed dose at 300-670 K in dry argon. The formation, accumulation and annihilation of radiation-induced defects (RD) were analysed by electron spin resonance (ESR) spectroscopy.

By using ESR spectroscopy it was determined that in the modified Li$_4$SiO$_4$ pebbles several, characteristic paramagnetic species of electron and hole type RD are formed, like E’ centres ($\text{SiO}_3^{2-}/\text{TiO}_3^{2-}$), HC$_2$ centres ($\text{SiO}_4^{2-}/\text{TiO}_4^{2-}$), probably peroxide radicals (=Si-O-O$^-$) and un-identified RD (possibly Ti$^{3+}$ ions etc.). The total concentration (a) and annihilation (b) of accumulated paramagnetic RD in the reference and modified Li$_4$SiO$_4$ pebbles after irradiation up to 5000 MGy absorbed dose at 300-730 K is shown in Fig. 1. On basis of obtained preliminary results, it was concluded that the modified Li$_4$SiO$_4$ pebbles have comparable radiation stability with reference pebbles. As well as it has been suggested that the modified Li$_4$SiO$_4$ pebbles have potential to combine the advantages of Li$_4$SiO$_4$ and Li$_2$TiO$_3$ as a tritium breeding ceramic.


Figure 1. The total concentration of paramagnetic RD in the reference Li$_4$SiO$_4$ pebbles with 10 mol% Li$_2$SiO$_3$ and the modified Li$_4$SiO$_4$ pebbles with 10-30 mol% Li$_2$TiO$_3$ after irradiation with accelerated electrons ($E = 5$ MeV) up to 5000 MGy absorbed dose at different irradiation temperature (a). The annihilation of paramagnetic RD in the irradiated (accelerated electrons, $E = 5$ MeV, $D = 5000$ MGy, $T = 380-650$ K, dry argon) reference Li$_4$SiO$_4$ pebbles with 10 mol% Li$_2$SiO$_3$ and the modified Li$_4$SiO$_4$ pebbles with 10 mol% Li$_2$TiO$_3$ (b).
Formation and decay of the incommensurate phase in ferroelectrics TlInS$_2$

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The low-dimensional crystals TlInS$_2$ exhibit ferroelectric as well semiconductor properties. Despite numerous studies the existing data on the mechanisms and temperatures of the paraelectric - incommensurate phase (IP) transition and the incommensurate - commensurate phase transition, based on the measurements of photoconductivity, dielectric susceptibility, velocities of ultrasonic waves propagation and heat capacity are rather contradictory [1]. Therefore the direct X-ray diffraction studies of the modulated structures in TlInS$_2$ acquire particular importance. So, in the present report the IP transformations in c- polytype of TlInS$_2$ are studied by means of the single-crystal four-circle X-ray diffraction method in the temperature range 180–300 K. In the present work X-ray scanning of c-TlInS$_2$ single-crystal samples was performed using X-ray diffractometer DRON-4-07 with four-circle goniometer head GP-15. Co and Ni K$_\alpha$ lines were allocated by pyrolytic graphite monochromator. The temperature was maintained with an accuracy of 0.5 K (taking into account possible temperature gradients along the sample). The X-ray scanning of the c- polytype samples was performed in (00l), (h0l) and (hhl) planes of reciprocal space under cooling and subsequent heating in the temperature range T=185 - 300 K.

An unexpected result is the arising of the IP satellites under cooling at temperature $T_{1d}$=238 K in plane (h0l)* as weak lines with wave vectors $q(\mp\delta,0,\pm0.25)$ ($\delta = 0.04$). At each temperature the index $h$ of $q(4+\delta,0,4.75)$ satellite maximum and its integrated intensity were determined. Under cooling from 238 K to 218 K the satellite intensity slightly increases, the increase being more pronounced in the temperature range of 217 K - 213 K. The intensity sharply increases on cooling below 213 K and 196 K of the increase becomes weaker. Appreciable changes in the dependencies $I(T)$ at temperatures 213 K and 196 K are in good agreement with the known data on the phase transitions in TlInS$_2$: paraelectric - incommensurate phase at $T_i$=214 K and incommensurate - commensurate phase at $T_c$=197 K [1]. Upon heating the small hysteresis appears on the dependence $I(T)$, especially in the vicinity of $T_c$. An unexpected result is the beginning of incommensurate phase formation at substantially higher temperature $T_{1d} > T_c$. We assume that the weak incommensurate phase satellites at temperatures $T_{1d} > T_c$ may be due to a distortion of the soft mode in local regions of crystal, which contains structural defects (point defects, impurity atoms and stacking faults).

It was observed the monotonically decreasing of incommensurability parameter $\delta$ at temperatures T<204 K. At temperature 195 K $\delta \rightarrow 0$, the commensurate phase is formed with the modulation vectors $q(0,0,\pm0.25)$. This dependence may indicate the transition from the sinusoidal modulation to the “soliton” regime at which the distance between domain walls increases. It is typical for the incommensurate - commensurate phase transformation in incommensurate systems of type I, i.e., improper ferroelectrics with Lifshitz invariant. The model of incommensurate phase formation in c-polytypes was proposed.

Dielectric properties of the \((1-x)(NaBi)_{1/2}TiO_3 - xBiCoO_3\) perovskite ferroelectric ceramics

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Bismuth-containing perovskite oxide systems have attracted researcher’s attention in connection with the search for advanced ferroelectric and piezoelectric materials that would be free of lead and have a high Curie temperature.

In this work, we present results of studies of crystal structure and dielectric properties of the \((1-x)(NaBi)_{1/2}TiO_3 - xBiCoO_3\) solid solutions in the composition range of \(0 \leq x \leq 0.2\). The solid solutions were synthesized by solid state reaction from the stoichiometric mixture of \(Bi_2O_3, TiO_2, Co_2O_3\) and \(Na_2CO_3\). The crystal structure was studied using powder x-ray diffraction. The obtained perovskite compositions were found to have a rhombohedrally distorted (sp. gr. \(R\bar{3}c\)) structure. The unit-cell parameters \(a_H\) and \(c_H\) (hexagonal setting) linearly increase with increasing the \(BiCoO_3\) content, while the octahedral tilt angle slightly decreases.

The real \((\varepsilon')\) and imaginary \((\varepsilon''\)) parts of the relative dielectric permittivity were measured as a function of temperature. The \(\varepsilon'(T)\) curves of the ceramics at high frequencies demonstrate a prominent peak, whose position \((T_m)\) is 590-620 K slightly depending on frequency (Figure 1).

![Figure 1](image)

The \(\varepsilon'(T)\) behavior at temperatures above \(T_m\) is characteristic of a diffuse ferroelectric phase transition. Below \(T_m\), \((NaBi)_{1/2}TiO_3\) undergoes a transition into a ferroelectric relaxor state. Small additions of \(BiCoO_3\) (\(\sim 5\) mol.%) were revealed to result in degeneration of the relaxor state.

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Structure and Dielectric Properties of Multiferroic Pb\(_{1-x}\)Sr\(_x\)Fe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) Solid Solution Ceramics

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Multiferroics are of great interest as promising multifunctional materials. An important task is the search for the route of changing the temperatures of ferroelectric and magnetic phase transitions. Recently a new multiferroic PbFe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) with a double perovskite structure was obtained under high pressure. It was found to possess unusual magnetic and dielectric properties [1]. In the present work the results of structural and dielectric studies of Pb\(_{1-x}\)Sr\(_x\)Fe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) solid solution ceramics are reported.

Pb\(_{1-x}\)Sr\(_x\)Fe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) solid solution compositions with \(x < 0.8\) were synthesized at 1400–1500 K under high pressure of 6 GPa while those with \(x > 0.8\) – at ambient pressure. It was established that a continuous series of solid solutions with cubic double perovskite structure (sp. gr. \(Fm\bar{3}m\)) at room temperature is formed in this system. The unit cell parameter decreases linearly with increasing Sr content. In the whole range of compositions a high degree of long-range order (0.75 - 0.90) in the arrangement of Fe\(^{3+}\) and Sb\(^{5+}\) cations is observed. From the analysis of the profiles of X-ray diffraction peaks it was found out that the size of the ordered regions is less than the size of ceramic’s grains.

For PbFe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) a diffused maximum of the real part of dielectric permittivity \(\varepsilon'\) marks a ferroelectric phase transition (Figure 1 a). For Pb\(_{1-x}\)Sr\(_x\)Fe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) compositions the \(\varepsilon'(T)\) maximum shifts to lower temperatures and becomes much more diffused as \(x\) grows (Figure 1 b). Such behavior is typical of A-site - substituted lead-containing perovskites [2]. However the temperature \(T_m\) of the \(\varepsilon'(T)\) maximum exhibits only a weak frequency dependence.

