

**Institute of Solid State Physics
University of Latvia**



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2013

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2014

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INTRODUCTION

The research in solid state physics at the University of Latvia restarted after World War II. The **Institute of Solid State Physics** (ISSP) of the University of Latvia was established on the basis of Laboratory of *Semiconductor Research* and Laboratory of *Ferro- and Piezoelectric Research* in 1978. Since 1986 the ISSP has the status of an independent organization of the University and now is the main material science institute in Latvia.

Four laboratories from the Institute of Physics of the Latvian Academy of Sciences joined our Institute in 1995. Twenty scientists of the former Nuclear Research Centre joined the ISSP in 1999 and established Laboratory of Radiation Physics. In 2004 scientists from the Institute of Physical Energetics joined ISSP and established Laboratory of Organic Materials (Table 1).

In mid 90-ties the ISSP has intensified its **teaching activities**. A number of researcher have been elected as professors of the University of Latvia. Post-graduate and graduate curricula were offered in solid state physics, material physics, chemical physics, physics of condensed matter, semiconductor physics, and experimental methods and instruments. In 2002 the Chair of Solid State and Material Physics University of Latvia was established at ISSP.

Research and training in optometry and vision science is taking place in the Laboratory of Visual Perception of the ISSP since 1992. Co-located with the Institute, the Optometry Centre has been established in 1995 with facilities for primary eye care and serving as a technological research basis for students and staff.

In December 2000 the ISSP was awarded the **Centre of Excellence of the European Commission** (Centre of Excellence for Advanced Material Research and Technologies). This honorary recognition with the accompanying financial support of 0,7 million EUR has increased our research activities, particularly extending the list of our research partners and scientists who come to work to our Institute from the leading European research centres.

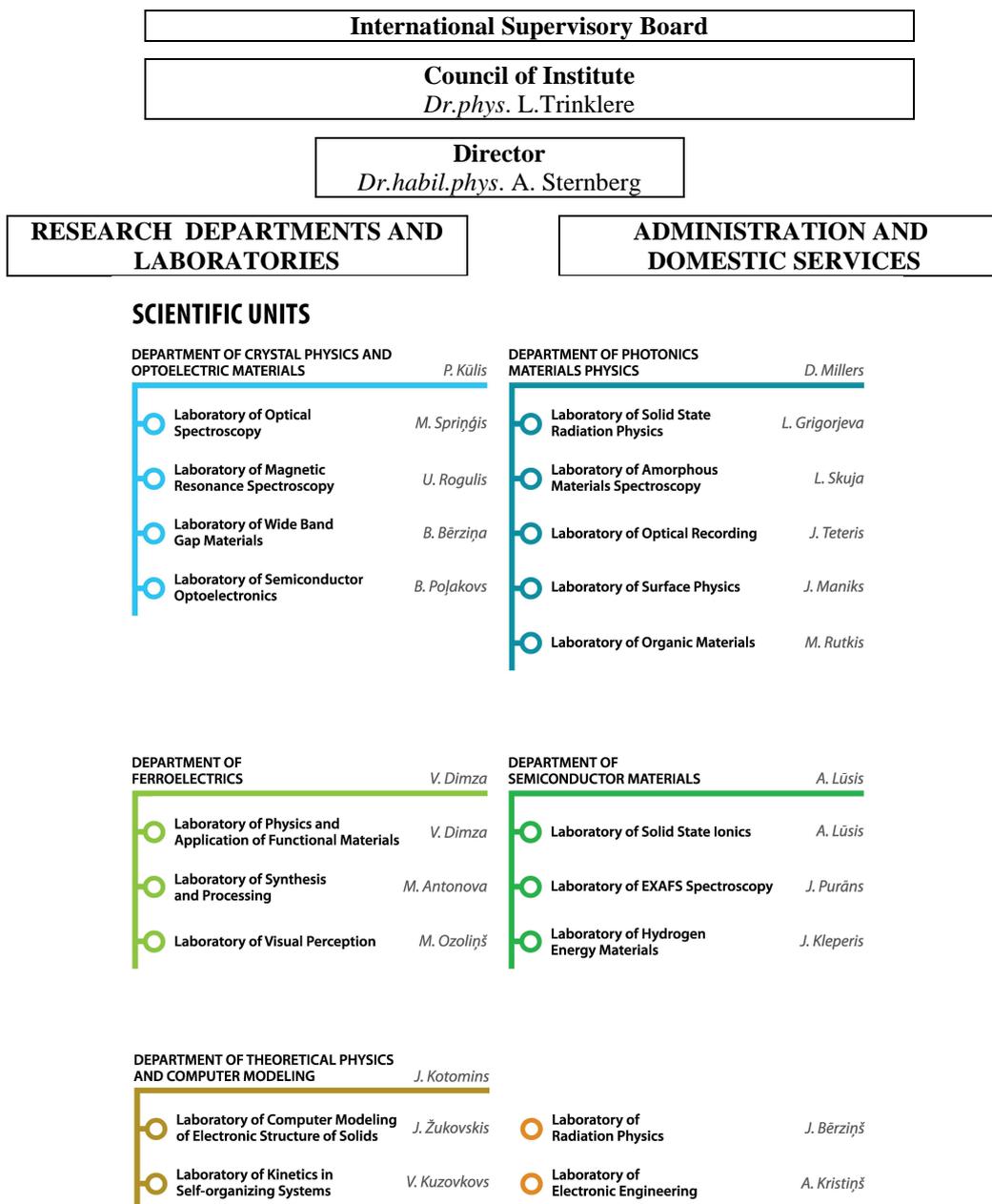
The research of the ISSP includes:

- electron and ion process in wide-gap materials with different degree of ordering;
- functional organic molecules and polymers for photonics and organic electronics;
- multifunctional and hybrid materials for energy applications: light emitting diodes, photovoltaic elements and coatings for solar baterries, storage of hydrogen for fuel cell devices;
- electrodes and plasma technologies for hydrogen production, polymer membranes with ionic conduction for fuel cells and gas separations;
- inorganic single crystals, ceramics, glasses, thin films, and nano-structured surfaces for application in optics, electronics, photonics and energetics.

The highest decision-making body of the Institute is the **Scientific Council** of 21 members elected by the employees of the Institute (Table 2). Presently Dr. phys. L.Trinklere is the elected chairperson of the ISSP Council. The Council appoints director and its deputies.

Table 1

ORGANIZATIONAL STRUCTURE OF THE ISSP IN 2013



ADMINISTRATION AND DOMESTIC SERVICES

ADMINISTRATION	<i>A. Šternbergs</i>		DOMESTIC SERVICES
Deputy director of Science	<i>M. Rutkis</i>	<i>D. Popele</i>	Human Resources
Deputy director of Studies	<i>A. Šarakovskis</i>	<i>R. Siatkovskis</i>	Procurement Department
Scientific Secretary	<i>L. Grīnberga</i>	<i>J. Ruhmanis</i>	Main Power Engineer Department
Accounting Department	<i>A. Jozepa</i>	<i>L. Rihtere</i>	Library
		<i>V. Ivanovs</i>	Main Engineer and Mechanical Workshops

The interdisciplinary approach of research at the ISSP is reflected by its **highly qualified staff**. At present there are 176 employees working at the Institute, 26 of 103 members of the research staff hold Dr.habil.degrees, 66 hold Dr. or PhD. At the end of 2013 there were 21 PhD students and 46 undergraduate and graduate students in physics and optometry programmes working at the ISSP.

Table 2

The Scientific Council of the Institute

1. Laima Trinklere, Dr.phys., chairperson of the Council
2. Marcis Auzins, Dr.habil.phys., UL
3. Gunars Bajars, Dr.chem.
4. Larisa Grigorjeva, Dr.habil.phys.
5. Jurgis Grube, PhD student
6. Anastasija Jozepa
7. Andris Krumins, Prof., Dr.habil.phys.
8. Peteris Kulis, Dr.phys.
9. Aleksejs Kuzmins, Dr.phys.
10. Kaiva Luse, PhD student
11. Juris Purans, Dr.phys.
12. Uldis Rogulis, Dr.habil.phys.
13. Martins Rutkis, Dr.phys.
14. Andrejs Silins, Prof., Dr.habil.phys.
15. Linards Skuja, Dr.habil.phys.
16. Anatolijs Sharakovskis, Dr.phys.
17. Andris Sternbergs, Dr.habil.phys.
18. Janis Teteris, Dr.phys.
19. Anatolijs Truhins, Dr.habil.phys.
20. Nils Veidemanis, A/S "Sidrabe"
21. Guntars Zvejnieks, Dr.phys.

The annual report summarizes the research activities of the ISSP in 2013. The staff of the Institute has succeeded in **5 national science grants** and in **two national cooperation projects** with the total financing 225 thous. Ls (ca. 315 thous. EUR).

Since 2008 the budgetary increase of science was focused on scientific infrastructure financing and launching of National Research Programmes (NRP). One of the scientific priorities in Latvia is **materials science**. ISSP became coordinating institution for the Materials NRP and collaborates as well in the NRP "Energetics" attracting 266.8 thous. Ls budget in 2013. The infrastructure financing for ISSP in 2013 was 390.1 thous. Ls. and it was partly used also for the salaries of the scientific and maintenance staff of the Institute. (Table 3).

Main awards, received at 2013:

No	Author	Award
1.	Dr.habil.phys. J.Purans	Member of Latvian Academy of Science
2.	J.Jansons	Honourary Doktor of Latvian Academy of Science
3.	Dr.phys. J.Banys (Lithuania)	The International Member of Latvian Academy of Science
4.	Dr.phys. N.Christensen	The International Member of Latvian Academy of

	(Denmark)	Science
5.	L.Shirmane	The L'OREAL-UNESCO sholarship „For Women in science 2013”
6.	Dr.habil.phys. A.Sternbergs	Award of Baltic Academy of Science
7.	J.Purāns, A.Kuzmins, J.Kalinko, J.Kotomins	Authors of the best scientific achievement (from Latvian Academy of Science)
8.	A.Vembris, M.Rutkis, A.Tokmakovs	Authors of the best scientific achievement (from Latvian Academy of Science)

At the end of 2013, more than 60 students, master's candidates and doctoral candidates worked in our Institute under the supervising of our scientists. The Institute has always strived to be actively involved in student teaching on all levels. During 2006 – 2008 a teaching module “Functional material and nanotechnologies” was introduced in bachelor and master physics curricula. This project was supported by European Social Fund. Many co-workers of the Institute were involved in preparation of lecture courses.

In 2013 **two international conferences** have been organised at the Institute:

1. International Young Scientist Conference “Developments in Optics and Communications 2013”, April 10 – 12, 2013, Riga, Latvia;
2. Saules kauss 2013, May 18, Riga, Latvia.

Table 3

INCOME OF ISSP, THOUSAND Ls, FROM 2007 - 2013

Year	Total financing	Grants and programmes from budget	Other financing from budget	Contracts, market oriented research	Internat. funds	Structural funds from EU
2007	3 236,5	721,9	1110,2	98,7	92,6	1201,7
2008	4 261,3	1 024,4	1 088,8	155,9	291,8	1 691,1
2009	1717,4	631,6	578,1	64,2	162,4	281,1
2010	2135,6	446,2	675,4	83,3	118,8	814,7
2011	2719,1	448,0	515,5	104,6	121,1	1530,0
2012	3462,0	462,3	552,1	120,0	41,5	2322,1
2013	2473,1	492,2	553,3	163,2	276,5	987,9

*) – investment for building reconstruction

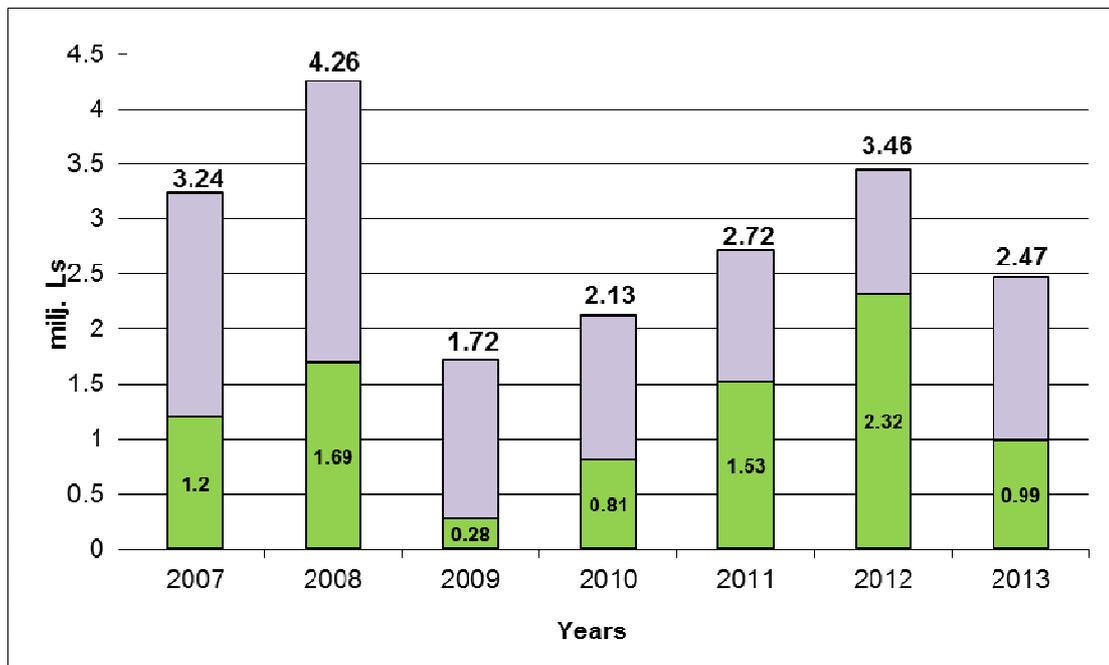


Fig.1. Total financing of the ISSP milj. LVL from 2007 to 2013

 - financing from EU Structural funds

The main source for **international funding** were three EC 7th Framework Programme contracts:

- 5 EURATOM projects – 134,5thous. EUR;
- GREEN-CC project – 116,0 thous. EUR;
- H2ESOT project – 64,7 thous. EUR.

Main achievements in 2013:

1. 121 SCI papers published by the staff of Institute;
2. 12 patent applications;
3. 29 B.sc. thesis and 13 M.Sc. thesis in physics, optometry and chemistry were defended under the supervision of our scientists;
4. I.Smeltere and A.Shvede were acquired degree of doctor of physics (PhD);
5. The development of “National Research Centre for nanostructures and multifunctional materials, constructions and technologies” by the ISSP (ERDF project).
6. The International evaluation of scientific institutions of Latvia by Technopolis took place at the end of 2013. In this evaluation the ISSP got a second place out of 150 scientific institutions of Latvia. The evaluation report for ISSP is in the next chapter.

Many thanks to everybody who contributed to this report as well as to the organizations that supported the Institute financially: Science Department of the Latvian Ministry of Education and Science, Latvian Council of Science, University of Latvia, EC 7th Framework Programme, Programme of EU Structural funds, COST Programme, and to many foreign Universities and institutions for cooperation.