![Figure 1](image-url)

Figure 1 \(\varepsilon'(T)\) dependences for Pb\(_{1-x}\)Sr\(_x\)Fe\(_{0.5}\)Sb\(_{0.5}\)O\(_3\) ceramic compositions with \(x = 0\) (a) and \(x = 0.1\) (b).

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Structure and dielectric properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$ solid solutions

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Discussions about the phase diagram of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ extend over the years. Still the existing conclusions are mutually contradicting. Different states comparing structure of poled and depoled Na$_{0.5}$Bi$_{0.5}$TiO$_3$, established during the latest studies, make this problem even more complicated.

In this work Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$ solid solutions are studied. CaTiO$_3$, being an orthorhombic perovskite, already in a small concentration causes remarkable changes in the temperature dependence of dielectric permittivity of Na$_{0.5}$Bi$_{0.5}$TiO$_3$. Coexistence of rhombohedral and orthorhombic structures is clearly identified in x-ray diffraction patterns for Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$. Changes in the structure correlate well with the jump of the temperature dependence of dielectric permittivity, allowing construction of a meaningful phase diagram. Differences of structure in poled in depoled states are extracted, the temperature dependence of the unit cell parameters is considered for both states. The obtained results allow us to make conclusions about the phase diagram of the pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$. 
Charge disproportionation as origin of ferroelectricity in Sn₂P₂S₆ type compounds

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The ferroelectricity in Sn₂P₂S₆ family compounds is related to tin cation stereoactivity that appeared with local three - well potential for the spontaneous polarization fluctuations [1]. This mechanism of phase transition could be described [2] in the frame of well-known second - order Jahn - Teller effect. For Pb₂P₂S₆ crystal, the paraelectric phase with P₂/c symmetry (that is isostuctural to Sn₂P₂S₆ paraelectric phase) exists at cooling until liquid helium temperature [3]. By first - principles calculations in GGA approach of density functional theory we found that full energy of Pb₂P₂S₆ paraelectric phase is only by 0.002 eV smaller than such energy for possible ferroelectric phase with Pc symmetry. In calculated phonon spectra of paraelectric phase, a very low energy polar optic mode with Ba symmetry at Brillouin zone center have been found. By Raman scattering, some softening of optical modes was observed in this crystal with cooling, what give evidence about growth of lattice anharmonicity. Such increase of Pb₂P₂S₆ crystal anharmonicity at cooling was also observed earlier as growth of Gruneisen parameter determined at elastic properties investigations by Brillouin scattering [4]. Finally, our dielectric measurements show an increasing of susceptibility in Pb₂P₂S₆ crystal at cooling from 400 K to 20 K.

Observed behavior of Pb₂P₂S₆ compound could be related to the charge disproportionation phenomenon of type P⁴⁺ + P⁴⁺ → P³⁺ + P⁵⁺ for the case of nominal charge states of Sn³⁺, P⁴⁺ and S²⁻ ions. On the matter of known valence skipping [5], the 3s¹ electronic configuration is metastable, so it follow that the closed shell 3s⁰ and 3s² electronic configurations are favorable. Obviously in reality, by covalence influence, only small recharging of phosphorus ions occurs. This process could be presented as hole polarons formation with their wave function mostly distributed around sulfur ions in the PS₆ structural groups. Interaction between polarons which are located at neighbor anions (P₂S₆)⁶ determines the bonding band formation at the top of valence band, at this related antibonding band at the bottom of conduction zone is placed. The itinerant electrons could be localized at the phosphorous ions – P³⁺ states with 3s² configuration are realized. Such electronic localization could be considered as Kondo like behavior with participation of phonons [6, 7]. At cooling the Kondo behavior appears as the valence skipping – phosphorus electronic configuration 3s¹ transforms into 3s² and 3s⁰. Below Kondo temperature the dielectric susceptibility could increase with cooling and reach some value at T → 0 K. The Kondo temperature could be estimated as T_K ≈ 10²/D, where D is a width of the conduction band. According to GGA calculations, the lowest conduction band for Pb₂P₂S₆ crystal has width near 1 eV, and T_K ≈ 100 K could be found. This estimation qualitatively explains experimentally observed growth of Pb₂P₂S₆ crystal dielectric susceptibility at cooling in wide temperature range - from 400 K till 20 K. This observation gives evidences that the electronic entropy realizes at conditions of local anharmonic potential, and by this determines a growth of Pb₂P₂S₆ paraelectric phase lattice polarizability at cooling across several hundreds of Kelvins. In general, observed Kondo like behavior for Pb₂P₂S₆ crystal mean that the charge disproportionation could be considered as origin of ferroelectricity in whole family of Sn₂P₂S₆ type functional materials.

Alkali halide crystals exciton-like luminescence buildup at a lattice symmetry decrease by elastic deformation and light cation

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Currently, in the global energy experiments on registration of dark matter the scintillation detectors based on alkali halide crystals are successfully used [1]. In these experiments all means for the registration of hyperweak flash signals with the lossless maximum efficiency are established (the increase of detector size to 230 kg and the low temperature - 4.2 K) [1]. The main mechanism to ensure the transformation of the energy of dark matter into a flash is irradiative relaxation of exciton-like electronic excitations. Thus, the problem remains for scintillators to achieve maximum luminescence quantum yield, especially at room temperature.

It should be noted that at low temperatures, the quantum yield of luminescence in iodides of alkali metals approaches a maximum value ($\eta \rightarrow 1$, CsI). With temperature increase the temperature quenching of luminescence is observed, which occurs due to the predominance of the nonradiative decay of electronic excitations, mainly, with the formation of radiation-induced defects [2].

However, the effect of intensity enhancing of intrinsic luminescence of alkali halide crystals at lattice symmetry lowering by low temperature uniaxial deformation is demonstrated [3]. We have defined the nature of the luminescence, which is self-trapped dihalogen exciton emission by reducing the mean free path of monohalogen exciton (NaI, KI, RbI, NaBr) and correlated tunneling charge of radiation defects (KBr, KCl). On the basis of the continuum approximation the reduction of the potential barrier between monohalogen and dihalogen exciton states in alkali halide crystals at low temperature uniaxial strain is established.

An interesting effect in crystals whose mean free path unrelaxed hole increases with increasing temperature is found. In case of a crystal KCl-Na registration the self-trapped excitons intensification is demonstrated experimentally by X-ray spectra of in the sodium light cation with a peak at 2.8 eV in the temperature range from 100 K to 300 K. Moreover, at room temperature the intensity has a maximum value which is extremely important for scintillation detectors. Let us remind that the range of the free exciton in KCl at 80 K has only 2a [2]. The luminescence intensity of the self-trapped exciton (2.3 eV) in KCl in the specified temperature range (120-300 K) is undergoing a complete temperature quenching, and therefore, it is necessary to eliminate the process of self-trapped exciton radiative relaxation in the regular lattice sites. This effect is interpreted by the assembly of electron-hole pairs near the sodium light cation, which acts as a catalyst due to the self-trapping of unrelaxed hole. The activation energy (60 meV) is determined due to temperature dependence of the luminescence intensity gain (2.8 eV). Apparently, it is the assembly energy of self-trapped exciton-like formation through the recombination of electrons with self-trapped holes in sodium field, since the holes in the lattice are self-trapped with no barrier.

Thus, the lattice symmetry lowering by light cation and elastic deformation provides opportunities to control luminescence characteristics of alkali halide crystals in a given direction.

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Simulation of current-voltage characteristics and the dynamic conductivity of the ballistic contacts based on superconductors with weak oscillation order parameter

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In some high-temperature superconductors the energy gap is oscillatory due to the active electron-phonon interaction [1]. (Oscillation energy parameters in this energy range is observed in the Eliashberg spectra). The calculation of the current-voltage characteristics (CVC) and dynamic conductivity of the ballistic SNS-contact was made with the help of the scattering matrix [2], which converts the state of free quasiparticles incident on the region of interaction with each other (or obstacle) in the state after the interaction of flying particles. Current-voltage characteristic of ballistic SNS-contact is defined by the equation:

$$I_s = \frac{e}{\pi \hbar} e V \delta_{i0} - \int d\varepsilon \tanh \left( \frac{\varepsilon}{2T} \right) \left[ J(\varepsilon) \left( a_{s0} A^+_s + a_{s2} A^+_s \right) \right] + \sum_{n} \left[ 1 + a_{s2} A^+_s B^*_{s2n} \right] \left( A_{s2n} - B_{s2n} \right),$$

(1)

where $\hbar$ – Plank constant, $V$ – voltage, $\varepsilon$ – energy, $T = (1 + i \cdot \hbar^{-1})^{-1}$ – value that determines the transparency of the system ( $\hbar$ - barrier height), $J(\varepsilon) = \sqrt{1 - |a(\varepsilon)|^2}$, $a(\varepsilon)$ – Andreyev reflection coefficient, $A$, $B$ – probability of amplitudes of Andreyev and normal reflection of quasiparticles). The results of numerical modeling of the CVC and $dI/dV$ - spectra of the ballistic SNS-contact according to the equation (1) taking into account the coefficient of Andreyev reflection for oscillating order parameter in the range 60-100 meV are presented at the barrier transparency 0.98 (barrier height $\hbar = 0.144$), 0.95 ( $\hbar = 0.229$), 0.9 ( $\hbar = 0.33$) on Fig. 1.

![Figure 1 Current-voltage characteristics and the dynamic conductivity of SNS-contact with transparency of the barrier 0.9 (curve 1), 0.95 (curve 2), 0.98 (curve 3) (1)](image)

The features of the subharmonic gap structure of SNS-contact with the values from 1 to 8 for the case $D = 0.9; 0.95; 0.98$ were determined; it was revealed that in these objects the significant changes of Andreyev spectra are observed, namely, the transformation of a maximum in a minima of five Andreyev features ($n = 5$) with an increase in the transmission coefficient, and minimizing of the sixth features peak ($n = 6$) with the transmission coefficient decreasing.

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Optical and electrical properties of LiGaO$_2$ as lattice-matched substrate for ZnO thin films

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A wurtzite-like β-LiGaO$_2$ (LGO) structure has attracted great interest as lattice-matched substrate for ZnO heteroepitaxy [1]. Also, LGO has a wide bandgap (5.6 eV) compared to ZnO (3.3 eV), and is optimal for growing nonpolar ZnO thin films. LGO samples studied were grown along [100], [010], and [001] axes by Czochralski method. The structural and optical characterisation of LGO has been carried out recently [2]. In this work, LGO material is studied in more detail by means of photoluminescence (PL), PL excitation (PLE), spectroscopic ellipsometry (SE), and time-resolved pump-probe techniques.

Low-temperature PL spectra (Figure 1 (a)) of (100) LGO sample contain several bands centered at 280 nm (4.43 eV; 1-band), 325 nm (3.82 eV; 2-band), 520 nm (2.38 eV; 3-band), and 700 nm (1.77 eV; 4-band). The excitation energy varied from above to below the bandgap of LGO, i.e. 197 nm (6.29 eV; dominates 1-band), 212 nm (5.85 eV; dominates 2-band), and 250 nm (4.96 eV; dominate 3,4-bands). The energy values of the recorded bands qualitatively resemble the cathodoluminescence spectra for (001) LGO single crystal [2].

Temperature-dependent PL revealed monotonous decrease of 325 and 700 nm bands (325 nm band), and 250 nm band, and 520 nm band exhibited a maximum at 60 K and then rapidly decreased disappearing at 140 K. The physical origin of the observed PL bands is still under investigation.

The optical response of LGO was studied in the photon energy range 0.7 – 5 eV by spectroscopic ellipsometry technique. The experimental ellipsometric data were analyzed by critical point parabolic band dispersion model. The deduced real part of complex refractive index $\bar{n} = n + i\kappa$ of LGO shown in Figure 1 (b). These data are in a good agreement with those of Leno [3]. The imaginary part was determined to be zero within error over the entire examined spectral region and it is not shown.

Pump-probe techniques using picosecond laser pulses at 213 nm (pump) and 1064 nm (probe) wavelengths were used for probing of excited carrier dynamics. Temperature-dependent differential transmission (Figure 1 (c)) provided thermal activation energy of ~200 meV. Latter pointed out to activation of near bandgap defects, while remaining tail at highest temperatures should indicate for the deeper defects. Light induced transient grating technique provided considerably faster decays, indicating for partial excitation of free carriers (1-band) and their capture to defects. Their lifetime reduced from 100 to 30 ps with excitation. Differential reflectivity also provided fast decay of free carriers competing with slow decay of traps.

![Figure 1](image)

Figure 1 PL spectra of (100) LGO at 10 K temperature (a). Refractive index of LGO crystal as a function of photon energy (b). Differential transmission decays for 213 nm excitation at various temperatures (c).

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Properties of Al-doped ZnO films grown by atmospheric pressure MOCVD on different orientation sapphire substrates

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Doped ZnO films are the most promising transparent conducting oxide (TCO) electrodes to replace indium tin oxide (ITO) electrodes in optoelectronic applications [1-3]. The search for alternative TCOs for industrial applications is motivated mainly by the scarcity and high price of In, the principal component of ITO. Although different properties of TCO films are important for technological applications, the main requirements for such films are low electrical resistivity (close to $1\times10^{-4}$ $\Omega$cm) and high optical transparency ($\geq 90\%$) in the visible spectral range. For some applications, the high optical transparency of TCO films should be extended into the ultraviolet (UV) and infrared (IR) spectral ranges. The quality of the deposited TCO films highly depends on the deposition method. Although Physical Vapor Deposition (PVD) techniques still allow for the growth of doped ZnO films with better properties, the use of Chemical Vapor Deposition (CVD) methods seems to be more desirable from a technological point of view because CVD methods exhibit high growth rates, uniform and conformal coverage of large areas of uneven or structured surfaces, and are simpler and more flexible in the tuning of the film composition (e.g., doping level). Application of atmospheric pressure CVD techniques additionally simplifies the deposition process because complicated and expensive vacuum equipment is not required. Film properties highly depend on deposition conditions, which should be carefully optimized. A possible additional way to improve properties of CVD grown doped-ZnO films is the choice of an appropriate procedure of post-deposition treatment, which may markedly improve the carrier concentration and carrier mobility in films.

Films of Al-doped ZnO were grown on different orientation sapphire substrates at atmospheric pressure via the aerosol-assisted MOCVD technique. Air-stable metal-organic compounds Zn(thd)$_2$ and Al(thd)$_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) were used as precursor materials. Aerosol was generated from solutions of precursors’ mixture in 1,2-dimethoxyethane. The depositions were performed at 400-500 $^\circ$C. Properties of the deposited films were investigated using various characterisation techniques: XRD, SEM, AFM, UV–Vis and FT-IR spectroscopies, and Hall measurements.

The influence of the orientation of sapphire substrate on the properties of Al-doped ZnO films was investigated. Epitaxial films grown on sapphire-R substrates exhibited the best electrical properties: carrier mobility 50-60 cm$^2$ V$^{-1}$ s$^{-1}$, resistivity <10$^{-5}$ $\Omega$ cm. Because the low resistivity of Al-doped films was mainly determined by the high carrier mobility, the optical transmittance was high in both the visible ($\leq 90\%$) and the mid-IR ($\approx 90\%$ at $\lambda=2.5$ $\mu$m) spectral ranges. High transmittance in the mid-IR spectral range makes these films suitable for use as transparent electrodes in applications of the IR optoelectronic devices. Annealing of films in an argon-hydrogen mixture resulted in a marked improvement of electrical properties independently of substrate orientation.

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Piezoresponse Force Microscopy Study of local ferroelectric properties of Bi(Fe,Sc)O$_3$

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Perovskite bismuth ferrite (BiFeO$_3$) has attracted an immense attention as a rare room-temperature single-phase multiferroics. There have been many attempts to control properties of BiFeO$_3$ by cationic substitutions either in A- or in B-site of the perovskite structure. Application of the high-pressure synthesis method enables to extend the solubility and thereby the perovskite phase existence ranges. Recently, a new perovskite composition BiFe$_{0.5}$Sc$_{0.5}$O$_3$ was successfully synthesized under high pressure [1]. Depending on the synthesis conditions, it appears in different polymorphs. The phase obtained by quenching under pressure is antipolar (antiferroelectric-like) one. However, thermal cycling at normal pressure irreversibly turns this phase into polar (ferroelectric-like) one. The resulting polar modification is a rare example of perovskite phase where canted ferroelectricity coexists with a ferromagnetic component.

To get more insight in properties of Bi(Fe,Sc)O$_3$ ceramics prepared under high pressure and to address local ferroelectric properties in these materials we have applied piezoresponse force microscopy (PFM). The post-annealed Bi(Fe$_{0.5}$Sc$_{0.5}$)O$_3$ ceramics show strong PFM signal and posses a well-developed domain pattern typical of a ferroelectric state. The quenched ceramics, however, demonstrate no piezoresponse that is in line with suggestion on the antiferroelectric state. However, this state can be transferred to a ferroelectric one by application of a local electric field. In Bi(Fe$_{0.6}$Sc$_{0.4}$)O$_3$ ceramics a coexistence of ferroelectric and antiferroelectric grains was observed. In latter a ferroelectric state could be induced by electric poling. The temporal and temperature stability of the induced states was studied. Mechanisms of antiferroelectric-ferroelectric transformation are discussed.