Prof. Dr. A.Krumins

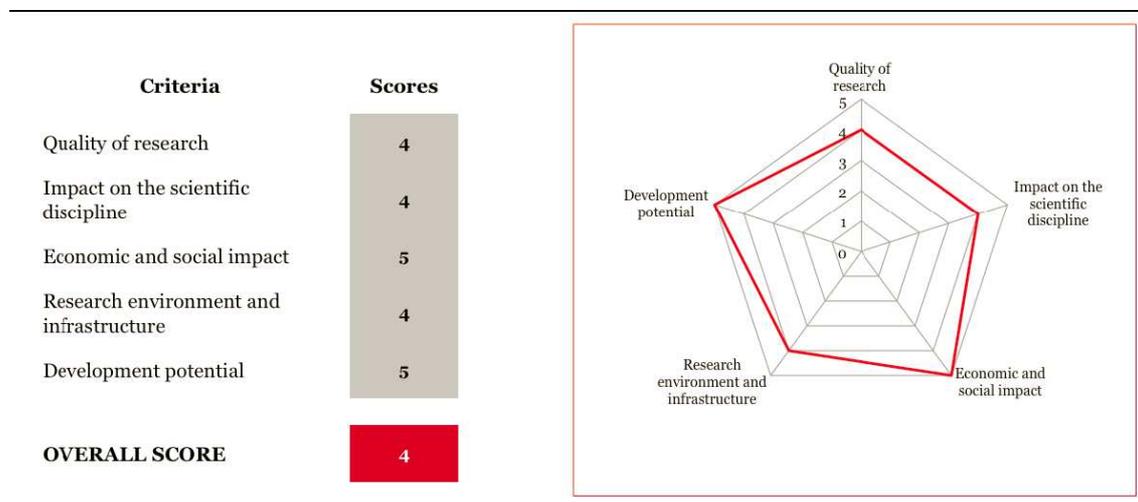
THE INTERNATIONAL EVALUATION REPORT FOR ISSP (Technopolis, 2013)

Name of the institution	Institute of Solid State Physics
Name of university	University of Latvia
Type of institution	Institute established by HEI

The Institute of Solid State Physics is one of the largest institutes in Latvia. The main field of its research is material science, with emphasis on nanoscience and nanotechnology of new advanced functional materials, with a special focus on materials applicable for sustainable energetics. The Institute is modern and well-run. A major concern of its management and staff is regarding further development, which is understood as the realisation of important and up-to date research topics, ongoing collaboration with other national and international centres and continuous involvement of the young generation in the performed work. The Institute is a national coordinator and leader in several projects. It has an active International Supervisory Board consisting of internationally recognised experts. The Board plays an important advisory role.

The mission of the Institute is to carry out high-level scientific activity, and to use its knowledge in the fields of education and innovation. The Society of Students and Young Scientists founded at the Institute helps students in their studies and professional development; and it also organises popularisation activities.

Figure 24 Assessment of the Research Quality of the Institute of Solid State Physics



Overall Score

The Institute of Solid State Physics is a leading Latvian centre in modern technology and materials research, combined with high-level education. It is visible internationally and carries out respectable activities. The Institute can provide an internationally comparable excellent research environment in materials science, educate students in modern technology and material studies, and provide innovative solutions for industrial applications. It constitutes a link for Latvia to world cutting-edge technology and science.

Quality of the research

Research performed at the Institute is of high level, and it involves topics which are generally considered as important and up-to date in materials science and in the related interdisciplinary areas. The Institute is following research priorities set by the European Commission and the Latvian Ministry. The publication output is good; the Institute produces papers mostly in international journals and with high impact factor. It had several invited papers at very good international conferences. Projects of applied character are also implemented. The Institute is a non-questionable national leader in its field of research – the total number of research outputs and total number of citations for Scopus outputs are by far the highest among all Latvian institutions assessed by the Panel - and it is a coordinator and leader in important nation-wide projects such as in the National Research Programme in Materials Science, the National Research Centre of functional and construction materials and their technologies, including the development of the Latvian Nanostructured Material Centre LATNANO-C. and also Latvian leader in big EU programmes, like EURATOM and Fusion for Energy. There is high involvement of PhD students in the research performed.

A criticism regarding the self-assessment report is that it does not show the research topics which were born in the Institute and are a local specialty. The main directions of the research are not described in detail, they are only listed. The full description is provided in the information booklet edited by the Institute in 2013, which was given to the Panel Members during the institutional visit.

Impact on the scientific discipline

The international competence of the Institute was confirmed already in 2001 by the status of "Excellence Centre of Advanced Materials Research and Technology" awarded by the European Commission. The international level of the institution is also corroborated by the large number of international collaborations, which has produced many joint publications with European and world scientists working in materials research. The Institute offers to its international partners a high-level human potential – e.g. in computer modelling and characterization of advanced materials – further to its technological and characterisation infrastructure. The infrastructure has been substantially modernised in the recent years and is still under development - due to the European funds and also to Latvian contribution - which has allowed the Institute to be competitive at the international level. The Institute has also strong collaboration with European large-scale materials research centres. It participates in quite a large number of EU projects. The world-scale impact of the laboratory's scientific results can be seen from the high number of invited talks at prestigious international conferences.

Researchers from the Institute are taking part in edition of several international journals, and the Institute is very active in organisation of international scientific meetings.

Economic and social impact

The Institute is a leading research centre in material science at Latvian scale, and plays an important role in education in the areas of modern technology and material research. Topics of research performed at the Institute are very important for modern society, for example the innovative materials and technologies, also applied for energy and environment issues. The Institute is a national leader in several big projects in materials science. It tries to use its high level of scientific activity for education and innovation. Some of the staff members are responsible for teaching of fundamental physics and solid state physics at all study levels at the University of Latvia and Riga

Technical University, and several MSc and PhD theses are performed in the Institute. Worth mentioning is the Institute's care about PhD students and young scientists, which goes beyond pure science. The Institute tries to help the students in problems associated with their studies and also in their professional development; it is done partially through the Society of Students and Young Scientists founded at the Institute. A number of spin-off companies have been established as a result of technological and scientific research. There are many common projects realised at the Institute with these and other industrial partners, regarding different applied research. The Institute participates also in other national and international (EUREKA) support programmes for market oriented research projects. It takes an active role in popularisation of science in press, radio and TV and also by organising events for school children.

Research environment and infrastructure

The Institute is able to provide an internationally comparable excellent research environment to high-level international researchers in materials science - it offers skilled personnel, interesting research topics and good infrastructure. It has already taken its chance in attracting European funds, and has substantially modernised the infrastructure, which is available to all of the Institute's scientific staff, as well as Latvian and international partners working on joint national and international projects. Upon successful competition for funding, the infrastructure of the Institute will be further developed. For example they have already started on an experimental basis the construction of "cleanrooms", which are essential for the development of nanotechnology and extension will be added if more funds will be obtained. The Institute has a clear strategy to become an excellent institute in novel materials science on a world scale, which is presented in the very well written self-assessment report and in the Institute's modern forward-looking strategy. The research goals of the Institute were developed to align with the European and national priorities identified in materials science. Current availability of support personnel is quite good. The Institute understands the need for continued employment of young and active researchers, and strongly supports these intentions. There is no doubt about the present and future status of the Institute as a very good research centre, as long as the national funding is on satisfactory level.

Development potential

The Institute has potential to become a really strong international player and even a global leader. It is already on a good track to achieve this goal. It has high-level researchers with internationally recognised scientific outputs (L. Skuja, J. Purans, A. Truhins, I. Tale, V. Kuzovkov) and modern infrastructure. It is active in fundraising from competitive sources. It has clearly defined its research goals, which involve important, up to date topics. It has made a competitive and realistic SWOT-analysis, and a carefully considered plan to manage weaknesses, threats and opportunities. It has world-wide collaboration in material research, also involving PhD student exchange. The Institute takes special care of young scientist generation and knows well that its future depends on them - their interest to continue research career in the most efficient way. The Institute has critical mass, and can be or will soon be attractive for PhD students and scientists from abroad. It should continue its role as a leading centre of Latvian research in material science.

Conclusions and recommendations

This institution is one of the best - arguably *the* best institution evaluated by Panel M. It has all the qualities to continue its role as the leading centre of Latvian

research in material science. Securing funding for the Institute should be of highest priority for the Latvian Government and Latvian research funding agencies.

DEPARTMENT OF CRYSTALS PHYSICS AND OPTOELECTRONIC MATERIALS

Head of Department Dr. phys. P. Kulis

LABORATORY OF OPTICAL SPECTROSCOPY

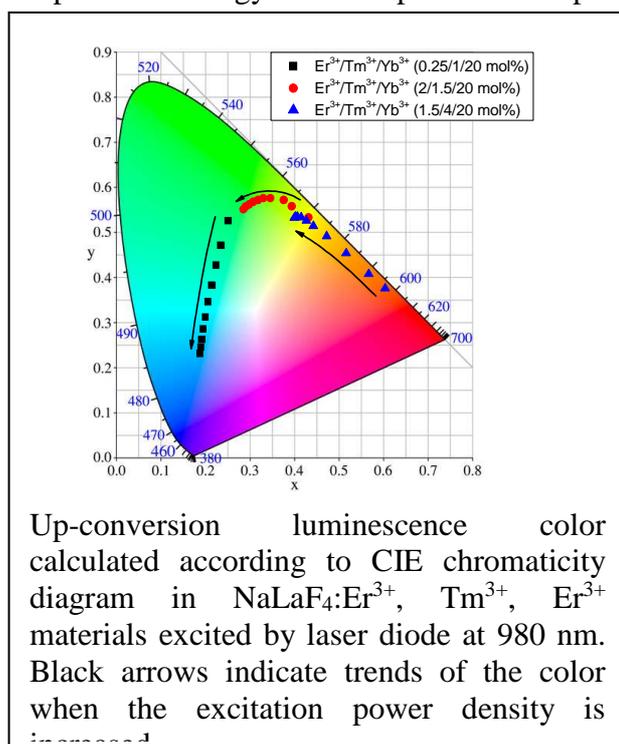
Head of Laboratory Dr.habil.phys. M.Springis

RESEARCH TOPICS

Synthesis of rare-earth doped fluoride and oxyfluoride nanocomposites; studies of radiation energy transfer and relaxation mechanisms in doped nanocomposites by means of optical spectroscopy methods; optical spectroscopy of defects in nanocomposites including studies of up-conversion luminescence.

The impact of defects (including radiation) on spectroscopic properties of several complex fluorides structures (LaF_3 , NaYF_4 , NaLaF_4) was studied. Along with the mentioned activities a new research topic related to the luminescence processes in rare-earth (RE) doped fluoride and oxyfluoride materials was initiated. The studies are organized in two directions: development of synthesis process of different fluoride nanostructures and studies of spectroscopic properties as well as radiation energy relaxation mechanisms in the materials. Special attention is paid to the studies of up-conversion process, i.e. studies of visible or even ultraviolet luminescence excited by several lower-energy photons absorption.

SiO_2 based glasses and nanostructured glass ceramics with RE doped (Er^{3+} , Yb^{3+} , Tm^{3+}) LaF_3 nanocrystals were synthesized. Mechanisms of the up-conversion luminescence in these materials were studied at different temperatures. It was found that in silicate glass ceramics with $\text{LaF}_3:\text{Er}^{3+}$ the main mechanism responsible for the up-conversion luminescence at room temperature is excited state absorption while at lower temperatures energy transfer up-conversion prevails.



A synthesis procedure of $\text{NaLaF}_4:\text{RE}^{3+}$ was elaborated and systematic studies of the material were performed. It was concluded, that $\text{NaLaF}_4:\text{RE}^{3+}$ is a perspective material for efficient up-conversion luminescence solutions due to its particularly low phonon energy. Possible applications involve efficient transformation of the infrared radiation into visible (visualization of infrared radiation, enhancement of Solar cells efficiency) and generation of different light colors (light sources).

The staff of the laboratory is taking part in the preparation and supervision of practical works in spectroscopy of solid state physics courses for Master students at the

University of Latvia (Dr. hab. phys. M. Springis, M. Sc. J. Grube). Dr.phys. A. Sarakovskis is a lector at the Faculty of Physics and Mathematics University of Latvia (courses: “Materials in Nature and Technics” and “Spectroscopy of Solid State”).

LABORATORY EQUIPMENT

Picosecond wavelength-tunable laser (EKSPLA) excited luminescence measurement equipment with streak-camera (HAMAMATSU). The equipment allows measurement of time-resolved luminescence spectra at different temperatures (10 K – 300 K) in a broad time range (50 ps – 10 ms)

Spectrometer (ANDOR) equipped with CCD camera (ANDOR) for traditional and up-conversion luminescence spectra measurements at different temperatures (10 K – 300 K), excited by Xe lamp or laser diode (808 nm and 980 nm, power up to 1 W).

Scientific Staff

Dr.hab.phys. Maris Springis
Dr.phys. Anatolijs Sarakovskis

PhD Students

M.Sc. Jurgis Grube
M.Sc. Guna Doke

Students

E. Pauksts
G. Krieķe

SCIENTIFIC VISITS ABROAD

M. Springis (1 week Estonia)
A. Sarakovskis (1 week Estonia)
G. Doke (1 week Lithuania, 1 week Estonia)
J. Grube (1 week Estonia, 1 week Poland)

COOPERATION

Latvia

Riga Technical University (Prof. A. Medvid).
RTU Institute of Nonorganical Chemistry (Dr. J. Grabis, Dr. D. Jankovica).

Switzerland

University of Bern, Department of Chemistry, Bern (Prof. K. Kraemer)

Russia

The Joint Institute for Nuclear Research, Dubna (Prof. G. Arzumanyan)

MAIN RESULTS

IMPACT OF SYNTHESIS CONDITIONS ON THE PROPERTIES OF UPCONVERSION LUMINESCENCE OF NaLaF₄:Er³⁺

G.Doke, J.Grube, A.Sarakovskis, M.Springis

Highly efficient up-conversion (UC) luminescence can be observed in several rare-earth doped materials. Numerous fluoride and complex fluoride materials are considered as very promising for a research of UC mechanisms and applications;

however there are some synthesis related problems with these materials. One of the most important problems of fluorides is emerging of oxygen-related defects which can act as luminescence “killers”. Additionally, the presence of oxygen defects in fluorides may disturb the energy transfer (ET) processes which are particularly important in the case of UC because excited state absorption (ESA) via ET is one of the most effective UC mechanisms.

In this research $\text{NaLaF}_4:\text{Er}^{3+}$ were synthesized in different atmospheres (air or fluorine). For these samples UC spectra, kinetics, excitation spectra as well as other optical measurements and X-ray diffraction analysis were performed. The analysis of the obtained data showed that, the dominant UC mechanism of the “green” (540nm) luminescence depends on the synthesis atmosphere. For the sample synthesized in the air atmosphere the dominant UC mechanism is ESA, while for the sample synthesized in fluorine atmosphere the UC process is governed by ET between Er^{3+} ions.

LUMINESCENCE OF OXYFLUORIDE GLASS AND GLASS CERAMICS DOPED WITH Eu AND Ce IONS

I. Brice, U. Rogulis, E. Elsts, J. Grube

Oxyfluorides are interesting compounds and they have drawn attention by combining the low-fluoride phonon energy with the thermal, mechanical and chemical stability of the silica glass. Oxyfluoride materials have broad applications possibilities in photonics by doping the material with appropriate rare earth activators. New better visible light phosphors are still being sought that could be used in LED lamps because when compared to incandescent lamps, they are much more energy-efficient. In our work, activated oxyfluoride glass and ceramic samples are prepared doped with Ce^{3+} and Eu^{2+} ions. The luminescence bands of these ions are not only intense but also wide, and are studied from the visible light luminophores application point of view.

Glass samples of $\text{SiAl}_2\text{ZnSrO}_3\text{F}_4$: Eu containing 1% mol EuF_3 , the sample is colourless and transparent, and 2% mol EuF_3 , the sample is semi-transparent, were made as well as glass ceramic samples by heating glass samples to 700 °C and 800 °C. These samples are studied by comparing their luminescence intensity and luminescence spectra.

LUMINESCENCE OF NaLaF_4 DOPED WITH Tm AND Yb

J. Grube, G. Doke, A. Sarakovskis, M. Springis

Our previous studies have showed that NaLaF_4 doped with rare-earth elements is a perspective material for up-conversion luminescence. It is possible to obtain upconversion luminescence in a wide spectral region (red, blue, UV) using this material doped with Tm^{3+} and Yb^{3+} . Therefore polycrystalline NaLaF_4 doped with Tm^{3+} and Yb^{3+} ions was synthesized. There was observed intensive blue up-conversion luminescence under 980nm excitation of these samples. When the samples were treated in different ways, for example grinding or deposited on a substrate using laser ablation technique, we could achieve also relative intensive ultraviolet up-conversion luminescence. Based on the experimental results peculiarities of different processes which take place in $\text{NaLaF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ ions will be discussed.