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Thermophysical properties of $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ multiferroics

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We research the thermal diffusion, thermal conductivity, and heat capacity of $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ multiferroics ($x = 0 - 0.40$) in temperature intervals from 130 K to 1200 K. The substitution of a small amount of rare earth element Eu for bismuth leads to a change in temperature anomalies of the thermal diffusion and the thermal conductivity in an antiferromagnetic phase transition region, an increase of the heat capacity in a wide temperature range, and a temperature displacement of the antiferromagnetic transition. It is established that the temperature dependence of the excess heat capacity is related to the Schottky effect for three level states that appear as a result of structure distortions in the rare earth doped compositions.

The analysis of the results obtained in this work together with the structural and acoustic data indicates, that local distortions of the crystal lattice, which are caused by the distortions of oxygen octahedra of $\text{FeO}_6$ and polar shifts of $\text{Bi}^{3+}$ and $\text{Fe}^{3+}$ ions from their initial positions, constitute the main mechanism of the scattering of phonons in $\text{BiFeO}_3$ and $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ multiferroics. It has been found that doping with a rare-earth element Eu leads to a significant change in the temperature anomalies of the thermal diffusion and heat conductivity near phase transitions, namely, to the smearing of the ferroelectric transition $T_c$ and the appearance of a minimum in the region of the antiferromagnetic transition $T_N$.

The dominant mechanisms of phonon heat transfer in the region of ferroelectric and antiferromagnetic phase transitions have been revealed. The temperature dependence of the mean free path of phonons has been determined.
Lead-free (1-x)Na$_{0.5}$Bi$_{0.5}$TiO$_3$-xSrTiO$_3$ ((1-x)NBT-xST) ceramics (x=0, 0.02, 0.04 and 0.06) were prepared by conventional solid state method. The structural, dielectric and ferroelectric measurements of these ceramics have been made in a wide temperature range. The obtained samples show pure perovskite structure with rhombohedral symmetry at room temperature and with increasing temperature its undergoes two successive phase transitions: from rhombohedral to tetragonal at about 240-260°C and from tetragonal to cubic at about 500-540°C. Low frequency (100 Hz – 1 MHz) investigations reveal the diffuse phase transitions. The main broad anomaly of electric permittivity at $T_m$ = 290-310°C and additional small anomaly at $T_d$ = 180-190°C were observed. It was concluded, that as for pure NBT, the main anomaly is related to electromechanical interaction of polar regions with nonpolar matrix and small anomaly is related to decay of long-range ferroelectric state. The pyroelectric and hysteresis loops measurements show that obtained ceramics possess ferroelectric behaviour with the relatively large remanent polarization (15-22 $\mu$C/cm$^2$) and the coercive field (20-40 kV/cm). The NBT-ST system is expected to be a new promising candidate for lead-free electronic crystals.
Local atomic environment of Fe in mixed perovskite-type ferroelectrics

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In recent years much attention has been given to the structural studies of mixed perovskites displaying advanced dielectric characteristics, however the origin of their properties is still not clear. We have performed a comparative study of Fe local atomic environment in PbFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\) (PFN) SrFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\) (SFN) and BaFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\) (BFN) using X-ray absorption spectra of the compounds. All the materials exhibit a high dielectric constant over a wide temperature range in spite of quite substantial difference in their structure and symmetry: PFN has a monoclinic structure, SFN shows a tetragonal distortion whereas BFN has a cubic symmetry.

X-ray absorption spectra have been recorded at the Fe \(K\)-edge in the transmission mode at the beamline "Structural Materials Science" of the Kurchatov Center for Synchrotron Radiation and Nanotechnology (KCSRNT, Moscow, Russia). Fourier transformation of the \(k^2\)-weighted EXAFS functions has been made over the \(k\) range of 2.6 – 12.7 Å\(^{-1}\). The non-linear fit of theoretical spectra to experimental ones has been performed to estimate interatomic distances. Fe\(_2\)O\(_3\) has been used as a reference compound.

At the EXAFS Fourier transforms for all the examined compounds including BFN (Figure 1), the amplitude of the first peak, which corresponds to the Fe-O bonds, appeared to be very close to that of Fe\(_2\)O\(_3\), in which Fe is shifted off-center by about 0.12 Å. The fits to EXAFS spectra, assuming 1-shell model, which suggests that Fe atoms occupy the central positions within oxygen octahedron, were unsuccessful. Considerable improvement of the fits has been achieved within 2-shell model, and the displacements of the Fe ions from the centers oxygen octahedra for all the compounds were estimated to be about 0.1 – 0.13 Å.

The results show, that the local symmetry of BFN on the B-site does not match the long-range cubic symmetry and the compound possesses quite substantial local dipole moments which may give rise to its dielectric properties.
Influence of axial pressure on electric properties of Na$_{1-x}$Li$_x$NbO$_3$ (x= 0.08, 0.1, and 0.2) ceramics

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The materials based on the solid solutions of the Na$_{1-x}$Li$_x$NbO$_3$ system are often used in electronic devices using high frequencies [1,2]. Ceramics Na$_{1-x}$Li$_x$NbO$_3$ (x= 0.08, 0.1, and 0.2) were synthesized by conventional solid-state processing. The structural and dielectric measurements of these ceramics were performed in the temperature range from room temperature to 600°C, frequency range from 100 Hz to 2 MHz and axial pressure to 1500 bars. The XRD investigations and micrographs show that the simples have a pure perovskite structure, were good sintered and the grains are well-formed. Dielectric investigations show that the axial pressure greatly influences on the intensity of the peaks in the $\varepsilon(T)$, peaks became diffused and shift to lower temperatures. The values of tanδ change also significantly. The obtained results of the performed investigations of this materials show that the Na$_{1-x}$Li$_x$NbO$_3$ (x= 0.08, 0.1, and 0.2) are a good candidate for lead-free electroceramics.


Observation of local Piezo- and Ferroelectricity in Lysozyme protein by means of PFM technique

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Organic ferroelectrics - are light, flexible, and nontoxic molecular base systems which possessed intrinsic biocompatibility and were accepted as a following milestone in ferroelectricity development after rigid and heavyweight, contain toxic lead and require high temperature processing perovskite oxides such as PZT and BTO [1]. Thus, the observation of ferroelectricity in organic systems fills an important link in bioelectric, molecular ferroelectric and electronic phenomena.

One of promising organic ferroelectric material is lysozyme, an abundant cationic antimicrobial protein that plays an important role in pulmonary host defense [2]. In this work we present the results of piezoelectric and ferroelectric behavior investigations of tetragonal and monoclinic crystallographic structured lysozyme film samples by means of the Piezoresponse Force Microscopy technique.

For tetragonal sample a strong piezoresponse that naturally comes from the +NH₃-CH₂-COO- zwitterions via a hydrogen-bonds network was confirmed. Besides, there was an additional strain response related to the elastic nature of the sample (third rank stress tensor). Thus, for tetragonal lysozyme sample a strong piezoresponse with distinct hysteresis behavior was confirmed. The piezoresponse coefficient has been calculated equal to 15 pm/V.

For monoclinic lysozyme sample only piezoresponse without evident manifestation of hysteresis loop was confirmed. This fact could indicate a significant role of pinned polarization in the sample. The piezoresponse coefficient has been calculated equal to 1 pm/V.

For both tetragonal and monoclinic protein samples, the piezoelectric effect was also observed on the macroscale via the Berlincourt Method. The inherent piezoelectric and biocompatible properties of lysozyme combined with the possibility of chemical modification using molecular engineering could allow applications such as biocompatible non-volatile memories, optical switches or in biomedical energy-harvesting devices.

Use of ultrasonic vibrations for mechanoactivation and compaction of ceramic powders

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Ceramic powder compaction by application of ultrasonic vibrations allows obtaining of denser structure. This leads to improvement of physical and mechanical properties and performance characteristics of ceramic items. Preliminary ultrasonic treatment of powder in liquid medium, particularly under high hydrostatic pressure, also significantly affects physical and mechanical properties of ceramics [1].

This paper presents the results of studies of physical and mechanical properties of barium zirconate titanate ceramics, obtained by mechanoactivation and compaction of powder using ultrasonic vibrations. Mechanoactivation was carried out in an ethyl alcohol medium under hydrostatic pressure 2•10⁵ Pa in the cavitation mode. Ultrasonic compaction was performed according to the scheme [2].

The grain refinements of the powder after ultrasonic treatment and major structural defects have been defined. The dielectric constant increases at frequency of 500 kHz and 1 MHz which is likely due to structural changes in ceramics at the expense of powerful ultrasonic influence (Fig. 1.).