SYNTHESIS AND PHOTOLUMINESCENCE IN NaLaF₄:Eu³⁺ MATERIAL

G.Doke, M. Voss, J. Grube, A. Sarakovskis, M. Springis

It is known that most of the fluoride and complex fluoride materials have relatively high chemical stability, moreover, these materials have small phonon energy which suppresses the rate of nonradiative transitions. These properties make fluorides very attractive as host materials for optically active trivalent rare-earth ions. Numerous studies on optical properties of fluoride and complex fluoride materials have been conducted for several decades, however not much information can be found about processes in europium doped NaLaF₄ material.

One of the most important problems of fluorides is oxygen-related defects which emerge as result of synthesis of the material. The presence of oxygen defects in fluorides may have negative effect on photoluminescence intensity and the quantum yield .

In this work NaLaF₄:Eu³⁺ samples with different Eu³⁺ concentrations were synthesized by solid-state reaction. The synthesis was performed using different annealing temperatures and atmospheres (air or fluorine). For these samples photoluminescence spectra, excitation spectra, luminescence decay kinetics and X-ray diffraction patterns were measured.

From the analysis of the obtained experimental data conclusions about composition and optical properties of the material were made. Optical transitions and cross-relaxation processes in the activator system as well as formation of oxygen related defects and their impact on material optical properties are discussed.

UP-CONVERSION LUMINESCENCE OF NaLaF₄ DOPED WITH Tm³⁺ AND Yb³⁺

Jurgis Grube, Guna Doke, Anatolijš Sarakovskis, Maris Springis

Our previous studies have showed that NaLaF₄ doped with rare-earth elements is a perspective material for up-conversion luminescence [1]. It is possible to obtain up-conversion luminescence in a wide spectral region (red, blue, UV) using this material doped with Tm³⁺ and Yb³⁺.

Therefore polycrystalline NaLaF₄ doped with Tm³⁺ and Yb³⁺ ions was synthesized. An intensive blue up-conversion luminescence under 980nm excitation was observed in these samples. When the samples were treated in different ways, for example grinding or deposited on a substrate using laser ablation technique, we could achieve also relative intensive ultraviolet up-conversion luminescence (Fig. 1).

Based on the experimental results peculiarities of different processes which take place in NaLaF₄:Tm³⁺, Yb³⁺ ions will be discussed.

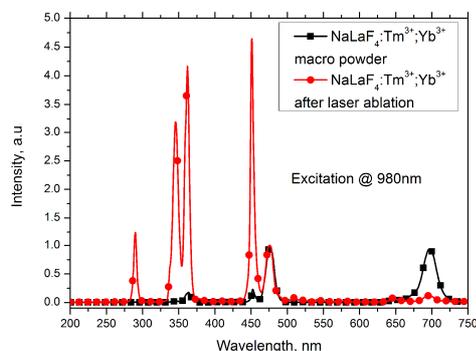


Fig.1 Up-conversion luminescence spectra for NaLaF₄ doped with Tm³⁺ (2mol%) and Yb³⁺ (20mol%) as macro powder and after laser ablation, excitation at 980nm. Spectra are normalized to 480nm up-conversion luminescence band

**X-RAY ABSORPTION SPECTROSCOPY AND SECOND HARMONIC
GENERATION ANALYSIS OF SRTI18O3**

A.Anspoks, D.Bočarovs, J.Purāns, F.Rocca¹, **A.Šarakovskis**, V.Trepakov²

Institute of Solid State Physics, University of Latvia

¹ IFN-CNR, Institute for Photonics and Nanotechnologies, Unit 'FBK-Photonics' of

Trento, Povo (Trento), Italy

² Institute of Physics, AS CR, Prague, Czech Republic

SrTiO₃ is well known quantum paraelectric material where ferroelectric ordering is suppressed by zero-point vibrations. By controlling exchanging ¹⁶O with ¹⁸O this material shows so-called quantum ferroelectricity.

In the present study we performed an X-ray absorption spectroscopy study and an optical second harmonic generation studies of ¹⁸O-exchanged SrTiO₃ in temperature range from 20-300K. Combining these data we can clarify role and character of the phase transitions and their influence on the local structure of Ti. We have identified 3 temperature regions which correspond to 3 different phases of SrTi₁₈O₃: so called cubic, tetragonal paraelectric and tetragonal ferroelectric.

**OXYGEN RELATED DEFECTS AND THEIR IMPACT ON UPCONVERSION
PROCESSES IN NaLaF₄:Er³⁺**

Anatolijs Sarakovskis, Guna Doke, Jurgis Grube, Maris Springis

Due to their relatively small effective phonon energy that suppresses the rate of nonradiative transitions numerous rare-earth doped fluoride and complex fluoride materials are considered to be promising materials for various up-conversion luminescence applications. The fluorides however suffer from oxygen-related defects emerging if no precautions are taken during the synthesis of these materials. The presence of oxygen defects in fluorides may disturb the energy-transfer processes which are particularly important in the case of up-conversion because energy transfer is one of the most effective up-conversion mechanisms. In this work NaLaF₄: Er³⁺ has been synthesized in different atmospheres (air and fluorine). The samples have been characterized by both stationary and time-resolved up-conversion luminescence spectra. Excitation spectra for the dominant luminescence bands have also been measured and analyzed. The analysis of the obtained data shows that the synthesis atmosphere is crucial for obtaining of high quality efficient up-conversion phosphor. Additionally it has been found that the prevailing mechanism of the “green” up conversion luminescence of Er³⁺ in NaLaF₄ depends on the synthesis conditions: in the sample synthesized in fluorine atmosphere the dominant up-conversion mechanism is energy-transfer between Er³⁺, while the up-conversion luminescence in the sample synthesized in the air atmosphere is governed by excited-state-absorption process.

GREEN LUMINESCENCE DECAY KINETICS ANALYSIS IN NaLaF₄:Er³⁺

Maris Springis, Jurgis Grube, Anatolijs Sarakovskis

In this work luminescence spectra and kinetics of NaLaF₄:Er³⁺ material at different Er³⁺ concentration are studied under excitation in UV, VIS and IR spectral region at different temperatures. A luminescence spectrum for NaLaF₄:Er³⁺ (0.2mol%) at

489 nm excitation reveals characteristic Er^{3+} ion luminescence bands in the green (540 nm), red (640 nm) and infrared (980 nm) spectral regions. The green luminescence band responsible for the transition $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ is dominating the spectrum. As the concentration of the activator is increased the positions and the shapes of the luminescence bands do not vary remarkably while the intensity of all luminescence bands changes significantly. The proportional increase of the red band intensity with increasing Er^{3+} concentration under direct excitation should be caused by the increase of the number of the activator ions. The superlinear increase of infrared luminescence intensity with the increase of Er^{3+} concentration as well as the quenching of the green luminescence for the concentrations higher than 2 mol% can be attributed to the cross-relaxation process between the activator ions. The green luminescence decay kinetics under pulsed direct excitation reveals rather complicated, nonexponential behavior and can be divided in several sequential stages. Both activator concentration and temperature dependence of the green luminescence decay kinetics are discussed in the frame of various energy relaxation models, involving direct relaxation at short times and small activator concentration, migration accelerated relaxation at higher activator concentration and migration-limited relaxation at longer times.

SCIENTIFIC PUBLICATIONS

1. **G. Doke, A. Sarakovskis, J. Grube, M. Springis**, Photoluminescence of neodymium and erbium doped NaLaF_4 material, (2013), Radiation measurements, 56, p. 27-30.
2. Rogulis, U., Elsts, E., Jansons, J., **Sarakovskis, A., Doke, G.**, Stunda, A., Smits, K.
3. Cathodoluminescence of oxyfluoride glass-ceramics, (2013), Radiation Measurements, 56, pp. 120-123.
4. Smits, K., Jankovica, D., **Sarakovskis, A.**, Millers, D. Up-conversion luminescence dependence on structure in zirconia nanocrystals, (2013), Optical Materials, 35 (3), pp. 462-466.

LECTURES ON CONFERENCES

29th Scientific Conference of the Institute of Solid State Physics, University of Latvia, Riga, 2013, February 20-22.

1. **G. Doke, J. Grube, A. Šarakovskis, M. Springis**. Impact of Synthesis Conditions on the Properties of Upconversion Luminescence of $\text{NaLaF}_4:\text{Er}^{3+}$. Abstracts of the 29th Scientific Conference ISSP LU, 2013, p. 10.
2. I. Brice, U. Rogulis, E. Elsts, **J. Grube**. Luminescence of Oxyfluoride Glass and Glass Ceramics Doped with Eu and Ce ions. Abstracts of the 29th Scientific Conference ISSP LU, 2013, p. 52.
3. **J. Grube, G. Doke, A. Sarakovskis, M. Springis**. Luminescence of NaLaF_4 Doped with Tm and Yb. Abstracts of the 29th Scientific Conference ISSP LU, 2013, p. 53.
4. A. Anspoks, D. Bočarovs, J. Purāns, F. Rocca, **A. Šarakovskis**, V. Trepakov. X-Ray Absorption Spectroscopy and Second Harmonic Generation Analysis of SRTI18O_3 . Abstracts of the 29th Scientific Conference ISSP LU, 2013, p. 85.

International conference “Functional materials and nanotechnologies” FM&NT, Tartu, Estonia, 2013, April 21-24.

1. **G. Doke, M. Voss, J. Grube, A. Sarakovskis, M. Springis** „Synthesis and photoluminescence in Eu³⁺ doped NaLaF₄ material”. Book of abstracts, p. 245.
2. **J. Grube, G. Doke, A. Sarakovskis, M. Springis** „Up-conversion Luminescence of LaF₄ doped with Tm³⁺ AND Yb³⁺”, Book of Abstracts, p. 235.
3. **Maris Springis, Jurgis Grube, Anatolijs Sarakovskis** „Green Luminescence decay kinetics analysis in NaLaF₄:Er³⁺”, Book of Abstracts, p. 211.
4. **Anatolijs Sarakovskis, Guna Doke, Jurgis Grube, Maris Springis** „Oxygen related Defects and their Impact on Up-conversion Processes in NaLaF₄:Er³⁺”, Book of Abstracts, p. 63.

The Fourth International Workshop on Advanced Spectroscopy and Optical Materials, Gdańsk, Poland, 2013, July 14-19.

Jurgis Grube, Guna Doke, Anatolijs Sarakovskis, Maris Springis „Up-conversion Luminescence of NaLaF₄ doped with Tm³⁺ and Yb³⁺”. Book of Abstracts P67.

International conference EcoBalt 2013, Vilnius, Lithuania, October 25.-27.

G. Doke, M. Voss, J. Grube, A. Sarakovskis, M. Springis. „Synthesis and photoluminescence in NaLaF₄:Eu³⁺-material”. Book of abstracts, p. 80.

Bachelor thesis

Edgars Pauksts. Up-conversion Luminescence of Oxyfluoride Glass and Glass Ceramics doped with SrF₂:Er³⁺.

LABORATORY OF MAGNETIC RESONANCE SPECTROSCOPY

Head of Laboratory Prof., Dr. habil. phys. U. Rogulis

RESEARCH TOPICS

Research of defect structure, luminescence centres and mechanisms using magnetic resonance spectroscopy techniques (EPR, ODMR).

Research of intrinsic and activator-related defects in oxyfluoride composites, fluoride micro- and nano-crystals in glass matrixes.

Investigations of luminescence properties of oxyfluoride glass and glass-ceramics, as well as application possibilities of these materials.

LABORATORY EQUIPMENT

ODMR spectrometer: Oxford Instruments Magneto-optical cryostat with magnetic fields up to 7 T at temperatures 1.5-4.2 K, spectral range 200-800 nm and microwave frequencies 36 and 45 GHz.

EPR spectrometer: X-Band (9.3 GHz), magnetic fields up to 0.7 T, temperature range 6-300 K.

Scientific staff

Prof., Dr. habil. phys. U. Rogulis
Dr. Phys. A. Fedotovs
Dr. Phys. E. Elsts

PhD students

1. Dz. Bērziņš
2. O. Kiseļova

Students

1. I. Brice
2. A. Antuzevičs
3. A. Cvetkovs
4. K. Bulindžs
5. U. Balmaks

SCIENTIFIC VISITS ABROAD

U. Rogulis (1 week, Estonia)

COOPERATION

Latvia

1. Department of Physics, Faculty of Physics and Mathematics, LU
2. Laboratory of Semiconductor Physics, Institute of Technical Physics, Riga Technical University (Prof. A. Medvids)

Germany

1. Fachhochschule Südwestfalen, Soest (Prof. Dr. S. Schweizer)
2. University of Paderborn (Prof. Dr. S. Greulich-Weber)

Romania

1. National Institute for Material Physics (INCDFM), Bucharest, Romania (Dr. M. Secu)
2. National Institute for Research and Development for Optoelectronics INOE 2000, Bucharest, Romania (Dr. I. C. Vasiliu)

MAIN RESULTS

CATHODOLUMINESCENCE OF OXYFLUORIDE GLASS CERAMICS

U. Rogulis, E. Elsts, J. Jansons, A. Sarakovskis, G. Doke, A. Stunda, K. Smits

Tb, Ce, Eu activated oxyfluoride glass-ceramics with the composition $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O} \cdot \text{LaF}_3$ have been studied by cathodoluminescence (CL). We compared CL intensities and decay times of the Tb, Ce, Eu activated glass-ceramic samples and observed that the Tb activated sample has the most intense luminescence, but the Ce activated sample has the shortest decay times. The creation of trap centers in the glass-ceramics has been observed after X-ray irradiation of samples.

ADVANCES IN OXYFLUORIDE GLASS-CERAMICS

U. Rogulis, A. Sarakovskis, E. Elsts, A. Fedotovs, I. Brice

Besides being a good medium for up-conversion displays, oxyfluoride glass-ceramics have shown several new prospective application directions. For investigations of the up-conversion mechanisms, the comparison of the optical spectra of the glass-ceramics and corresponding fluoride macrocrystals has been fruitful. We compared cathodoluminescence decay times for terbium-, cerium- and europium-doped oxyfluoride glass-ceramics and obtained that cerium-doped glass-ceramics have shortest decay times. Formation of fluoride crystallites in the oxyfluoride glass-ceramics could be tracked by the EPR hyperfine structure of impurity ions. Activator ions in the oxyfluoride glass-ceramics could be embedded in the oxide glass as well as in the fluoride crystal parts of the ceramics, revealing new possibilities of the construction of the spectral shape for solid state lighting.

SCIENTIFIC PUBLICATIONS

1. **U. Rogulis, E. Elsts, J. Jansons, A. Sarakovskis, G. Doke, A. Stunda, K. Smits**, Cathodoluminescence of oxyfluoride glass-ceramics, *Radiation Measurements*, 2013, vol. 56, pp. 120-123; DOI 10.1016/j.radmeas.2012.12.020

LECTURES ON CONFERENCES

1. **U. Rogulis, A. Sarakovskis, E. Elsts, A. Fedotovs, I. Brice**, Advances in oxyfluoride glass-ceramics, Abstracts of the International conference "Functional Materials and Nanotechnologies FM&NT-2013", Tartu, Estonia, 2013, p. 44.
2. **Dz. Bērziņš, A. Fedotovs, U. Rogulis, A. Medvids, P. Onufrijevs**, Optiski detektējamās magnētiskās rezonanses spektri ZnO, LU CFI 29. zinātniskās konferences tēzes, 2013, 12. lpp.

3. **E. Elsts, O. Kiseļova, U. Rogulis, K. Bulindžs, A. Zolotarjovs, L. Trinklere,** Radiācijas defektu pētījumi oksifluorīdu stiklos un stikla keramikās, LU CFI 29. zinātniskās konferences tēzes, 2013, 8. lpp.
4. **I. Brice, U. Rogulis, E. Elsts, J. Grūbe,** Ar Ce un Eu joniem aktivētu oksifluorīdu stiklu un stikla keramiku kuminescences pētījumi, LU CFI 29. zinātniskās konferences tēzes, 2013, 52. lpp.
5. **A. Antuzevičs, A. Fedotovs, U. Rogulis,** EPR spektru leņķiskās atkarības LiYF_4 kristālā, LU CFI 29. zinātniskās konferences tēzes, 2013, 7. lpp.

Master thesis

Inga Brice, "The luminescence of oxyfluoride glass and glass ceramics doped by Ce and Eu ions", Rīga, UL.

Bachelor thesis

Kaspars Bulindžs, "Studies of radiation defects in oxyfluoride glasses and glass-ceramics", Rīga, LU.

Uģis Balmaks, "Luminescence of Cd-doped ZnO", Rīga, UL.

LABORATORY OF WIDE BAND GAP MATERIALS

Head of Laboratory *Dr. hab. phys., Assoc. prof. B. Berzina*

RESEARCH AREA AND POSSIBILITIES

The research interests of our laboratory are focused on light-induced processes and defect luminescence in wide band gap materials such as III group nitrides, oxides and others available in form of bulk and nanosize structures. The spectral characterization of materials is realized in order to reveal:

- defect-induced luminescence mechanisms as well as the defect structure and behavior in material;
- processes of energy transfer between defects and host lattice;
- influence of material size on luminescence properties (macrosize and nano-structures in 1D, 2D and 3D forms);
- estimation of practical applications of the materials for the UV light dosimeters, gas sensors, UV and visible light emitters;
- elaboration of new materials for white light emitters with defined properties;
- estimation of surface defect luminescence.

The research includes different spectral characterizations of materials in temperature range 8 K – 300 K, such as absorption spectra within the spectral range 190 nm – 1100 nm, photoluminescence spectra (250 nm – 1500 nm), its excitation spectra, luminescence polarization and optically and thermally stimulated luminescence.

Scientific Staff:

1. Baiba Berzina, Dr.hab.phys, senior researcher, head of lab.
2. Laima Trinkler, Dr. phys., senior researcher,
3. Valdis Korsaks, Dr. phys., researcher.

Students - Technicians:

1. Paula Jankovska, student,
2. Roberts Kirsteins, student,
3. Jana Grigorjeva, student.

COLLABORATIONS

Latvia

Laboratories and departments of ISSP University of Latvia (Drs. J.Maniks, D. Millers, L.Skuja, K.Kundzins, L.Grigorjeva, Y. Zhukovskii, S. Piskunov).
Institute of Inorganic Chemistry, Riga Technical University (Prof. J. Grabis).
Institute of Technical Physics, Riga Technical University (Profs. A.Medvid, M.Knite).

Lithuania.

Institute of Applied Research, Department of Semiconductor Optoelectronics, Vilnius University (Dr. K. Jarasiunas)

Taiwan

National Taiwan University, Taipei (Profs. Li-Chyong Chen, Kuei-Hsien Chen)

MAIN INVESTIGATIONS AND RESULTS

LUMINESCENCE PROPERTIES OF AlN CERAMICS

L.Trinkler, B.Berzina

Photoluminescence (PL), thermoluminescence (TL) and afterglow luminescence (AGL) produced by UV irradiation were studied in AlN ceramics in the 10-300 K temperature range. The luminescence properties of AlN ceramics revealed under UV irradiation are determined mainly by oxygen-related centres, giving rise to the UV (around 3.18 eV) and the Blue (2.58 eV) bands, which are observed in PL, AGL, TL and optically stimulated luminescence spectra. It was found that the UV irradiation-generated donor acceptor pairs (DAPs), responsible for the UV emission band, are randomly distributed with regard to separation distance. Luminescence properties of AlN are interpreted basing on the model of localised recombination involving electron tunnel transitions from the excited state of D to the ground state of A, proposed by Jain et al., (2012). The observed features of PL, afterglow and TL of AlN ceramics are explained by dependence of tunnelling recombination probability on separation distance between D and A implied by the used model. Presence of a mutual peak in the glow curves for all selected emission bands confirms that localised recombination also contributes to the TL process in AlN, thus implying coexistence of localised and delocalised transitions in luminescence of this material.

These studies were performed within a support of European project ERDF 2010/0253/2DP / 2.1.1.1.0/10/APIA/VIAA/079.

BLUE LUMINESCENCE OF HEXAGONAL BORON NITRIDE

V.Korsak, B. Berzina, L.Trinkler

Blue luminescence of hexagonal boron nitride (hBN) was studied. Photoluminescence spectra and its excitation spectra were studied within a wide temperature range between 8K and room temperature. It was found that the intensity of the 400 nm luminescence in hBN depends on oxygen content in ambient atmosphere surrounding the sample. It allows conclusion that the material defects responsible for the 400 nm luminescence are located at or near material surface. This feature allows propose hBN as a material applicable for oxygen sensors.

These studies were performed within a support of European project ERDF 2010/0253/2DP / 2.1.1.1.0/10/APIA/VIAA/079.

SPECTRAL CHARACTERIZATION OF Al_xGa_{1-x}N MATERIAL

B.Berzina, L.Trinkler, V.Korsaks

Compound materials Al_xGa_{1-x}N in form of thin layers are synthesized in National Taiwan University (Dr. Li-Chyong Chen). The band gap of the material depends on parameter x which varies between 3% and 12%. The photoluminescence spectra of Al_xGa_{1-x}N were studied within a temperature range between 8 K and 300 K. The exciton-induced luminescence demonstrating the band gap variations dependent on material content is observed in UV spectral region and its properties are studied.

These studies were performed within a support of collaboration project between Taiwan-Lithuania-Latvia and of European project ERDF 2010/0253/2DP / 2.1.1.1.0/10/APIA/VIAA/079.

WHITE LIGHT EMMITER BASED ON DOPED AlN POWDERS

B.Berzina, V.Korsaks, L.Trinkler, R.Kirsteins, P.Jankovska

A white light emitter was worked out based on some sorts of AlN nanopowders being as grown or containing Mn and Tb impurities. Materials were synthesized in Institute of Inorganic Chemistry, Riga Technical University. Spectral characterization of AlN, AlN-Tb, AlN-Mn powders have been done. It was found that a mixture of these powders emits white light under UV light excitation within the spectral region between 250 – 270 nm. A quality of light “whiteness” depends on proportions of the components forming the mixture and an optimal composition was worked out. To fix the powder grains the composite material was formed based on PMMA matrix.

These studies were performed within a support of European project ERDF 2010/0253/2DP / 2.1.1.1.0/10/APIA/VIAA/079.

SCIENTIFIC PUBLICATIONS

1. P.Ščajev, **L.Trinkler**, **B.Berzina**, E.Ivakin, K.Jarašiunas, „*Influence of boron on donor-acceptor pair recombination in type IIa HPHT diamonds*”, *Diam. Relat. Mater.* 36 (2013) 35-43.
2. V.Skvotcova, N.Mironova-Ulmane, **L.Trinkler**, G.Chikvaidze, “*Optical properties of natural topaz*”, *IOP Conf. Ser.: Mater. Sci. Eng.* **49** (2013) 012051. doi:10.1088/1757-899X/49/1/012051.
3. Sutka, A., Mezinskis, G., Jakovlevs, D., **Korsaks, V.**, “*Sol-gel combustion synthesis of CdFe₂O₄ ferrite by using various reducing agents*”, *Journal of the Australian Ceramic Society* 49 (2) (2013) , pp. 136-140.
4. **L.Trinkler**, **B.Berzina**. „*Localised transitions in luminescence of AlN ceramics*”, *Radiation Measurements*, (article in press).
5. **Laima Trinkler**, **Baiba Berzina** „*Recombination luminescence in aluminum nitride ceramics*”, *Phys. Status Solidi B* **251**, No 3, 542-548 (2014); DOI 10.1002/pssb.201350090. (submitted 2013).

PATENTS

1. European patent, No EP13196564.2, submitted 10.12.2013.
„White light emitter compound material for luminescent lamps and method for making same”.
Submitter –Institute of Solid State Physics, University of Latvia.
Authors: **Baiba Berzina**, **Valdis Korsaks**, **Laima Trinkler**, Maris Knite, Janis Grabis.

Student Thesis

1. Jana Grigorjeva „Luminescence of nanostructured $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ”; Thesis of magister work, supervisor B.Berzina.
2. Roberts Kirsteins „Luminescence of dopped AlN powders”; Thesis of bachelor work, supervisor V. Korsaks.

LECTURES ON CONFERENCES

29th LU Scientific Conference of Institute of Solid State Physics, University of Latvia, February 20 - 22, 2013, Riga, Latvia

1. R. Kirsteins, V.Korsaks, L.Trinkler, B.Berziņa, J.Grabis , “*Luminescence of Al-Mn powder*”, Book of Abstracts, 2013, p.11.
2. J. Grigorjeva, V. Korsaks, L. Trinkler, B. Berzina, L.C. Chen, „*Luminescence of nanostructured compound AlGaN*”, Book of Abstracts, 2013, p. 44.

International Conference on Material Sciences and Technology (MST-S) 2013, May 31 - June 2, 2013, Wuhan, China.

3. L.Trinkler, B.Berzina, „*Luminescence properties of Al_2O_3 nanopowders with different phases*”, (oral).
4. B.Berzina, V.Korsaks, L.Trinkler, „*Blue luminescence of hexagonal boron nitride*”, (oral).

Scientific Workshop, National Taiwan University, 2013, April 23 – 26; Taipei, Taiwan.

5. B. Berzina, L. Trinkler, V. Korsaks, „*One dimentional nanostructures of ternary AlGaN with tunable bandgaps: optical properties*”, (oral).
6. L. Trinkler, B.Berzina, V. Korsaks, “*Luminescence properties of AlN ceramics* “ (oral).

17th International Conference on Solid state Dosimetry, September 22-27, 2013., Recife-Brazil

7. L.Trinkler, B.Berzina, “*Photo and thermoluminescence in AlN ceramics in broad temperature range*”, Abstract book, p.69.

International Conference of Nanomaterials annd Nanotechnologies (N&N) 2013, September 30 – October 4, Frascati, Italy.

8. B.Berzina, L.Trinkler, V.Korsaks, L.c.chen, K.H.Chen, K.Jarasiunas, “*Excitonic luminescence of ternary AlGaN*”, (oral).

LABORATORY OF SEMICONDUCTOR OPTOELECTRONICS

Head of Laboratory Dr. phys. B.Polakovs

RESEARCH AREA AND MAIN PROBLEMS

1. Laser processing of amorphous hydrogenised silicon thin films for solar cell applications. Investigation of effects of pulsed laser processing on electric, structural, morphological and photoconductive properties of a-Si:H films. Development of hybrid and tandem solar cell prototypes.
2. Laser scribing and laser processing of pyrolytic graphite, advanced methods of graphene printing on solid substrates. Optical microscopy, Atomic force microscopy and Scanning Electron microscopy investigation of printed graphene structures.
3. Synthesis of metal and semiconductor nanocrystals and nanowires for photonic, electronic and nanomechanical applications. Investigation of structural, optical, mechanical and other properties of nanomaterials.
4. Real-time manipulations of nanowires inside Scanning Electron Microscope. Investigation of tribological aspects of nanowire manipulation, nanoindentation experiments, mechanical characterization (Young modulus, bending strength and yield strength) of semiconducting and metallic nanowires. Scientific cooperation with Institute of Physics (University of Tartu) and Estonian Nanotechnology Competence Centre.

Scientific Staff

Dr. Habil. Phys. I. Tale
Dr. Phys. P. Kulis
Dr. Phys. J. Butikova
Dr. Phys. L. Dimitrocnko
Dr. Phys. B. Polyakov
Dr. Phys. S. Vlassov (visiting
researcher)
M. Sc. J. Jansons

PhD Students

M.Sc. G. Marcins
M.Sc. A.Voitkāns

Students

B. Sc. E. Butanovs
B. Sc. J. Pervenecka

COOPERATION

Latvia

Joint stock company "Alfa"
Institute of Biomedical Engineering and Nanotechnologies, Riga Technical University
G. Liberts Innovative Microscopy Center, University of Daugavpils

Germany

University of Rostock, Rostock
Company "Aixtron", Achen
Max Plank Institute of Plasma Physics, Garching

Estonia

Institute of Physics, University of Tartu
Estonian Nanotechnology Competence Centre, Tartu

MAIN RESULTS

LASER CRYSTALLIZATION OF A-SI:H FOR SOLAR CELL APPLICATIONS

G. Marcins, J. Butikova, J. Pervenecka, B. Polyakov, A. Muhin, I. Tale

The key of perspective manufacturing of thin film amorphous silicon solar cells lies in the improving of performance of the solar cells and reducing the production costs. Occurrence of metastable light-induced defects leads to dramatic decrease of efficiency of amorphous silicon solar cells with time due. Laser crystallization helps to prevent this effect. Primary effects of laser crystallization of a-silicon are dopants activation, and increase of charge carrier mobility due to higher crystallinity of laser-processed silicon. Silicon crystallization experiments had demonstrated that visible light irradiation facilitates super lateral growth of polysilicon grains. Additional effect is texturing of an initially smooth surface, which leads to reduction of back reflection of incident light and significant improvement of efficiency of a solar cell.

Laser crystallization has been successfully applied for processing of the whole p-i-n structure of total thickness around 300 nm. A significant improvement of solar cell output parameters in comparison to a non-processed cell was achieved. The highest mobility levels and the best cell performance has been demonstrated by the cells crystallized with the 2nd harmonics of Nd:YAG laser.

GRAPHENE STAMP PRINTING

J. Butikova, E. Butanovs, B. Polyakov, A. Kuzmin, L. Dimitrocenko, I. Tale

Graphene as a single monolayer of covalently bonded carbon atoms is an intriguing material for both fundamental and applied science. Due to its outstanding electronic and thermal properties (high charge carrier mobility, high heat conductance, etc.) graphene raised huge interest in the last decade, and became a real candidate as a successor of silicon in future microelectronics. There is plenty of graphene synthesis methods, however, the best electric properties were demonstrated by graphene mechanically cleaved from HOPG. Cleaved HOPG graphene sheets, nevertheless, are usually irregular in shape and thickness, and therefore are not suitable for integration in microelectronics devices.

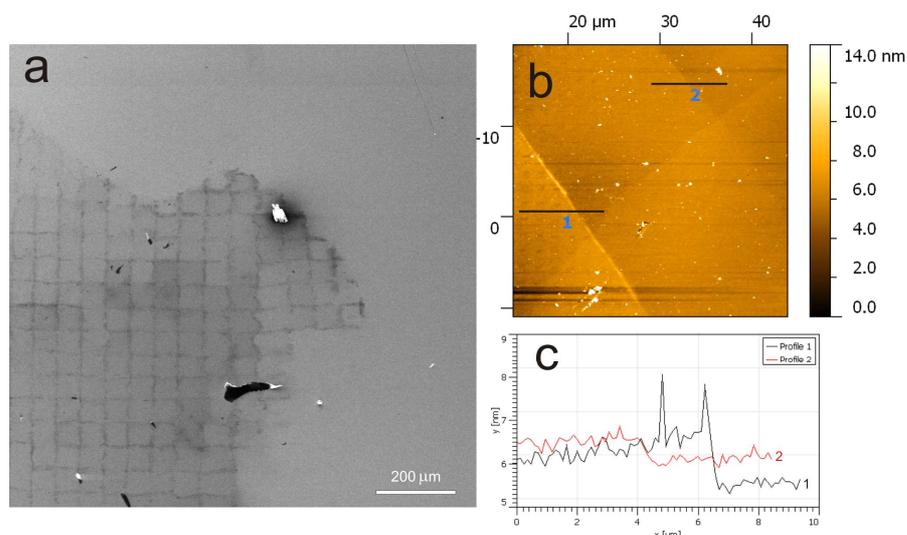


Fig.1. SEM image of stamp printed graphene sheets on oxidized silicon wafer (a). AFM image of the area marked by red rectangle on the SEM image (b). Cross sections demonstrating few- (Profile 1) and single-layer (Profile 2) graphene (c).