Characteristic of osteopontin, osteocalcin and osteoprotegerin expression in rabbit bone tissue after the implantation of hydroxyapatite-containing biomaterials

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Calcium phosphate biomaterials, particularly hydroxyapatite (HAP) are of great interest as bone replacement and repairing materials, and especially in studies related to stomatology. HAP is often used as pure monophasic material, biphasic material and it can be covered with medication substances, polyesters like polycaprolactone (PCL) and with other materials. Bone cell activity marker osteoprotegerin (OPG), bone matrix proteins osteopontin (OP) and osteocalcin (OC) are indicators of reactivity and biocompatibility occurring during bone substitution [1-3]. The aim of our study was to assess the changes in the distribution and appearance of bone biomarkers OP, OC and OPG in the lower jaws of rabbits after the implantation of pure HAP, biphasic α-tricalcium phosphate/HAP (α-TCP/HAP) and HAP covered with PCL (HAP/PCL). Californian rabbits were used in the study, and the study protocol was approved by the Animal Ethics Committee of Food and Veterinary Administration of Latvia, 2010. The biomaterials used in this experiment were manufactured in Rudolfs Cimdins Riga Biomaterials Innovation and Development Centre of Riga Technical University of Latvia. The biomaterial implantation was carried out in two experiments, each of them lasted three months. Pure HAP and HAP/PCL in the first experiment was used, but in the second one – pure HAP and α-TCP/HAP. Three months after the implantation of biomaterial the rabbits were euthanized by air embolisation and blocks of bone tissue from the experimental and control sides were obtained. Bone tissue was processed for routine morphological staining and for biotin-streptavidin immunohistochemistry. A semi-quantitative counting method was used to assess the relative amount of positively-stained osteocytes for each marker. The Mann-Whitney U-test was used to analyse the differences in average number of positively stained osteocytes between the experimental and control groups for each marker. Statistical analysis was performed using IBM SPSS Statistics 20.

Morphological results of both implantation periods showed different numbers of OPG-, OP- and OC-positive osteocytes in both experimental and control tissue. The most extensive number of the above mentioned cells were obtained in bone tissue with HAP/PCL from the first experiment. But in the second one – the most extensive number of OP- and OC-positive cells was observed in bone tissue with pure HAP, while the number of OPG-positive cells in tissue with pure HAP and α-TCP/HAP was low. Statistically significant difference in the means of OP, OC and OPG expression in osteocytes was not detected between experimental and control groups (Mann-Whitney U-test; p>0.05).

We conclude that the expression of OP and OC primarily is affected, probably, by individual reactions on the implanted biomaterial; the most extensive number of OP- and OC-positive osteocytes in bone tissue with pure HAP and HAP/PCL indicates on potential regeneration stimulated by these biomaterials. Low number of OPG-positive osteocytes in bone tissue with pure HAP and α-TCP/HAP probably indicates on preserved ability of bone resorption.

Effect of Ag catalyst atoms on adsorption, reduction and dissociation of oxygen molecules on LaMnO$_3$ (001) surface

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Numerous attempts had been made to explore new electrode materials and microstructures, and establish how and why electrode performance changes with time, temperature, thermal cycling, operating conditions, impurities, and other factors. One way to overcome operating temperature limitation SOFC may be adding to the cathode a certain amount of metallic catalysts, such as silver. The addition of catalysts to an active cathode layer is mainly used to enhance the oxygen reduction reaction.

We present and discuss the results of GGA+$U$ calculations of the atomic and molecular oxygen adsorption on the LaMnO$_3$ (001) surface, which serves as a model material for SOFC cathode, in the presence of Ag adsorbate with different coverages. The bond length and bond population of adsorbed O$_2$ molecules indicate that Ag induces O$_2$ dissociative adsorption. The most energetically favourable adsorption sites on both MnO$_2$- and LaO-terminations have been determined, the electron charge transfer between the O$_2$, Ag and LMO surface has been analyzed. The calculation of electronic properties of interaction demonstrated the formation a covalent bond between the O$_2$ molecule and the surface-Mn. It means that Ag pre-adsorbed facilitates O$_2$ adsorption on surface.
Non-Equilibrium Charge Dynamics in Functionalized Semiconductor Nanostructures

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We model dynamics of photo-excitations in functionalized semiconductor nano-structures. The modeling is performed by reduced density operator method in the basis of Kohn-Sham orbital's. Thermalized lattice vibrations are modeled through ab initio molecular dynamics of nuclei, forming a time-dependent trajectory. Non-adiabatic couplings in the basis of Kohn-Sham orbital’s are computed in a course of molecular dynamics, and are utilized to build autocorrelation functions and the Redfield dissipative part of the equation of motion for the reduced density operator. The latter one is solved in the frequency domain (i) and time domain (ii): in the frequency domain, the steady state solution illustrates formation of the density of an excited non-equilibrium state with contributions of multiple electron-hole pairs. Time domain solution for non-equilibrium initial state of the model shows how the energy of photo-excitation is dissipating due to interaction with lattice vibrations with the electron/hole part of an excitation relaxing to the bottom of conduction band /top of valence band. The methodology is applied to Al and P co-doped silicon quantum dots and titanium dioxide [1], doped by Ru atom [2] or functionalized by minimalistic Ru nano-cluster [3]. Solution for nonequilibrium density of electrons is used for determining the dynamics of formation of charge transfer state on the surface, computing surface photo-voltage, and rates of energy and charge transfer. Simulations of these models demonstrate the formation of charge transfer state. These results are of the importance for an optimal design of nano-materials for photo-catalytic water splitting and solar energy harvesting.

Synthesis and sintering of the BLT ceramics doped with Fe$^{3+}$

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Perovskites have been matters of interest to many scientists due to their unique properties and a wide range of potential applications. The valence of A and B ions affects the crystal structure and the physical properties of the materials. The introduction of La$^{3+}$ ion into Ba$^{2+}$ site causes a decrease in the number of covalence bonds; moreover Fe$^{3+}$ ion substitution into Ti$^{4+}$ site leads to the limitation of displacement in octahedron [1].

In hereby poster we would like to present the technology conditions of iron modified Ba$_{0.997}$La$_{0.003}$Ti$_{0.99925}$O$_3$ (BLTF0) ceramics obtaining. All samples of Ba$_{1-x}$La$_x$Ti$_{1-x/4}$O$_3$ for different Fe concentration $y = 0.1$ mol. % (BLTF1), $y = 0.2$ mol. % (BLTF2) and $y = 0.3$ mol. % (BLTF3), were synthesized by solid-phase synthesis reaction from the conventional mixture of oxides, viz. BaCO$_3$, La$_2$O$_3$, TiO$_2$ and Fe$_2$O$_3$ powders - sintered by mixed oxide method (MOM) and followed by free sintering method (FS).

The stoichiometric mixtures of powders were subjected to thermal analysis with Netzsch STA-409 system. The results of thermal analysis allowed to determine the optimal temperature of synthesis. Morphology of the ceramic material was observed by scanning electron microscopy. BLTF ceramics was studied in terms of its chemical composition. The EDS investigations showed that samples were prepared in optimum conditions and show the stoichiometry according to chemical composition formula. Quantitative analysis of the chemical composition was performed with a Noran Vantage software. One can see that small deviations from the theoretical composition of BLTF have occurred but they do not exceed a value of $\pm 5\%$ what is consistent with the resolution of the utilized method of investigation (Figure 1). The crystalline structure of the sintered samples were examined by X-ray diffraction. Microstructure and crystalline structure studies of ceramics were carried out at room temperature. The obtaining results were compared with the ones received for pure Ba$_{1-x}$La$_x$Ti$_{1-x/4}$O$_3$ for $x = 0.3$ mol. % ceramics[2,3].

![Figure 1. EDS spectrum and SEM images of BLTF synthesized powders.](image)


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The aims of the study were to design and obtain ferroelectric-ferromagnetic ceramic composites based on ferrite powder and PLZT powder. The synthesis of the composition of the PLZT material of chemical formula Pb$_{0.98}$La$_{0.02}$(Zr$_{0.90}$Ti$_{0.10}$)$_{0.995}$O$_3$ was carried out by conventional technology. The composite constituted 90% of PLZT powder and 10% of ferrite powder (Ni$_{0.64}$Zn$_{0.36}$Fe$_2$O$_4$). These two components (PLZT type and ferrite) were mixed in proportion 90% PLZT and 10% ferrite using Fritsch planetary ball mill for 15h (wet in ethyl alcohol). Subsequently the mixture was synthesized by calcination method under the following conditions: $T_{synth}$=1000°C, $t_{synth}$=4h. The synthesis temperature of the PLZT-NZF material was selected on the basis of differential thermal analysis DTA, as well as DTG and TG (Fig.1) using a Q-1500D derivatograph (with a Paulik–Paulik–Erdey system) in the temperature range from 20°C to 1030°C. Studies have shown that the above 750°C a further weight loss is not observed. In the whole temperature range the weight loss does not exceed 0.7%. The final sintering of the ceramic composite samples were conducted at $T_s$=1200°C (PLZT-NZF1) and 1250°C (PLZT-NZF2) for $t_s$=2 h.