Highly oriented pyrolytic graphite (HOPG) was scribed by the pulsed laser beam to produce square patterns. Patterning of HOPG surface facilitates the detachment of graphene layers during contact printing. Direct HOPG-to-substrate and glue-assisted stamp printing of a few-layers graphene was compared. Printed graphene sheets were visualized by optical and scanning electron microscopy (fig.1.). The number of graphene layers was measured by atomic force microscopy. Glue-assisted stamp printing allows printing relatively large graphene sheets ($40 \times 40 \mu\text{m}$) onto a silicon wafer. The presented method is easier to implement and is more flexible than the majority of existing ways of placing graphene sheets onto a substrate.

NANOWIRES AND NANOCRYSTALS SYNTHESIS FOR PHOTONIC APPLICATIONS

B. Polyakov, J. Butikova, A. Kuzmin, S. Vlassov, R. Zabels, P. Kulis

Metal nanoparticles and nanowires are novel and perspective nanomaterials having wide range of possible applications. These materials can be synthesized using simple wet chemical methods. Metal nanoparticles and nanowires (Ag and Au) can be used in photonics and plasmonics, for single or double photon luminescence yield enhancement, photon absorption enhancement in solar cells, etc. Moreover, percolating networks of metal nanowires can be used as transparent conductive electrode, which is a mandatory component of every thin film solar cell. Recent publications proved that silver nanowires networks have electrical and optical parameters similar to ITO electrodes, which is etalon material in photovoltaics.

We investigate mechanical, electroconductive and other properties of metal nanowires and hybrid core-shell (Ag/SiO₂ nanowires), as well as laser processing methods of metal nanowires. CV laser processing helps to weld percolating NWs and reduce sheet resistance. Pulsed laser processing can be used to melt NWs and produce spherical nanoparticles.

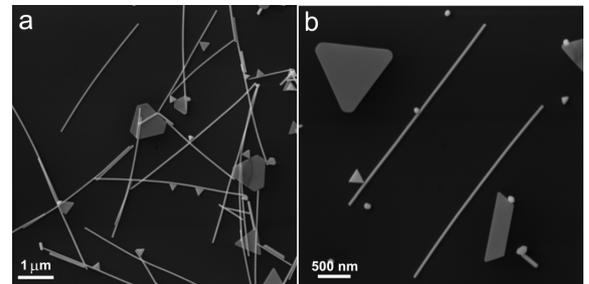


Fig. 2. SEM images of Au NWs and co-product nanostructures synthesized by wet chemical method.

TRIBOLOGICAL ASPECTS OF NANOWIRE MANIPULATION ON FLAT SUBSTRATE: EXPERIMENTAL METHODS AND MODELING

B.Polyakov, S.Vlassov, L.Dorogin, M.Antsov, R.Löhmus, I.Kink, A.Romanov

One-dimensional solids such as nanowires (NWs) and nanotubes (NTs) exhibit many unique optical, electrical, mechanical, and other properties that make them candidates for numerous future nanoscale devices. In many applications NWs are subjected to mechanical stresses and deformations. In flexible electrodes, as well as various nanoelectromechanical systems (NEMS) like, e.g., nanorelays, nanoswitches and nanoresonators, NWs are required to withstand numerous and severe deformations. The investigation of NWs mechanical characteristics is of a great importance for performance of the named systems.

The manipulation of NWs or NTs is frequently employed to position and assemble prototype nanodevices. Depending on the magnitude of its static friction and its ultimate strength, a NW may be displaced or broken as a result of manipulation. On small friction substrates (HOPG, for example) it is possible to move NW and measure kinetic friction force using NW itself as force sensor. At fig. 3 ZnO NW was moved on HOPG substrate by AFM tip inside SEM and kinetic friction was calculated from characteristic arc shape of the NW. It is possible to find static friction and bending strength of elastically deformed NW using characteristic bending profile and Young modulus of the NW. The method was demonstrated on copper oxide (CuO) and zinc oxide (ZnO) NWs on silicon and HOPG substrates, but it can be applied to any other elastic NWs.

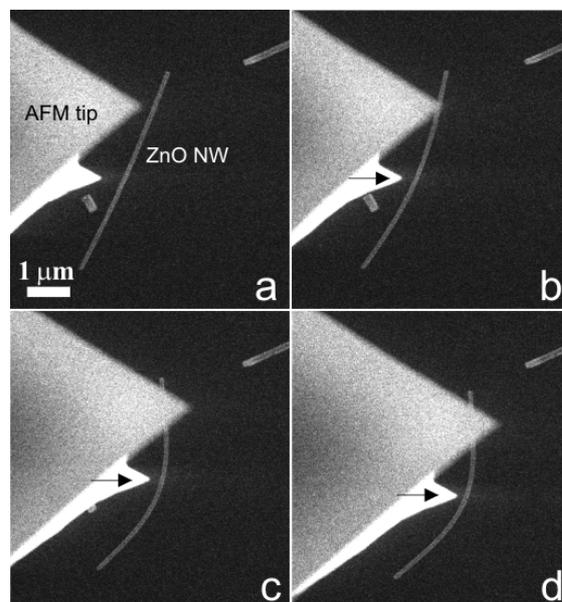


Figure 3. SEM images of the ZnO NW shape profile during the NW dragging on HOPG substrate (inverted contrast). The AFM tip contacts the intact NW, the arrow indicates the direction of tip movement (a); partially displaced NW (b); completely displaced NW (c); final characteristic shape corresponding to $\sigma_{kin}=0.6$ MPa (d).

SCIENTIFIC ARTICLES

1. **J. Butikova, B. Polyakov, L. Dimitrocnko, E. Butanovs, I. Tale.** Laser scribing on HOPG for graphene stamp printing on silicon wafer. *Central European Journal of Physics*. **11**, 580-583, 2013.
2. L. Dorogin, **S. Vlassov, B. Polyakov, M. Antsov, R. Lõhmus, I. Kink, A. Romanov.** Real-time manipulation of ZnO nanowires on a flat surface employed for tribological measurements: experimental methods and modeling. *Physics Status Solidi B*. **250**, 305–317, 2013.

LECTURES ON CONFERENCES

International conference “Functional materials and nanotechnologies” FM&NT, Tartu (Estonia), April 21 – 24, 2013

J. Pervenecka, J. Butikova G. Marcins, B. Polyakov, A. Voitkans, I. Tale. *Laser crystallization effects in amorphous silicon layers for solar cells.*

M. Antsov, **B. Polyakov, L. Dorogin, S.Vlassov, M.Vahtrus, S. Oras, I. Kink, R. Lõhmus.** *Static friction of CuO nanowires on substrates with varying roughness.*

M. Vahtrus, **S.Vlassov, M.Paalo, B.Polyakov, L. Dorogin, M. Antsov, R.Lõhmus, I. Kink.** *Two point electrical measurements of 1D nanostructures.*

MRS Spring Meeting&Exhibit, San Francisco (USA), April 1 – 5, 2013

G. Marcins, J. Butikova, B. Polyakov, A. Voitkans, I. Tale. *Comparison of pulsed laser and flash lamp assisted crystallization of amorphous Si:H thin films.*

International conference ImagineNano-2013, Bilbao (Spain), April 23-26, 2013

B. Polyakov, S.Vlassov, L. Dorogin, M. Antsov, I. Kink, R. Lohmus. *Silver nanowires for transparent conductive electrodes: In situ mechanical characterization.*

29th Scientific Conference of the Institute of Solid State Physics, University of Latvia, Riga, February 20-22, 2013

J. Butikova, B. Polyakov, L. Dimitroenco, E. Butanovs, **I. Tale**. *Laser scribing on HOPG for graphene stamp printing on silicon wafer.*

A.N. Trukhin, K. Smits, **J. Jansons**, L.A. Boatner . *Ultraviolet luminescence of ScPo₄, AlPo₄, GaPo₄ crystals.*

DEPARTMENT OF FERROELECTRICS

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Head of Laboratory Dr.habil.phys. V.Dimza

LABORATORY OF SYNTESIS AND PROCESSING

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REAEARCH AREAS

Materials

1. Production of new modified ferroelectric ceramics by doping with monoxides, developing binary or multicomponent solid solutions:
 - complex lead-containing perovskite family with general chemical formulas $PbB'_{1/2}B''_{1/2}O_3$ (where $B'=Sc^{+3}, Lu^{+3}, Yb^{+3}, Tm^{+3}$ etc.; $B''=Nb^{+5}, Ta^{+5}$) and $PbB'_{1/3}B''_{2/3}O_3$, (where $B'=Mg^{+2}, Zn^{+2}, Ni^{+2}, Cd^{+2}$ etc., $B''=Nb^{+5}, Ta^{+5}$ and etc);
 - modified $(Pb,La)(Zr,Ti)O_3$ (PLZT);
 - lead-free perovskite ceramics based on $(K_{0.5}Na_{0.5})NbO_3$, $(Na_{0.5}Bi_{0.5})NbO_3$, or $BaTiO_3$;
 - $BiFeO_3$, $Bi(Fe_{0.5}Cr_{0.5})O_3$, $SrMnO_3$,
2. Thin films, multiferroic materials, inorganic functional and nanomaterials

Methods

1. Investigation of kinetic parameters of synthesis and sintering proceses;
2. X-ray diffraction, atomic force microscopy, piezo-response force microscopy, electron scanning microscopy with EDX option, EPR and Raman spectroscopies, dielectric impedance and hysteresis measurement tools, ellipsometry and reflectometry techniques;
3. Investigation using synchrotron radiation based methods.

Properties: electromechanical properties; piezoelectric properties and field induced deformation, electrocaloric effect, thermal expansion, optical (absorbtion, luminescence), magnetic properties, electronic structure;

Problems

1. Phase transitions (including field-induced ferroelectric phase transitions) and ordering effects in “ordinary” ferroelectrics and ferroelectric *relaxors* along with new compositions (including 3d elements doping of ABO_3 perovskites); replacement of lead-containing materials in various applications
2. Investigation of electronic structure of prospective inorganic functional and nanomaterials using advanced synchrotron based methods.

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11. Voronezh State Technical University, Voronezh (Prof. S.A. Gridnev, Prof. L. Korotkov).
12. Moscow State Technical University of Radioengineering, Electronics and Automation (MIREA), Moscow (Prof. A.S. Sigov).

MAIN RESULTS

DIELECTRIC, ELASTIC AND MAGNETIC PROPERTIES OF

(1-X)BA_{0.95}PB_{0.05}TiO₃+XCO₂O₃ (X=0.1, 0.5, 1.0, 2.0 WT.%) CERAMICS

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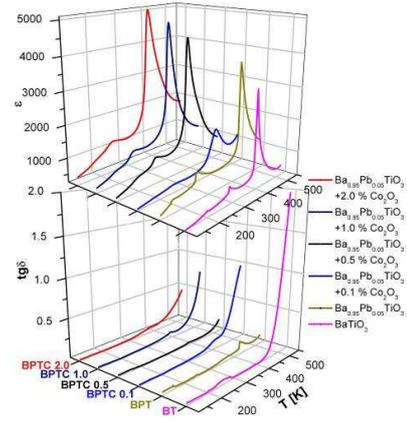
²*Institute of Molecular Physics, Polish Academy of Science,*

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$(1-x)\text{Ba}_{0.95}\text{Pb}_{0.05}\text{TiO}_3+x\text{Co}_2\text{O}_3$, ($x=0.1, 0.5, 1.0, 2.0$ wt.%) ceramics were prepared by a conventional sintering method. Samples have been characterized by X-ray diffraction in the laboratory Huber imaging plate Guinier camera G670 with $\text{CuK}\alpha_1$ radiation. Microstructures of the ceramics were studied by a Hitachi SU-70 scanning electron microscope equipped with X-ray microanalysis system for composition mapping. The dielectric measurements of the samples with gold-evaporated electrodes were carried out using an Alpha High Performance Frequency Analyzer in the temperature range 125–525 K at the frequencies varied from 1 Hz to 1 MHz. In order to designate the gap of the energy in these materials the diffuse reflectance measurements at the room temperature with using the Cary 5000 UV-VIS-NIR spectrophotometer were performed.



Application of ultrasonic method with using the INCO-VERITAS Ultrasonic Measuring Set UZP-1 allowed to determine main material parameters such as the Poisson ratio, the shear and the Young's modulus for the samples. The temperature dependences of ZFC and FC magnetization were measured for the ceramics in magnetic field up to 10 T and at temperatures from the range 2-500 K.

Ab initio calculations were performed on the cluster Zeus under PL-Grid Infrastructure with using the SIESTA 3.1 code.

Measurements showed the interesting effect of Pb and Co impurities on the properties of the BaTiO_3 perovskite.

ELECTRICAL CHARACTERIZATION OF FE DOPED BT CERAMICS BY IMPEDANCE SPECTROSCOPY

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³*Institute of Solid State Physics, University of Latvia*

The ABO_3 -type compounds with perovskite structure are one of the most interesting group of materials. Among them, the titanates are of great interest from the point of view of fundamental research as well as regarding their possible applications. Barium titanate (BaTiO_3 , BT) was the first developed piezoelectric ceramic and even now due to its excellent ferroelectric properties and the high electric permittivity at room temperature it is still widely used as capacitors, thermistors, chemical sensors, and piezoelectric devices.

The electric behavior of the Fe-doped and undoped BaTiO_3 were investigated as a function of frequency and temperature. These ceramics were prepared by solid state reaction using the conventional method. The microstructures were observed on the surface of the polycrystalline specimens, with use of a scanning electron microscopy Model Hitachi S4700 with a field emission and a Noran Vantage EDS system. The performed EDS investigations revealed that the all investigated samples were perfectly sintered. They contained a little glassy phase and their grains were well shaped. The impedance measurements were carried out in the temperature from 150K to 600K, and in the frequency range from 0.1Hz to 10MHz. All the electric measurements of the samples were performed with use of an Alfa - AN modular measurement system with a

temperature control system Quatro Krio 4.0 range from 0.1Hz to 1-MHz. Based on these parameters the electrical properties of the grains and grains boundaries were described. The grain and grain boundaries relaxation frequencies were shifted to higher frequency with increasing temperature. Bulk resistance of ceramics and the thermal activation energies were determined.

LUMINESCENCE AND ULTRAVIOLET EXCITATION SPECTROSCOPY OF SrI_2 AND $\text{SrI}_2:\text{Eu}^{2+}$

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R.T. Williams (*Wake Forest University, NC, USA*)

Despite the promising scintillator performance of $\text{SrI}_2:\text{Eu}^{2+}$, the fact remains that it is a very hygroscopic crystal and thus somewhat challenging to make certain physical measurements on. As a result, several of its important physical properties have not yet been measured or in some cases only recently measured for the first time. In this paper we report measurements of both undoped and 3% Eu-doped SrI_2 luminescence and ultraviolet excitation spectroscopy obtained using tunable ultraviolet synchrotron radiation at the SUPERLUMI station of DESY in Hamburg.

The main results of our experiments and associated analyses and interpretations contributing to the following: (1) Determination of the exciton energy and interband gap at $T=10$ K and 300 K by combined analysis of excitation spectra and optical transmission of a very thin crystal, (2) Tentative identification of the spin-orbit splitting of the valence band as expressed in the exciton spectrum, (3) Observation that nominally undoped powder and single crystal SrI_2 samples have trace Eu which appears associated with a defect, perhaps oxygen, broadening the Eu 5d-4f luminescence band by a factor x3, and (4) Spectra relating to the afore-mentioned search for self-trapped exciton luminescence.

COMPARATIVE STUDY OF THE LUMINESCENCE PROPERTIES OF MACRO- AND NANOCRYSTALLINE MGO USING SYNCHROTRON RADIATION

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MgO nano-powder with an average crystallite size of nanoparticles ranging 10–15 nm was synthesized using the extractive-pyrolytic method and was studied by room temperature VUV spectroscopy under synchrotron radiation excitation. Comparative analysis of their luminescent properties with that of macrocrystalline powder analogues and an MgO single crystal, grown by the arc-fusion method, has been performed under excitation by pulsed VUV synchrotron radiation. Special attention was paid to VUV spectral range, which is not reachable with commonly used lamp and laser sources. A considerable blue shift of about 0.3 eV in the excitation spectra of 2.95 eV emission band, was revealed in nanocrystalline MgO samples.

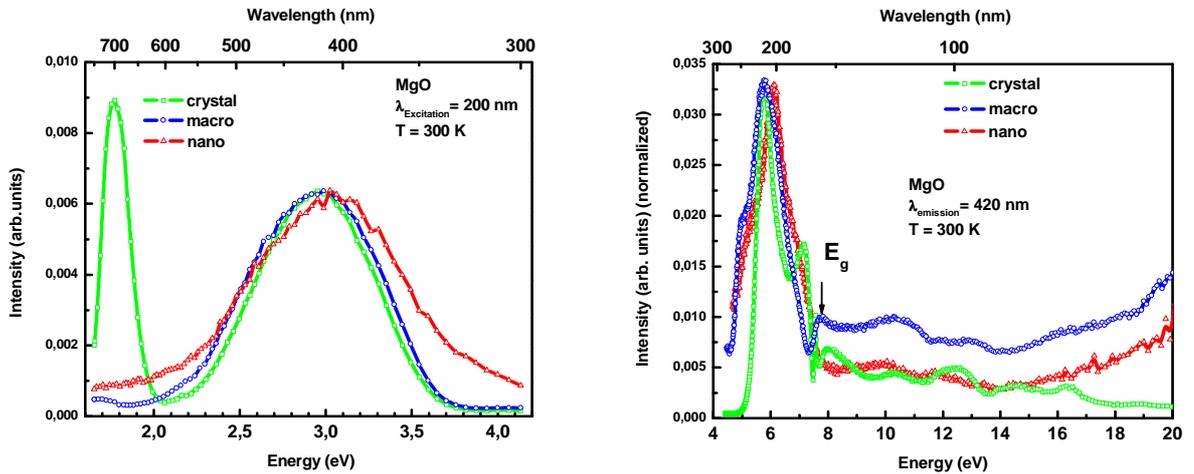


Figure 1. Emission (left) and excitation spectra of MgO single crystal, macroscopic and nanosized powders at room temperature obtained under synchrotron radiation.

RESISTANCE TO RADIATION OF LITHIUM NIOBATE CRYSTALS *)

M.N. Palatnikov, N.V. Sidorov, O.V. Makarova, and K. Bormanis

A series of lithium niobate crystals containing rare earth and alkaline elements – LiNbO_3 ; $\text{LiNbO}_3\text{:Y}$ (0.46 % mass); $\text{LiNbO}_3\text{:Y,Mg}$ (0.32, 0.24 % mass); $\text{LiNbO}_3\text{:Mg}$ (0.27 % mass); $\text{LiNbO}_3\text{:Gd}$ (0.004, 0.04, 0.26, 0.43 % mass) have been prepared along with ostensibly pure LiNbO_3 for the study of optical transmission before and after γ -irradiation. The features of optical transmission of the samples are determined with respect to the dosage of ionising radiation, the type and concentration of the admixture.

The change of the optical transmission by γ -irradiation of LiNbO_3 crystals containing admixtures is found to be substantially dependent on the type and concentration of the admixture while resistance to radiation compared with ostensibly pure LiNbO_3 crystal may be considerably higher or considerably lower. The strongest change of the optical transmission of the studied samples is observed in the case of Gd admixture ($\text{LiNbO}_3\text{:Gd}$, $[\text{Gd}] = 0.004\text{--}0.04$ % mass). In the same crystals a considerable shift of the edge of fundamental absorption to longer wavelengths is observed pointing to a remarkable amount of charged defects having emerged in the crystal structure.

The obtained data allow to propose using the change of optical transmission of the $\text{LiNbO}_3\text{:Gd}$ ($[\text{Gd}] = 0.004\text{--}0.04$ % mass) crystals in γ -dosimeters for the $\sim 1\text{--}160$ Gy range. The radiation colouring saturates at high doses of γ -radiation presumably due to irradiative annealing of defects. For instance, the change of transmission of the $\text{LiNbO}_3\text{:Gd}$ ($[\text{Gd}] = 0.04$ % mass) at ~ 160 Gy and $5 \cdot 10^4$ kGy is practically the same. Of the number of examined samples the most resistant to radiation are $\text{LiNbO}_3\text{:Gd}$ (0.26 % mass), $\text{LiNbO}_3\text{:Gd}$ (0.43 % mass), and $\text{LiNbO}_3\text{:Mg}$ (0.27 % mass) crystals the optical transmission of which practically does not change (≤ 3 %) at doses $\sim 5 \cdot 10^4$ kGy of γ -irradiation.

*) In cooperation with Institute of Chemistry, Kola Science Centre RAS, Apatity, Murmansk Region, Russia

ORDERING OF CATIONS IN THE LITHIUM NIOBATE FERROELECTRIC SINGLE CRYSTALS *)

N.V. Sidorov, M.N. Palatnikov, A.A. Janichev, A.A. Gabayn,
A.A. Kruk, and K. Bormanis

Obtaining nonlinear optical crystals of low photo-refractivity is an important problem of material science. Modification of congruent lithium niobate (LiNbO_3) crystal ($\text{Li/Nb} = 0.946$) by cations maintaining their charge under laser irradiation and resistant to optical damage (Zn^{2+} , Mg^{2+} , Gd^{3+} , B, In^{3+} , etc.) is one of ways to improve the optical strength of the crystal. The mentioned cations are able to suppress photo-refractivity by two orders of magnitude. The mechanism of embedding zinc in the structure of lithium niobate has a threshold depending on concentration of the Zn^{2+} ions. Refined studies of the features of restructuring of $\text{LiNbO}_3:\text{Zn}$ within the narrow range between the threshold concentrations of Zn^{2+} are of substantial interest beginning with the region of 0–2 mole % Zn^{2+} (the first threshold) where the strongest suppression of photo-refraction is observed.

Comparative Raman studies of structural features in ostensibly pure stoichiometric lithium niobate crystals ($\text{Li/Nb} = 1$) grown from melt of 58.6 mole % Li_2O , congruent lithium niobate crystals ($\text{Li/Nb} = 0.946$), and congruent lithium niobate crystals modified by Zn^{2+} cations within the range of 0.03 – 1.59 mole % are presented showing a region of enhanced order (compared with the congruent composition) in the sequence of basic and admixture cations and vacancies in the cation sub-lattice along the polar axis of the $\text{LiNbO}_3:\text{Zn}$ crystals. The shapes of NbO_6 are close to ideal octahedrons. The maximum ordering is observed at concentrations of Zn^{2+} ca. 0.05 – 0.94 mole %. Raman bands of $\text{LiNbO}_3:\text{Zn}$ (0.05 – 0.94 mole %) crystals are narrower compared with Raman spectra of the congruent crystal and closer to Raman bandwidth of the stoichiometric crystal the cation sub-lattice of which is the most ordered. At small concentrations of the Zn^{2+} admixture the modified $\text{LiNbO}_3:\text{Zn}$ crystals grow under the same technological conditions as the ostensibly pure congruent LiNbO_3 crystals.

*) In cooperation with Institute of Chemistry, Kola Science Centre RAS, Apatity, Russia

FEATURES OF LITHIUM NIOBATE SINGLE CRYSTALS MODIFIED BY RARE EARTH ADMIXTURES *)

M.N. Palatnikov, N.V. Sidorov, V.A. Sandler, K. Bormanis, and I. Smeltere

A number of anomalies of conductivity and of optical, dielectric and pyroelectric properties of lithium niobate crystals within a range of temperatures (300—400 K) has been observed by different authors. The lack of quantitative repeatability of the results depending on the history of the sample is typical to most studies of anomalous thermal behaviour of various physical parameters of ostensibly pure lithium niobate crystals and particularly of crystals containing admixtures.

Examining of the micro- and nano-structures of domains and specific structural ordering features of lithium niobate crystals containing admixture of rare earth elements ($\text{LiNbO}_3:\text{REE}$) and grown under stationary and non-stationary conditions has revealed formation of regular micron-scale domain structures (RDS) of changeable or fixed steps and periodic nano-size fractal structures of steps between 10 and 100 nm. A super-structural sub-lattice of clustered defects forming in the cation sub-lattice of REE-modified lithium niobate crystals is observed to have steps of the size of a few lattice translation periods.

Static and dynamic piezoelectric properties, dielectric dispersion and conductivity of lithium niobate crystals modified by REE (Gd, Er, Tm, and Gd:Mg), containing micro- and nano-structures, and grown under stationary and non-stationary conditions are studied within the 290 – 840 K and 0.5 – 10⁶ Hz range of temperature and frequency, respectively. Abrupt increase of the d₃₃ piezoelectric modulus up to the value of single domain ostensibly pure lithium niobate crystal is observed up to 340 K at heating poly-domain LiNbO₃:REE crystals. The actual observed values of physical parameters and kinetics of the processes to a considerable extent are determined by the particular micro- and nano-structure of the sample.

*) In cooperation with Institute of Chemistry, Kola Science Centre RAS, Apatity, Murmansk Region, and Ivanovo State University, Ivanovo, Russia.

LOW FREQUENCY DIELECTRIC PROPERTIES OF DOPED PMN-PNN CERAMICS *)

K. Bormanis, I.E. Tumanov, A.I. Burkhanov, A. Kalvane, and M. Antonova

A study of dielectric response within the range of the broad phase transition of lead-magnesium-nickel niobate ceramics containing lithium admixture (PMN+2wt.%Li₂O and 0.8PMN-0.2PNN+2wt.%Li₂O) prepared by conventional ceramics technology is reported. Silver-based conducting varnish coatings applied to the samples after heating up to 200 °C and slow cooling to room temperature are used as electrodes. Dielectric properties in weak fields were studied by means of a bridge circuit at frequencies from 1 Hz to 1000 Hz and in strong fields by Sawyer-Tower techniques at frequencies from 0.1 Hz to 10 Hz.

Dielectric response in strong fields is analysed on the basis of the amplitude and temperature curves of the effective parameters ϵ'_{eff} and ϵ''_{eff} obtained from polarisation loops. Nonlinearity of the dielectric response is found at temperatures considerably exceeding the temperature of the $\epsilon'(T)$ maximums.

A distinctive feature of the $\epsilon'_{\text{eff}}(T)$ curves in the PMN+2wt.%Li₂O and 0.8PMN-0.2PNN+2wt.%Li₂O ceramics presented in Figure 1 is existence of two regions of temperatures of different behaviour of ϵ'_{eff} with the temperature at field amplitudes between 1 kV/cm and 5 kV/cm. Two maximums of $\epsilon'_{\text{eff}}(T)$ are observed at 1 kV/cm: one of them around T_m corresponding to the maximum of the $\epsilon'(T)$ curve in weak fields, the other one – around 40 °C. Transition between the two maximums is presented by a broad plateau on the $\epsilon'_{\text{eff}}(T)$ curve gradually disappearing as the low-temperature maximum grows at raising the field amplitude. At higher fields (close to the maximum) the value of ϵ'_{eff} monotonously declines with increasing the temperature and $\epsilon'_{\text{eff}}(T)$ turns into the usual dielectric response specific to materials of broad phase transitions.

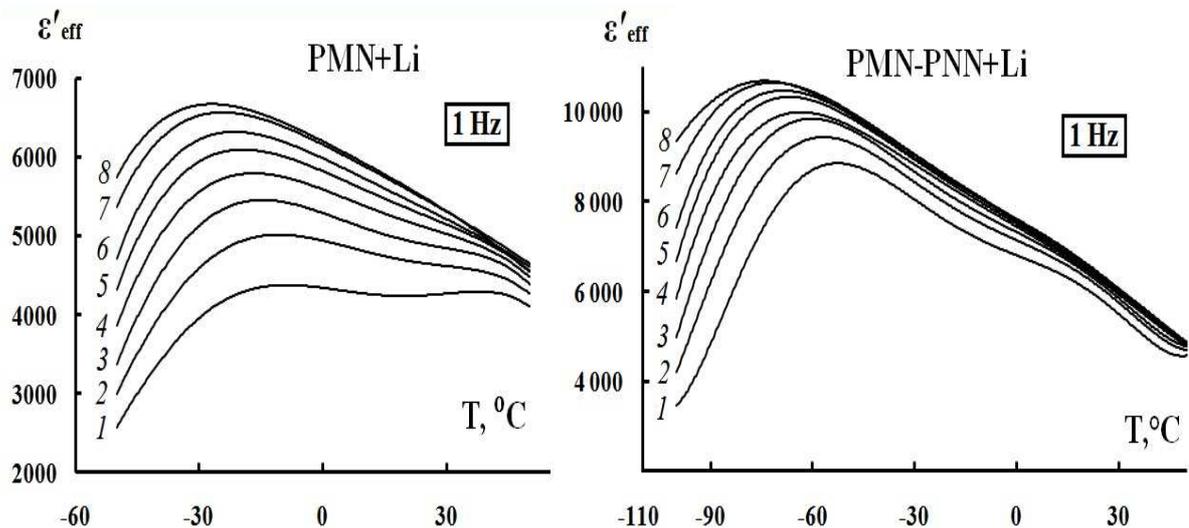


Figure 1. Effective dielectric permittivity at 1 Hz as function of temperature in PMN+2wt.%Li₂O and 0.8PMN-0.2PNN+2wt.%Li₂O at measurement field intensities of 1 (1), 2 (2), 3 (3), 4 (4), 5 (5), 6 (6), 8 (7), and 10 (8) kV/cm.

The obtained results are discussed within the existing approaches considering the broad phase transition as anomalously extended thermal range of coexisting polar and nonpolar phases and relaxation of phase boundaries being affected by a variety of defects in the material.

* In cooperation with Volgograd State Architectural and Engineering University, Volgograd, Russia

DIELECTRIC RESPONSE OF PLZTS CERAMICS OVER THE BROAD FERROELECTRIC-ANTIFERROELECTRIC PHASE TRANSITION *)

K. Bormanis, P.V. Bondarenko, A.I. Burkhanov, and A. Kalvane

The phase diagram of the complex perovskite $Pb_{(1-x)}La_x(Zr_{(1-y-z)}Ti_zSn_y)O_3$ (PLZTS) solid solution is of particular interest for the study of modern active dielectric materials. Depending on the molar concentration of admixtures (x, y, z), the PLZTS composition acquires either ferroelectric (FE) or antiferroelectric (AFE) properties. The present experimental study is made to reveal the features of dielectric nonlinearity in the PLZTS ceramics. For purposes of the study ceramic samples of $(Pb_{0.97}La_{0.02})(Zr_{0.53}Ti_{0.12}Sn_{0.35})O_3$ (PLZTS-35) belonging to the morphotropic region of coexisting FE and AFE phases were obtained by conventional ceramics technology and furnished with fired silver-paste electrodes.

The dielectric response of PLZTS-35 ceramic samples measured at a number of bias field intensities E_{-} is shown in Figure 1. The value of the $\epsilon'(T)$ maximum increases with the applied bias field intensity while shifting to a lower temperature. Most likely the observed behaviour of the dielectric response is a manifestation of the field-induced AFE-to-FE phase transitions in the material.