The article presents the technology and the results of a XRD measurement, a microstructure and the dielectric properties (Fig.2) of composite samples. The results of the PLZT-NFZ composite were also compared with the results of PLZT ceramics.
The ceramic samples of solid solution $(1-x)(0.5PZT-0.5PFW)-xPFN$ with $x=0; 0.1; 0.2$ have been obtained by conventional ceramic technology from oxides i.e. PbO, ZrO$_2$, TiO$_2$, Fe$_2$O$_3$, WO$_3$, Nb$_2$O$_5$. Basing on the literature data for individual components it can be expected that this material should have interesting multiferroic properties. The presented work is the first step in obtaining and investigating this solid solution. In presented paper it is described the technology and the dielectric properties of obtained samples. The calcined powders were crushed and next pressed into discs and sintered using free sintering (FS) method. For such obtained samples the following investigations have been done: EDS, XRD, the microstructure of fractured samples, dielectric measurements and the investigations of d.c. electric conductivity. As a result of relatively high electric conductivity of investigated samples the investigations of the $P$-$E$ hysteresis loop were not possible.
Dielectric Investigations of Polycrystalline Dysprosium Bismuth Ferrite Ceramic

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Nowadays investigations of multiferroic materials are a significant interest because of the co-existence of ferroelectric and ferromagnetic properties. The most popular multiferroic material is bismuth ferrite, especially doped with rare earth elements (Sc, Dy, Pr and others). The dysprosium substitution results in the R3c→Pnma phase transition, which is realized via the formation of an inhomogeneous structural state and is accompanied by vanishing of ferroelectric behavior and appearance of enhanced magnetization [1].

The present work is aimed to investigate the dielectric properties of dysprosium bismuth ferrite ceramic, Bi₁₋ₓDyₓFeO₃, by the broadband spectroscopy. The measurements were performed as a function of both temperature and frequency in the temperature range 10 K – 1000 K and in the frequency range 20 Hz — 1 MHz. The investigations were carried out for samples x = 0.1, 0.15 and 0.2. Obtained results can be divided into two parts: the low temperature part, where the dielectric dispersion occurs, and the high temperature part, where, especially at low frequencies, the conductivity processes dominate the dielectric spectra (Fig. 1). At higher temperatures (above 400 K) the dielectric properties of dysprosium bismuth ferrite ceramics are governed by Maxwell - Wagner relaxation (the peak of dielectric permittivity close to 650 K) and electrical conductivity. Polycrystalline samples Bi₁₋ₓDyₓFeO₃ (x = 0.1, 0.15, 0.2) were prepared by a two-stage solid-state reaction method using the oxides Bi₂O₃, Dy₂O₃ and Fe₂O₃ taken in desired cation ratio [1]. The dielectric relaxation in the investigated ceramics will be discussed.

![Graph showing dielectric properties](image)

**Fig. 1.** Temperature dependence of the real real (ε') and imaginary (ε'') parts of complex dielectric permittivity of Bi₁₋ₓDyₓFeO₃ ceramics at 1 MHz frequency.

A Monte Carlo study on coronene influence on self-assembly of tricarboxylic acids

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Recently, many diverse supramolecular planar formations have been prepared on solid surfaces. A large part of them are H-bonded molecular networks. A high degree of directionality, chemical selectivity and flexibility of H-bonds allow to organize open molecular networks with well-defined pores suitable for incorporation of guest molecules with different functional properties for industrial applications. The symmetric cyclic trimeric arrangement is also quite often observed in ordering of triangular molecules [1]. The detailed knowledge of intermolecular and substrate-molecule interactions is very important for design of molecular networks. Theoretical modeling allows to predict the possible ordering patterns. Molecular ordering can be simulated using statistical phase transition models. In such calculations a molecule is represented by a simple geometrical form with a minimal number of molecular orientations. Experimental findings, especially by STM, can be used as a starting point for construction of a model with appropriately chosen interactions.

Here we propose a 7-state model (with some exclusion rules) for ordering of triangular, reduced-symmetry molecules of biphenyl-3,4',5-tricarboxylic acid (BHTC) into planar molecular structures on a substrate lattice. The model is built on the basis of popular 3-state (orientation) Bell-Lavis model which can be used to describe the symmetric triangular molecules, mapped onto equilateral triangle with interacting vertices (carboxylic groups) [2]. Due to lower symmetry the BHTC molecule might be mapped onto isosceles triangle with interacting vertices. Reduction of molecular symmetry enables formation of a variety of honeycomb-like porous structures, H-bonded by dimeric and trimeric interactions. The pores of these structures can incorporate guest molecules, therefore the model is supplemented by guest-host interaction term which allows us to study the role of guest (coronene) in ordering of tricarboxylic acid molecules.

Occurrence of BHTC molecular networks with trimeric bonds is particularly interesting. We observed two such similar structures [3]. Experimentally observed C1 phase has four-molecule and six-molecule hexagonal pores at a ratio 3:1. Monte Carlo calculations also predict the formation of C2 structure that is characterized by alternating zigzag chains of four-molecule and five-molecule pores. Both of them can contain coronene in their pores, and they mix in different proportions depending on coronene concentration.

The effect of host-coronene interaction on ordering of higher-symmetry molecules of trimesic (TMA) and benzene-tribenzoic (BTB) acids is also studied. One of the most interesting results is the co-existence of coronene-filled honeycomb phase and coronene-free superflower phase in TMA molecular system. The pores in the BTB honeycomb phase are much larger and may contain up to three coronene molecules. We also demonstrate that coronene-host interaction might stimulate the formation of BTB superflower phase. Trimeric interaction is sufficient to independently create the phases with trimeric bonds at high molecular densities for TMA molecular system, while BHTC and BTB have lower conformational flexibility and need some support of host-guest interaction.

Three-component gyrotropic metamaterial

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We propose a comparatively simple way to fabricate a metamaterial which is both gyrotropic and of simultaneously negative permittivity and permeability. The idea is to make a mixture of three ingredients, where one of them would be responsible for the negativity of \( \mu \), while the other two would be responsible for the negativity of \( \varepsilon \). The first component of the mixture is the ‘swarm’ of single-domain ferromagnetic nanoparticles, immersed in a mixture of other two: silver and one of the following: mercury cadmium telluride, lead tin telluride, or lead tin selenide. In the work we carried out computer simulations in the frame of the proposed model in order to establish the domain of existence of such a material searching through the vast parameter space. The main result can be summarized as follows: in the framework of the model, we succeed in establishing the domains of gyrotropic metamaterial existence, relative to all parameters characterizing the model, parameters of nanoparticles, and the fraction of cadmium or tin in mercury cadmium telluride or lead tin telluride/selenide as well as the relative concentrations of the mixture components. Negative refraction and optical activity can be achieved only if the material is in external, however moderate magnetic field. On the other hand, in some circumstance, it could be an advantage, since switching magnetic field on and off, one can trigger off negative refraction.

Magnetic interactions in La$_{1-2x}$Sr$_{2x}$Mn$_{1-x}$Sb$_x$O$_3$ ($x \leq 0.2$) solid solutions

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Mixed-valence manganese perovskites have attracted great attention due to a strong interplay between crystal structure, magnetic interactions and transport properties [1]. The main model to describe magnetic properties and conductivity of the manganites is the double-exchange (DE) model [2] it assumes a real electron transfer from Mn$^{3+}$ to Mn$^{4+}$ ions. Orbitally disordered state occurred in parent LaMnO$_3$ above 750 K results in dominant ferromagnetic interactions as confirmed by a positive Weiss constant ($\theta \approx 160$ K) [3, 4]. It is assumed that orbital ordering leads to anisotropic superexchange interactions and antiferromagnetic order below 140 K [3]. It was found that ferromagnetic state can be stabilized in compounds with manganese ions being only in 3$^+$ oxidation state [4-6]. The long-range ferromagnetic component has been observed in LaMn$_{1-x}$Ga$_x$O$_3$ ($0.2 < x < 0.6$) and LaMn$_{1-x}$Cr$_x$O$_3$ ($0.4 < x < 0.6$) series containing only Mn$^{3+}$ species [6-12]. Both these series show gradual transition into orbitally disordered state upon substitution with Ga$^{3+}$ ($x > 0.5$) or Cr$^{3+}$ ($x > 0.35$) accompanied by increase in ferromagnetic component.

It is known, that in manganites with Mn ions only in 3$^+$ oxidation state the type of magnetic interactions is strongly dependent on the angle Mn – O – Mn [7]. This angle governs the strength of hybridization of $e_g$ orbitals of manganese ions and 2$p$ orbitals of the oxygen ions and thus determines the type of Mn – O chemical bond character. It is considered that magnetic properties of manganites having Mn ions only in 3$^+$ oxidation state could be explained in terms of superexchange interactions where magnetic interactions are caused by Mn – O chemical bond character. In order to clarify the origin of ferromagnetic properties of manganites having only isovalent Mn$^{3+}$ ions we have performed analysis of the crystal structure and magnetic properties of the Ln$_{1-2x}$Sr$_{2x}$Mn$_{1-x}$O$_3$.

It has been shown that chemical substitution with Sb and Sr ions stabilize 3$^+$ oxidation state of the manganese ions and magnetic properties of the compounds are determined by magnetic sublattice of the manganese ions. Crystal structure data obtained by neutron diffraction measurements have testified rhombohedral phase of the compounds La$_{1-2x}$Sr$_{2x}$Mn$_{1-x}$Sb$_x$O$_3$ ($0.1 < x < 0.2$) at room temperature, temperature decrease leads to the structural transition to orbitally disordered orthorhombic phase (Fig.1). The compounds are ferromagnets, the magnetic transition temperature decreases with chemical doping (~175 K for $x=0.1$; ~90 K for $x=0.2$). It is considered that ferromagnetism of the components is caused by dominance of the positive superexchange interactions between Mn$^{3+}$ ions; Mn–O–Mn bond angle becomes wider in doped compounds and thus increases covalency of the Mn – O bond and stabilizes ferromagnetic interactions.

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Electromechanical properties of 
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$-$\text{SrTiO}_3$-$\text{PbTiO}_3$ solid solutions

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Development of relaxor properties in $0.4\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$-(0.6-$x$)$\text{SrTiO}_3$-$x\text{PbTiO}_3$ solid solutions with respect to $x$ resembles well-known relaxor ferroelectric PbMg$_{1/3}$Nb$_{2/3}$O$_3$-$\text{PbTiO}_3$ [1]. The latter one was recognized as a promising material for electromechanical applications which require large electric field-induced deformations without hysteresis.

In this work, electric field-induced deformations are studied in $0.4\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$-(0.6-$x$)$\text{SrTiO}_3$-$x\text{PbTiO}_3$ system. Measurements of the electromechanical properties were performed by aixACCT TF2000 analyzer.

Deformation as a function of polarization ($u_{33}(P)$) can be expressed by pure electrostrictive behaviour (i.e. $u_{33} = Q'_{33} P^2$) in the concentration range where ferroelectric state cannot be reached even in the presence of electric field ($x \leq 0.05$). These results are consistent with previous data on relaxor ferroelectrics [2]. The value of fictive coefficient of electrostriction ($Q'_{33}$) weakly depends on concentration and temperature and is similar to the values found earlier in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ [2].

The ferroelectric phase can be induced in $0.4\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$-$0.5\text{SrTiO}_3$-$0.1\text{PbTiO}_3$ sample by electric field. Considering stability of relaxor and ferroelectric states, it resembles PbMg$_{1/3}$Nb$_{2/3}$O$_3$. For this composition, the same $u_{33}=Q'_{33} P^2$ dependence is observed in the temperature region above the electric field-induced phase transition. It has similar values of $Q'_{33}$ comparing with the compositions $x \leq 0.05$. Below the temperature of the phase transition, where the composition is in ferroelectric state, $u_{33}(P)$ can be described by electrostriction, but just in the part of hysteresis loops $P(E)$ from the maximum value of electric field $E_{\text{max}}$ to the point where the electric field equals zero ($E = 0$). Here $Q'_{33}$ values are higher, comparing with the relaxor state.

In the compositions with $x \geq 0.10$, piezoelectric coefficient was determined in the temperature range of the stable ferroelectric state. At room temperature, $d_{33}(x)$ decreases upon increasing of PbTiO$_3$ concentration, which is related to the increase of the phase transition temperature. The $d_{33}$ values and electromechanical coupling constants, measured by resonance-antiresonance method, are also considered.

Properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ ceramics after Ba$^{2+}$ doping

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Over the past half century, most piezoelectric devices were fabricated by using lead-based ceramics (PZT), due to their high piezoelectric response and the tailoring of their properties through composition. Unfortunately, the use of lead-based materials has caused serious environmental pollution. In the last few years, Na$_{0.5}$Bi$_{0.5}$TiO$_3$-based compositions have shown greater advantages than other lead-free piezoelectric candidate materials.

The (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics were fabricated by conventional solid phase sintering process. The samples were characterized by the bulk density which exceeds 95% of the theoretical density. The X-ray diffraction analysis shows an increase of size and volume of oxygen octahedra with the rise in Ba$^{2+}$ content. The electric permittivity broad anomaly is shifted to low temperature after Ba doping of NBT. The pyroelectric and hysteresis loops measurements also show changes in comparison to pure NBT. The obtained results are discussed in terms of ions/lattice imperfections, which create local electromechanical fields.
Investigation of dielectric and ultrasonic behavior of PVDF based polymer composites with ferroelectric fillers

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Ferroelectric polymers can be doped with various fillers in order to modify their properties [1, 2]. In this work we present experimental study on the impact of piezoelectric fillers on the ferroelectric and the ultrasonic properties of a ferroelectric conventional ferroelectric copolymer based composite. We used polyvinylidene fluoride / trifluoroethylene (P(VDF-TrFE)) copolymer with a molar ratio 70/30 as the composite matrix to be filled with PZT family (Pb₀.₇₅Ba₀.₂₄Sr₀.₀₁(Zr₀.₅₃Ti₀.₄₇)O₃ (BPZT)) and BaTiO₃ (BTO) fillers. Composites of different piezoelectric filler concentrations are studied (up to 50 vol. % in the case of BPZT and 15 vol. % in the case of BTO). The impact of filler concentration on the shape of ferroelectric hysteresis loop has been investigated by TF Analyzer 2000 aixACCT measurement system.

![Ferroelectric Loops of Pure P(VDF-TrFE) and Composites](image)

It is shown that in the case of BPZT and BTO coercive electric field is dependent on the filler volume fraction similarly as the dielectric permittivity and obeys the Lichteneckers mixing rule. Experimental study of ultrasonic wave attenuation, velocity and piezovoltage in these composites has been performed over wide temperature range (100 K – 410 K) using ultrasonic automatic pulse-echo technique. The temperature dependences of ultrasonic velocity and attenuation showed anomalies attributed to the glass transition and paraelectric-ferroelectric phase transition. The ultrasonic attenuation of longitudinal wave propagating in the composite below the ferroelectric phase transition can be well described by the Landau-Khalatnikov theory.

Thermal, Raman and electric studies of 0.95Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.05PbTiO$_3$ ceramics

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Materials which have relaxor ferroelectric bahaviour are very attracted due to possibility of their use to production of transducers and other electromechanical devices. On the other hand, such properties occur more often in lead-based ceramics. Lead titanate-zirconate ceramics are one of the most used ferroelectric materials [1]. The downside this ceramics is toxicity of lead and its high vapour pressure during processing. Low-lead and lead-free ceramics can be used instead of lead-based materials if their properties will be promising.

0.95Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.05PbTiO$_3$ ceramics have been prepared by conventional solid phase sintering process. X-ray diffraction analysis show that obtained specimens possesses the perovskite structure. The microstructure study showed a dense structure in good agreement with that of above 95% relative density determined by the Archimedes method. The crystal structure, phase transitions behaviour, thermal and electric properties of these ceramics were investigated. The maximum of electric permittivity was observed at about $T_m \approx 290 \, ^\circ C$ (on cooling, at 100 kHz). The transitions temperature observed by means of DSC measurements are in good agreement with those obtained from dielectric study.

Bidomain lithium niobate and lithium tantalate: the perspective materials for precision actuation

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Nowadays, there is an increasing trend of usage nanotechnology in different fields of science and engineering. Thus, the necessity to provide ultra-precision displacements with sub-nanometer accuracy exists. Actuators that utilize transverse piezoelectric effect are mainly used for this purpose. However, PZT (lead zirconate-titanate) ceramics, which the actuators are based on, demonstrates such disadvantages as creep, hysteresis and non-linearity of the displacement dependence on the applied operating voltage. Low Curie temperature and thermal instability of piezoelectric coefficients inherent in piezoceramics also complicate usage of the actuators.

Single crystalline materials do not have these negative properties but their piezoelectric modules are low so they are not used for actuators. One way to increase displacements is to use a bimorph actuator based on ferroelectric single crystal. In order to create such bimorph structure it is necessary to form two domains with opposite orientations of the spontaneous polarization vector in one crystal plate. This bidomain structure keeps all the advantages of a ferroelectric single crystal and has higher electromechanical conversion coefficient.