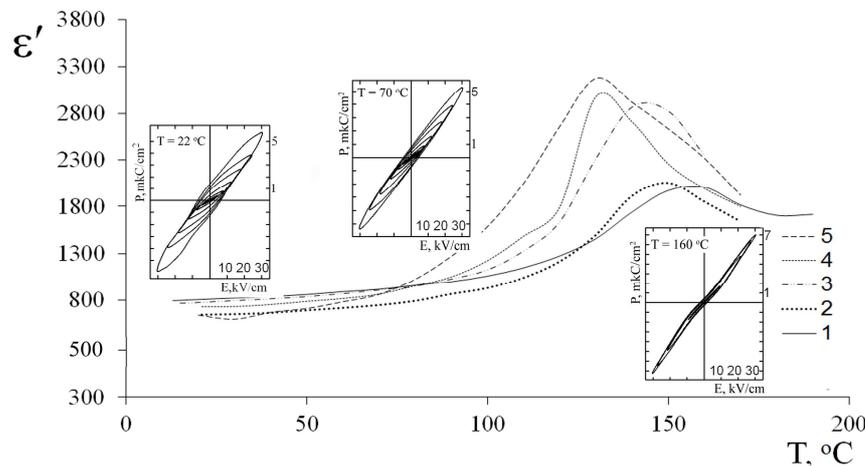


Figure 1. Dielectric permittivity ϵ' at 1 kHz as function of temperature in PLZTS - 35 ceramics at bias field intensities of 0 (1), 10 (2), 15 (3), 23 (4), and 30 (5) kV/cm.

Insert: polarization loops at different amplitudes of the AC measuring field at 0.1 Hz.

In the range of temperatures far below T_m corresponding to the temperature of the $\epsilon'(T)$ maximum, the value of ϵ' decreases with the bias field intensity E (Figure 1, $T < 70$ °C). The value of the field $E_{-} = 10$ kV/cm is close to the critical field at which the AFE phase is transformed into the FE phase. At such field-induced phase transitions the microstructure and the domain structure of the material are change.

Coexistence of the AFE and FE phases may be detected by the unusual polarization loops observed at these temperatures. So, at low E the ordinary ferroelectric polarization loops are displayed while triple loops – at amplitudes above 15 kV/cm (Figure 1, inset) indicating that up to a certain field value ($E < E_{cr}$) response to the action

of the field is determined only by the part of the sample presenting the FE phase while the AFE phase in the rest of the sample bulk to be transformed into the FE state requires field intensities $E > E_{cr}$.

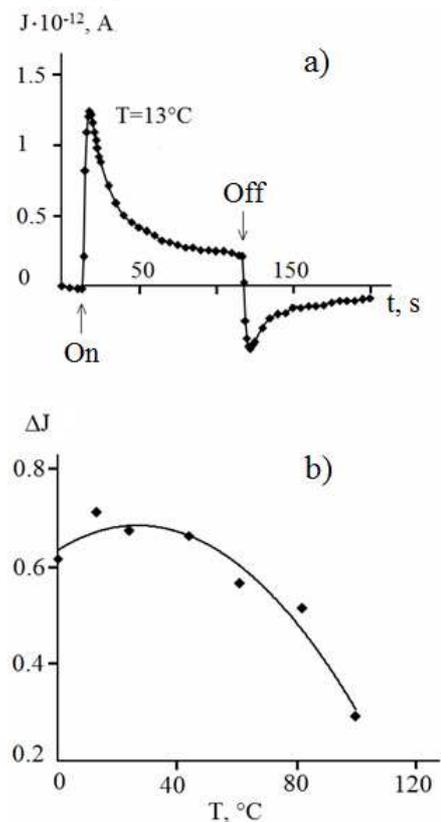
The type of polarization loops and behaviour of $\epsilon'(T)$ observed in PLZTS-35 are consistent with phenomena of coexisting antiferroelectric, ferroelectric and paraelectric phases over a rather wide temperature range.

*) In cooperation with Volgograd State University of Architectural and Civil Engineering, Volgograd, Russia

PHOTOELECTRICAL PROPERTIES OF THE SBN RELAXOR CERAMICS IN THE RANGE OF THE BROAD PHASE TRANSITION *)

K. Bormanis, A.I. Burkhanov, Luu Thi Nhan, A.G. Shein, S.V. Mednikov, and M. Antonova

A study of photocurrent in shortcut sample of $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN-75) ceramics at irradiation by “white” light of 0.15 W/cm^2 generated by LED 5034W2C-DSA-A is presented. The incident light beam is perpendicular to the surface of punctured electrode. Since penetration depth of visible radiation of such intensity into opaque ceramics is negligible, the effects of illumination are assumed to show up mainly within surface layers adjacent to the electrode. Similar techniques have been used studying photovoltaic effects in ferroelectric films [1].



Kinetics of photocurrent in the SBN-75 depolarised ceramics at 13°C – much below the temperature of the dielectric permeability $\epsilon'(T)$ maximum ($T_m = 110^\circ\text{C}$ at 1000 Hz [2]), is shown in Fig. 1a.

Some local heating of the material is possible with the start of illumination changing the polarization and causing appearance of pyroelectric current, formation of space charge and, consequently, Maxwellian relaxation of the magnitude of the photo-current to some stationary value [3] as a result. A parameter referred to as transition current defined by $\Delta J = (J_{max} - J_{end})/J_{max}$, where J_{max} is the maximum value of the photocurrent and J_{end} – the value at the end of the transition ($0.1 J_{max}$ at fast drop of the current) is introduced to account for the process. Experiments within the temperature range of $0 - 100^\circ\text{C}$ show that transition may last as long as 60 s.

Fig. 1. Photocurrent (a) and parameter of transition current (b) in the SBN-75 ceramics as functions of temperature.

Dependence on temperature $\Delta J(T)$ is found to have a maximum at some $T < T_m$ (Fig. 1b) possibly indicating to a contribution of pyroelectric current regardless to the

small intensity of radiation. Analysis of the behaviour of the stationary photo-current with temperature reveals thermal activation of it.

Kinetics of the photocurrent increase $J=a-b\cdot\exp(t/\tau)$ and decrease $J=A+B\cdot\exp(-t/\tau)$ is presented in Fig. 2. The obtained approximations are in good agreement with the data of other materials and confirm Maxwellian relaxation of the photovoltaic current caused by space charge emerging at the beginning of illumination.

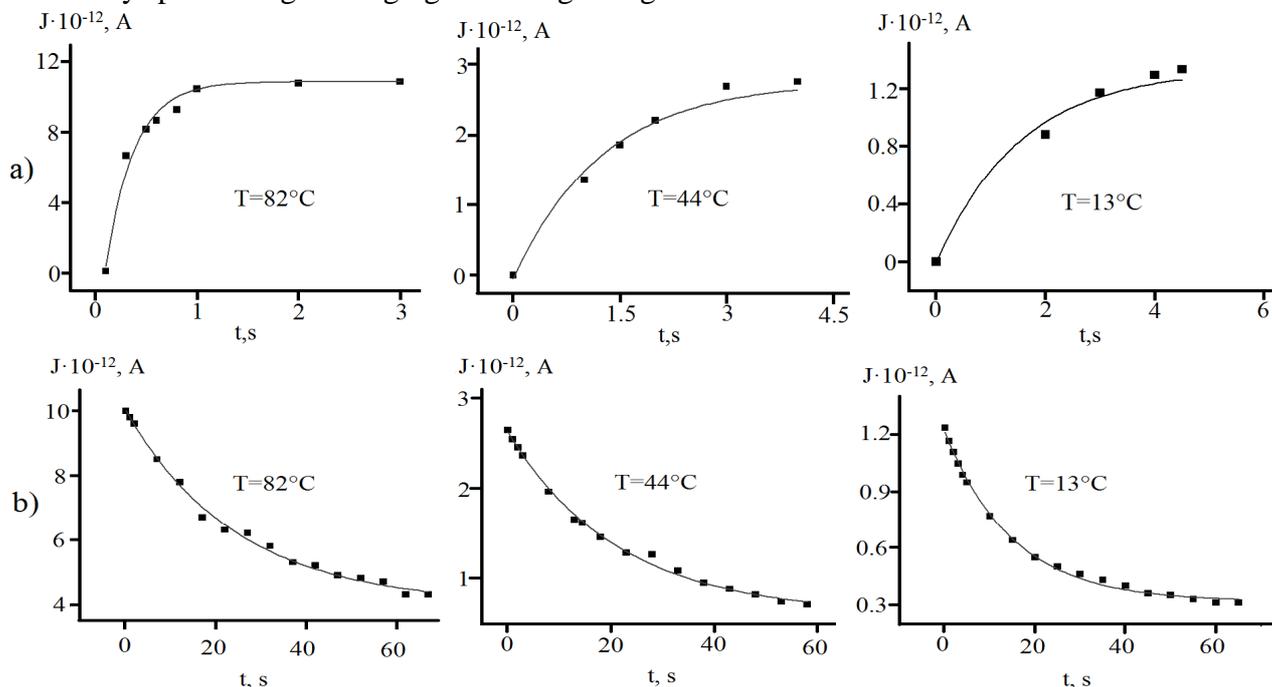


Fig. 2. Kinetics of the ascent and descent of photocurrent in the SBN-75 ceramics: a) within the time interval between the start of illumination and reaching the maximum; b) within the time interval between turning off the light and the end of fast drop of the current (~ 1 min). Solid lines – approximations of the increasing $J=a-b\cdot\exp(t/\tau)$ and decreasing $J=A+B\cdot\exp(-t/\tau)$ currents; a, b, A, B – experimental constants, τ – relaxation time.

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*) In cooperation with Volgograd State Architectural and Engineering University and Volgograd State Technical University, Volgograd, Russia

FIELD-INDUCED EMISSION OF LIGHT BY PLZT CERAMICS *)

S.A. Sadykov, S.N. Kallaev, K. Bormanis, M. Antonova,
A.Sh. Agalarov, and S.M. Alieva

The paper presents results of a study of the intensity of luminescence at switching polarization in lead-lanthanum zirconate (PLZT 9/65/35) relaxor ceramics as a function of temperature over the 0 – 60 °C range including the maximum point of dielectric permittivity (~ 60 °C) under condition of fast rise (0.1 kV/cm per μ s) of a strong applied field.

Emission is found to be specified by two distinct features: (i) a pronounced sequence of a large number of discrete flashes and (ii) the integrated intensity of the

emission increasing with temperature as the intensity and the number of flashes during the switching time (0.1 – 0.5 μs per flash), it is – as the bulk fraction of nano-polar mass of a hetero-phase sample.

There is a critical (dynamic coercive) field E_c at which the domain reorientation starts (decreasing with rising the temperature), which is similar to ferroelectrics and indicates to decreasing internal bias fields. The temperature being higher the polarised state (determined from the duration of emission) at switching the strong applied field within $\sim 50 \mu\text{s}$ is achieved faster – formation and evolution of the relevant domain structure is intensified by temperature.

The discrete character of emission from PLZT within the entire range of temperatures studied is supposed to be related to temperature-induced variation in dimensions and the number of nano-polar regions increasing the number of charged phase boundaries when polar domains are split as the temperature increases. Under a rapidly growing applied field the microscopic regions of individual critical field intensities E_c are successively involved in formation of the domain structure and further rearrangement the distribution of the internal and coercive fields determining the scatter of separate emission peaks in time.

*) In cooperation with Daghestan State University and Institute of Physics of Daghestan Scientific Center, Russian Academy of Sciences, Makhachkala, Russia

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LECTURES ON CONFERENCES

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1. **Marija Dunce, Eriks Birks, Maija Antonova, Anatoly Mishnov, Maris Kundzinsh, Andris Sternbergs** Phase Transitions and Physical Properties in Ca Modified Na_{1/2}Bi_{1/2}TiO₃-SrTiO₃-PbTiO₃ Solid Solutions
2. **R. Ignatans, A. Plaude, M. Dunce, M. Antonova, E. Birks**, „Structure and dielectric properties of Na_{1/2}Bi_{1/2}TiO₃-BaTiO₃ solid solutions in the phase transition region,”
3. **V. Pankratov, L. Shirmane**, A. Kotlov, A. Kuzmanoski, C. Feldmann, “*Ionic Liquid Based Synthesis and Ultraviolet Excitation Spectroscopy of Luminescent Nanocrystals*”, p. 283 Book of Abstracts
4. W. Cao, **V. Pankratov**, M. Huttula, **L. Shirmane**, Y.R. Niu, F. Wang, “*Origins of room temperature ferromagnetism and photoluminescence in Co-concentrated Co_xZnO_{1-x}O films*”, p. 284 Book of Abstracts

5. A.I. Popov, **L. Shirmane**, **V. Pankratov**, **V. Dimza**, **M. Antonova**, **M. Livinsh**, A.Kotlov, J. Zimmermann, "VUV Synchrotron radiation spectroscopy of PLZT ceramics" p. 276 Book of Abstracts
6. N.V. Sidorov, A.V. Syuy, A.A. Janichev, A.A. Gabayn, M.N. Palatnikov, A.A. Kruk, and **K. Bormanis**. Photorefractive Light Scattering in LiNbO₃:B, LiNbO₃:Y, LiNbO₃:Y:Mg, and LiNbO₃:Ta:Mg Crystals. Book of Abstracts, PO-130.
7. **K. Bormanis**, S.N. Kallaev, Z.V. Omarov, R.G. Mitarov, S.A. Sadykov, A.R. Bilalov, and **A. Kalvane**. Ferroelectric Lead Nickel-Niobium Titanate Ceramics: Phase Transition Studies. Book of Abstracts, PO-131.
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1. P.V. Bondarenko, A.I. Burkhanov, **K. Bormanis**, and **A. Kalvane**. Dielectric Response of PLZTS Ceramics Over the Broad Ferroelectric-Antiferroelectric Phase Transition. Proceedings, St. Petersburg, Polytechnical University Publishing House, 2013, pp. 108-109.
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3. S. A. Sadykov, S. N. Kallaev, **K. Bormanis**, **M. Antonova**, A. Sh. Agalarov, and S. M. Alieva. Field-Induced Emission of Light by PLZT Ceramics. Abstracts, 0301, 463.
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LABORATORY OF VISUAL PERCEPTION

Head of Division Prof. M.Ozolins

Human vision is a complex phenomenon. Its optical part is essential, however optical image stays only at the very beginning of the visual pathway and information processing in the cortex. We see with our brains, and as a result in some provocative cases it is very hard for us to accept the final outcome. Laboratory is a joint between colleagues in institute and Department of Optometry and vision science of the University. Most of Department's Master thesis have been accomplished due to collaboration between units. In 2012 more than 20 Bachelor's and 10 Master's thesis have been completed under supervision of laboratory researchers.

RESEARCH IN LABORATORY IS FOCUSED ON FOLLOWING PROBLEMS:

- investigation of smart optical materials and designs with controllable optical, electrooptic, refractive properties such as pjezooptic and electrooptic materials in order to accomplish effective radiation wavefront control, modification of light scattering and other optical characteristics;
- effect of aberrations in eye structures and appliances on retinal image formation and on the psychophysically detected human visual response, accomplishing adaptive optics compensation of optical objects aberration errors with fast control feedback;
- studies of binocular and stereovision, suppression and rivalry mechanisms of binocular vision, evaluation of suppression strength and depth effect on quality of vision binocular functions;
- fast eye kinematics studies for children and adults without and with several disorders of visual perceptions, eye kinematics studies in sport vision.
- evaluation of accommodation/convergence mechanisms reading print materials and for regular computer users;
- digital visual stimuli image processing determinant for analyse of the human visual response;
- multispectral material surface reflectance and emission analysis in visible and near IR and UV range, and its visual recognition by humans with normal and colour deficient vision;
- providing illumination and material visual appearance testing expertise and quality of products correspondence according to standards.

Scientific staff

Prof. Maris Ozolins
Prof. Ivars Lacis
Dr.phys. Sergejs Fomins
Dr.phys. Varis Karitans
Asoc.prof. Gunta Krumina

Ph.D. students

Kaiva Juraševska (Lūse)
Renars Trukša

SCIENTIFIC PROJECTS

- LCScie State Programm VPP-15 Prog., „Designing of innovative multifunctional materials, signal processing and information technologies for competitive scientific advanced products” ;
- Project funded by EU ERAF 2DP/2.1.1.1.0/10/APIA/VIAA/137: „Technologies for digital multispectral control of materials and quality improvement”.