Previously, several techniques of forming of the bidomain structures in 180° ferroelectric lithium niobate were offered [1-3]. There are also some ways to create bimorphs made of single crystals by gluing [4] or direct bonding [5]. In this study, we used the stationary external heating method [3] to produce lithium niobate (plates of z- and y+127° cut were used) and lithium tantalate (plates of z-cut were used) bidomain structures.

Cantilevered bending displacements of the 40×5×0.5 mm3 lithium niobate bimorph were ≈±70 μm when the voltage was within ±300 V (Figure 1, a). These structures were also tested by cyclic loading under the variable electric field. After more than 10 million working cycles the bimorphs do not change their electromechanical properties and shape of the voltage-deformation dependence. We also revealed that there is saddle-like deformation of the single crystalline bidomain actuators due to their anisotropic nature (Figure 1, b).

![Figure 1 Bending cantilevered deformation of the single crystalline LN bimorph (a) and the dependence of the deformation on the rotation angle (b).](image)

From the point of view of applications, single crystalline LN bimorph actuators can be used for precise positioning in probe microscope techniques, for an adjustment of laser resonators and as wave guides with exact variable geometrical characteristics.

Nano-indentation studies and macro-scale mechanical testing of calcium modified \((\text{Pb}_{0.75}\text{Ba}_{0.25})(\text{Zr}_{0.70}\text{Ti}_{0.30})\text{O}_3\) ceramics

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The \((\text{Pb}_{0.75}\text{Ba}_{0.25})(\text{Zr}_{0.70}\text{Ti}_{0.30})\text{O}_3\) ceramics (PBZT 25/70/30) are one of the members of PBZT system. The investigations on the system were initiated by Smolensky et al [1], however the phase diagram was proposed by Ikeda [2]. Further investigation of dielectric and other properties, performed by Li, Heartling and others [3-4] revealed that solid solutions containing about 25 – 35 at% of Ba and with Zr/Ti ratios located near the boundary between ferroelectric (rhombohedral and tetragonal) and paraelectrical (cubic) phases belong to relaxor ferroelectrics. The dielectric and ferroelectric properties of pure PBZT 25/70/30 ceramics were widely described in our previously paper [5-6] as well as the paper of other authors [7-8]. The lack of information about the mechanical properties of discussed ceramics is visible in the literature. It was reason why the mechanical properties of the pure as well as calcium modified PBZT 25/70/30 ceramics have been studied in macro and nano-scales using two different methods. Specifically for macro-scale the ultrasonic velocity measurements were employed to evaluate the Young modulus (E), whereas for nano-scale the nanoindentation method was a very useful tool to obtain the elastic modulus and hardness. These results reveal the strong influence of calcium admixture on mechanical properties of the discussed material. The small amount of calcium admixture caused the decreasing of Young modulus. Whereas the concentration of Ca modifier overstep 1 at.% changed the tendency - value of Young modulus increased. The changes in E value are probably connected with the decreasing of the number of defects. Moreover, the described results show the significant differences in mechanical properties measured on nano and macro-scale. It is concluded that the knowledge of the mechanical properties of the ceramic material is completed only when we take into account both the macro and nano-scale.

**Keywords:** PBZT, Ceramics, Hardness, Nanoindentation, XRD measurements, Young Modulus,
Lanthanide Complexes as Probes of Local Temperature by NMR PARACHEST

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Magnetic Resonance Imaging (MRI) is routinely used in the clinic to visualize the structure and function of organs. For several applications, including tumor and cardiovascular imaging in clinic and in vivo studies, an enhancement in contrast is an absolute requirement to improve the sensitivity and the diagnostic contents of the images. For this, several contrast agents (CAs) have been developed over the past years, most of which incorporates paramagnetic gadolinium ions (Gd³⁺). Currently, complexes of the different lanthanides (Ln, other than Gd), remain largely unexplored as probes for nuclear magnetic resonance spectroscopy (NMR) and MRI.

Recent studies have demonstrated that MRI can be used as a tool for noninvasively assessing temperature changes in tissues associated with absorption of nonionizing radiation. As an example, we initially proposed the use of special NMR thermo-sensitive contrast reagents (NMR-TSCR) based on paramagnetic Ln complexes. This technique can diagnose conditions such as inflammatory reactions and cancer. The mechanism of action of NMR-TSCR is based on the substantial dependence of lanthanide-induced shifts (LIS) in NMR spectra on temperature. We here suggest using the spin saturation transfer method (so called PARACHEST) of dynamic NMR for determination LISs and local temperature.

This new approach is characterized by: (a) Non-invasive in comparison with the known methods of temperature microprobe, (b) the possibility of the temperature on almost any depth from the surface of the body as opposed to, for example, the fluorescence-based diagnostics (FD) and infrared (IR) diagnostics; (c) compatibility directly with the photo-dynamic therapy (PDT), neutron and proton capture therapy. According to our evaluations, temperature determination error (ΔT) is ~0.3 K and 3D resolution (ΔL) is ~30 mkm.

To solve the main problem requires answers to a number of interrelated issues (which will also be covered in the report): (1) development of the method of the molecular structure determination of paramagnetic Ln complexes in solution according to the combined analysis of LIS and of the paramagnetic spin-lattice relaxation enhancement; (2) development of the technique for the kinetic parameters determination of the intramolecular and intermolecular dynamics in paramagnetic Ln complexes based on the study the NMR signals lineshape (with temperature changes of LIS); (3) the information about the molecular structure and the dynamics of Ln coordination compounds with macrocyclic (cyclodextrins, crown-ethers and DOTA-like molecules) and acyclic (EDTA-like) ligands in solutions.
A simple model of “negative capacitance” phenomenon in inorganic-organic heterostructures

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An inductive behaviour in some semi-conductive devices, which are real – or not ideal – capacitors, has been known for years [1, 2]. The phenomenon is often referred to as “negative capacitance”. Interfacial traps, for instance impurities or dislocations, are essential for the effect. Injected charge carriers are delayed by the traps and this delay is responsible for the observation of “negative capacitance”. There are different explanations for the behaviour. In this work, a simple approach showing its origin in n-doped silicon/silicon dioxide/P(VDF-TrFE) heterostructures is presented [3]. It explains both time-domain and frequency-domain measurements.

Electromechanical properties of Bi$_{1-x}$Pr$_x$FeO$_3$ solid solutions within the phase boundary region

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Bismuth ferrite based materials attract persistent interest due to diverse phase diagram testifying multiple transitions affecting physical properties of the compounds. It is known that chemical substitution of bismuth ions in BiFeO$_3$ by large rare-earth elements drives structural transition from the rhombohedral phase to antipolar orthorhombic one and then to nonpolar orthorhombic phase [1, 2].

X-ray diffraction data recorded for the Bi$_{1-x}$Pr$_x$FeO$_3$ ceramics at room temperature testify concentration driven structural transition from the polar rhombohedral phase (R-phase) to anti-polar orthorhombic one (O$_2$-phase) as declared in the published studies [3]. The crystal structure of the compound with x=0.115 doping level is characterized by the dominant rhombohedral phase (90%) and small amount of the orthorhombic one (10%). Further increase of prasemydium content leads to a progressive decrease in the amount of the rhombohedral phase and to proportional increase of the orthorhombic phase. The XRD data recorded for the x=0.125 compound testifies the dominance of the rhombohedral phase while secondary orthorhombic phase is clearly detected. Structural analysis of the XRD data reveals that the compounds with x = 0.125, 0.135 and 0.15 are characterized by 75%, 50% and 10% of the amounts of the R-phase respectively.

The local piezoelectric hysteresis loops obtained for the x=0.11 compound are similar to those specific for initial BiFeO$_3$ [4, 5]. Hysteresis loops measured for the x=0.125 compound testify significant increase in the piezoelectric response. The PFM loops measured in different places over the sample surface reveal about 40% difference there the maximal piezoelectric signal is about two times larger than the signal observed for the x=0.11 compound (Figure). The hysteresis loops with maximal PFM signal are attributed to the local area with a dominance of the rhombohedral phase. Further increase of prasemydium concentration diminishes electromechanical properties of the compounds. The PFM data obtained for the x=0.15 compound demonstrate drastic degradation of the polar character of this solid solution, the registered signal is nearly negligible and it is most probably associated with electrostatic and related effects.

The obtained results testify the evolution of crystal structure and piezoelectric properties of the Bi$_{1-x}$Pr$_x$FeO$_3$ ceramics across the phase transition from the polar rhombohedral into the anti-polar orthorhombic structure. PFM measurements testify drastic increase of piezoelectric response for the compound characterized by the dominant rhombohedral phase and minor amount of the anti-polar orthorhombic phase. The authors consider the phase coexistence observed for x=0.125 compound to be specific structural state associated with increased structural instability associated with enhanced electromechanical properties.

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