PARTNERS ABROAD

<i>Spain</i>	Universidad Complutense Madrid, Spain (Prof. J. Alda) Laboratorio de Optica, Universidad de Murcia, Spain (Prof. P. Artal)
<i>Sweden</i>	Chalmers TH, Sweden (Prof. L.Komitov)
<i>Norway</i>	Buskerud HØgskolan, Institutt for optometri (Prof. J.R.Brueinich).
<i>Finland</i>	Colour Research Laboratory, University of Eastern Finland (Prof.J.Parkkinen)
<i>Germany</i>	<i>Institut fur Arbeitsphysiologie an der Universität Dortmund</i>
<i>The Netherlands</i>	Utrecht University (Prof. R. van Ee)
<i>France</i>	Laboratoire Régional des Ponts et Chaussées de Clermont-Ferrand (Dr.M.Colomb)
<i>Wales</i>	University of Cardiff, The School of Optometry and Vision science (Prof.T. Wess)

MAIN RESULTS

Modelling the appearance of chromatic environment using hyperspectral imaging. S. Fomins, M. Ozolinsh

Color of objects is a spectral composition of incident light source, reflection properties of the object itself, and spectral tuning of the eye. Light sources with different spectral characteristics can produce metameric representation of color; however most variable in this regard is vision. Pigments of color vision are continuously bleached by different stimuli and optical density of the pigment is changed, while continuous conditions provide an adaptation and perception of white. Special cases are color vision deficiencies which cover almost 8 % of male population in Europe. Hyperspectral imaging allows obtaining the spectra of the environment and modelling the performance of the dichromatic, anomalous trichromatic, as also normal trichromatic adapted behavior. First, CRI Nuance hyperspectral imaging system was spectrally calibrated for natural continuous spectral illumination of high color rendering index and narrow band fluorescent light sources. Full-scale images of color deficiency tests were acquired in the range of 420 to 720 nm to evaluate the modelling capacity for dichromatic and anomalous trichromatic vision. Hyperspectral images were turned to cone excitation images according to Stockman and Sharpe (2000) 1. Further, model was extended for anomalous trichromacy conditions. Cone sensitivity spectra were shifted by 4 nm according to each anomaly type. LWS and SWS cone signals were balanced in each condition to provide the appropriate appearance of colors in CIE system.

Multispectral analysis and cone signal modelling of pseudoisochromatic test plates

K. Luse, M. Ozolinsh, S. Fomins, and A. Gutmane

The aim of the study is to determine the consistency of the desired colour reproduction of the stimuli using calibrated printing technology available to anyone (*EpsonStylus Pro 7800* printer was). 24 colour vision assessment plates created in the University of Latvia were analysed right after their fabrication on August 2012 and after intense use for 7 months (colour vision screening on 700 people). Multispectral imagery results indicate that the alignment of the samples after seven months of use has maintained on the *CIExy* confusion lines of deutan deficiency type, but the shift towards achromatic area in the diagram indicates decrease in the total colour difference (ΔE^*ab) of test background (achromatic) areas and stimuli (chromatic) areas, thus affecting the testing outcome and deficiency severity level classification ability of the plates.

Vision science and psychology approach to adaptation processes

M. Ozolinsh, D. Lauva and O. Danilenko

We have experimentally studied visual adaptation processes and compared results in various visual perception tasks. Adaptation stimuli were demonstrated on computer screen and differed each from other by their luminance, colour, duration and dynamics related to the excited retinal and consequently the cortex neural cells and corresponding visual areas. Depth and characteristic times of adaptation processes depend on visual perception task. The slowest characteristic times (in range up to 10 sec and more) from studied processes are for adaptation to size of moving targets exciting retinal cells by equiluminant and isochrome stimuli, that are processed along parvocellular and magnocellular visual pathways. We assume that neural cell physiology lays on the base of this kind of size adaptation. Another kind of size adaptation where retinal cell excitation is static realizes in Ebbinghaus illusion. Here parallel to ongoing adaptation process brain uses also previously acquired knowledge to make shift in decision about stimuli size, and physiological effects dominate over psychological effects in perception of such stimuli. Over- or underestimating sizes in Ebbinghaus illusion with non-moving stimuli realizes much faster, and the degree of perception errors practically does not depend whether magnocellular or parvocellular visual pathway are activated – contrary to adaptation to dynamic moving targets.

Multicolour LEDs in educational demonstrations of physics and optometry

M. Ozolinsh and P. Paulins

LED light sources are used to design experimental setup for university courses teaching human color vision. The setup allows to demonstrate various vision characteristics and to apply for student practical exercises to study eye spectral sensitivity in different spectral range using heterochromatic flicker photometry. Technique can be used in laboratory works for students to acquire knowledge in visual perception, basics of electronics and measuring, or it can be applied as fully computer control experiment. Besides studies of the eye spectral sensitivity students can practice in trichromatic color matching and other visual perception tasks.

PUBLICATIONS

1. **S. Fomins, M. Ozolinsh**, Modelling the appearance of chromatic environment using hyperspectral imaging. *Proc. SPIE*, Vol.**9032**, Article number 903205 (2013).
2. **M. Ozolinsh**, D. Lauva and O. Danilenko, "Vision science and psychology approach to adaptation processes". *Eur.Scie.Journ.*, Vol.**9**(SE2), p.977-981 (2013).
<http://www.eujournal.org/index.php/esj/article/view/1422>; indexed: IndexCopernicus™, <http://journals.indexcopernicus.com/passport.php?id=6708>
3. **K. Luse, M. Ozolinsh, S. Fomins**, and A. Gutmane, "Multispectral analysis and cone signal modelling of pseudoisochromatic test plates". *IOP Conf. Ser.: Mater. Sci. Eng.*, Vol.**49**, 012041 (2013). doi:10.1088/1757-899X/49/1/012041
4. **S. Fomins, M. Ozoliņš**, Biologically inspired color vision deficit modelling with hyperspectral data. *Proc. 9th Baltic-Bulgarian Conference on Bionics and Prosthetics, Biomechanics and Mechanics, Mechatronics and Robotics*, Vol.**9**, pp.203-206 (2013).
5. **M. Ozolinsh**, P. Paulins, "Multicolour LEDs in educational demonstrations of physics and optometry". *Proc SPIE*. Vol.**9289**, "12th Education and Training in Optics and Photonics Conference, 92891D (July 17, 2014)"; doi:10.1117/12.2070522.
[http://spie.org/Documents/ETOP/2013/5_Training and Laboratory Demonstrations/ETOP2013_5-2.pdf](http://spie.org/Documents/ETOP/2013/5_Training_and_Laboratory_Demonstrations/ETOP2013_5-2.pdf)

PATENTS

Application - EP13193137.0 **S.Fomins, M.Ozoliņš**, MULTISPECTRALLY TESTED, PRINTED COLOUR VISION TEST FOR THE FINE EVALUATION OF THE DEGREE OF DEFICIENCY.

ABSTRACTS OF CONFERENCE PRESENTATION

1. B. Zutere, **K. Luse**, „Usability of psychophysical experiment scheme in colour vision deficiency characterization”. Abstract book “*Open Readings 2013*”, Vilnius, Lithuania, Riga, p.184(2013).
2. **K. Luse, M. Ozolinsh, S. Fomins**, A. Gutmane, B. Zutere, „Individual chromatic sensitivity threshold determination in case of red-green color deficiency”. Abstract book “*Developments in Optics and Communications - 2013*”, Riga, Latvia, p.78-79(2013).
3. **K. Luse, M. Ozolinsh, S. Fomins** and A. Gutmane, „Obtaining individual chromatic sensitivity thresholds in case of congenital red-green colour deficiency”. Abstr.book „*AIC 2013*”, p.239(2013).
4. **K. Luse, M. Ozolinsh, S. Fomins**, „Chromatic sensitivity variances along confusion lines for congenital red-green colour deficient individuals”. Abstr.book „*ICVS 2013*”, p.138(2013).
5. **K. Luse, M. Ozolinsh, S. Fomins**, A. Gutmane, “Evaluation of Pseudoisochromatic Plate Colour Fading”. Abstr.book „*AMT 2013*”, Palanga, Lithuania, p.112(2013).
6. **S. Fomins, M. Ozolins**, “Hyperspectral Imaging for Printed Matter, Construction Materials and Dyes Quality Assessment”. Abstr.book „*AMT 2013*”, Palanga, Lithuania, (2013).
7. **R. Trukša, S. Fomins**, “Computerized Color Vision Tests.” Abstr.book „*AMT 2013*”, Palanga, Lithuania, (2013).

8. **S. Fomins, M. Ozolins**, “Modelling the Appearance of Chromatic Environment Using
9. Hyperspectral Imaging.” Abstr.book „*Biophotonics - Riga 2013*”, Riga, Latvia (2013).

DEPARTMENT OF THEORETICAL PHYSICS AND COMPUTER MODELLING

Head of Department Dr. hab. phys. Eugene Kotomin

RESEARCH AREA AND MAIN PROBLEMS

Our theoretical research interests are focused on six classes of problems related to:

- kinetics of diffusion-controlled processes, with emphasis on pattern formation and catalytic surface reactions;
- the atomic and electronic structure of numerous advanced materials, with emphasis on calculations of properties of defects, surfaces, metal/insulator interfaces.
- theoretical simulations and experimental studies of nanostructures and nanomaterials;
- modeling of advanced functional materials for energy applications (fuel cells, ceramic membranes, Li batteries, fusion and fission reactors);
- stochastization of magnetic field lines in magnetized fusion plasma;
- gyrotron development for thermonuclear reactors .

We combine several different techniques, including analytical formalisms and large-scale computer simulations (quantum chemical methods, stochastic simulations as well as Monte Carlo/cellular automata modeling)—for more details see our homepage <http://www1.cfi.lu.lv/teor>

Staff

Laboratory of kinetics in self-organizing systems

Dr. O. Dumbrajs
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Dr. E. Klotins
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Dr.hab. V. Kuzovkov
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Laboratory of computer modeling of electronic structure of solids

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B.Sc. J. Kazerovskis
B.Sc. O. Lisovski
Dr. Yu. Mastrikov
Dr. S. Piskunov
Dr. hab. Yu. Shunin
M.Sc. A. Sorokin
Dr. Yu. Zhukovskii

SCIENTIFIC VISITS ABROAD

1. Dr. hab. E. Kotomin, Max-Planck Institut für Festkörperforschung, Stuttgart, Germany (9 months), Eurasian National University, Astana, Kazakhstan (2 weeks)
2. Dr. O. Dumbrajs, Karlsruhe Institute of technology (KIT) , Germany (7 weeks)
3. Dr. D. Gryaznov, Max-Planck Institut für Festkörperforschung, Stuttgart, Germany (9 months)
4. Dr hab. V. Kuzovkov, Northwestern University, Evanston, Illinois, USA (3 months)
5. Dr. A. Popov, Laue-Langevin Institute, Grenoble, France (1 month); Institute of Materials Science, Darmstadt University of Technology, Germany (5 weeks); Institute of Physics, University of Tartu, Estonia (2 weeks)

6. M.Sc. A. Sorokin, Technical University of Berlin, Germany (4.5 months)
7. M.Sc. A. Gopejenko, Institute for Applied Materials, Karlsruhe Institute of Technology Karlsruhe, Germany (3 months)
8. B.Sc. O. Lisovski, Uppsala University, Sweden (10 months)
9. B.Sc. J. Kazerovskis, University of Ulm, Germany (3.5 months)
10. Dr. Yu. Mastrikov, Institute of Applied Materials, Karlsruhe, Germany (1 month), Eurasian National University, Astana, Kazakhstan (2 weeks)
11. Dr. S. Piskunov, Laboratori Nazionali di Frascati, Italy (2.5 months); University of Duisburg-Essen, Germany (2 months), Institute of General and Inorganic Chemistry, Moscow, Russia (1 month)
12. Dr. hab. Yu. Shunin, Laboratori Nazionali di Frascati, Italy (5 weeks); Institute of Nuclear Problems, Belorussian State University, Minsk, Belarus (1 week)
13. Dr. Yu. Zhukovskii, St. Petersburg State University, Russia (1 month), Institute of Applied Materials, Karlsruhe, Germany (1 month)

INTERNATIONAL COOPERATION

Belarus	1. Institute of Nuclear Problems, Belarusian State University, Minsk (Prof. S.A. Maksimenko)
Estonia	2. Institute of Physics, University of Tartu (Prof. A. Lushchik)
Finland	3. Helsinki University of Technology (Dr. T. Kurki-Suonio)
France	4. Laue-Langevin Institute, Grenoble (Dr. G.J. McIntyre, Dr. H. Schober)
Germany	5. Max Planck Institut für Festkörperforschung, Stuttgart (Prof. Dr. J. Maier) 6. Deutsches Elektronen-Synchrotron DESY, Hamburg (Dr. A. Kotlov) 7. Darmstadt University of Technology, Darmstadt (Dr. J. Zimmermann) 8. Max Planck Institut für Plasmaphysik, Garching (Dr. V. Igochine, Prof. Dr. K. Lackner, Dr. R. Mayer-Spasche, Prof. Dr. H. Zohm) 9. Institut für Hochleistungsimpuls & Mikrowellentechnik (KIT), Karlsruhe (Drs. S. Kern, B. Piosczyk) 10. Institut für Angewandte Materialien (KIT), Karlsruhe (Drs. A. Möslang, P. Vladimirov) 11. Department of Theoretical Chemistry, University of Duisburg-Essen, (Prof. E. Spohr)
Greece	12. School of Electrical and Computer Engineering, National Technical University of Athens, Zographou (Dr. K. Avramides)
Israel	13. Ben Gurion University, Beer Sheeva (Prof. A. Aharony, Prof. D. Fuks)
Italy	14. Laboratori Nazionali di Frascati (Rome) (Dr. S. Bellucci, Dr. M. Cestelli-Guidi)
Kazakhstan	15. Gumilyov National University, Astana (Prof. A. Akilbekov)
Japan	16. FIR Center, University of Fukui (Prof. T. Idehara)
Lithuania	17. Institute of Semiconductor Physics (SPI), Vilnius (Dr. E. Tornau)
Poland	18. Warsaw University, Dept of Chemistry (Dr A. Huczko)
Romania	19. University of Craiova (Dr. D. Constantinescu)
Russia	20. St. Petersburg State University (Prof. R.A. Evarestov) 21. Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow (Prof. P.N. Dyachkov)
UK	22. University College London (Prof. A.L. Shluger)
Ukraine	23. National University, Lviv (Prof. I. Bolesta, Drs. I. Karbovnyk, V. Lesivtsiv, S. Velgosh and I. Rovetsky) 24. Institute for Scintillator Materials, Kharkov (Prof. A. Gektin)

-
- USA
25. Northwestern University, Evanston, Illinois (Prof. M. Olvera de la Cruz)
 26. University of Maryland, College Park (Dr. G.S. Nusinovich, Dr. M.M. Kukulja)
 27. Lawrence Berkeley National Laboratory, Berkeley, California (Dr. G.A. Bizarri)
 28. Wake Forest University, Winston-Salem, North Carolina (Prof. R.T. Williams)
-

MAIN RESULTS

ELECTRONIC STRUCTURE CALCULATIONS FOR ADVANCED MATERIALS

ELECTRONIC AND THERMODYNAMIC PROPERTIES OF WURTZITE-TYPE ZnO CRYSTAL CONTAINING OXYGEN VACANCIES OR IMPURITY ATOMS AND Al_{Zn} SUBSTITUTE ATOMS

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Our *ab initio* LCAO calculations performed using the hybrid PBE0 exchange correlation functional (with the standard HF exact exchange contribution of 0.25) show good agreement of the electronic and phonon properties of V_O -containing wurtzite-type ZnO crystal (Fig. 1) with the corresponding experimental results. The calculated Raman- and infrared-active phonon frequencies in defect-free hexagonal ZnO were found to be in a

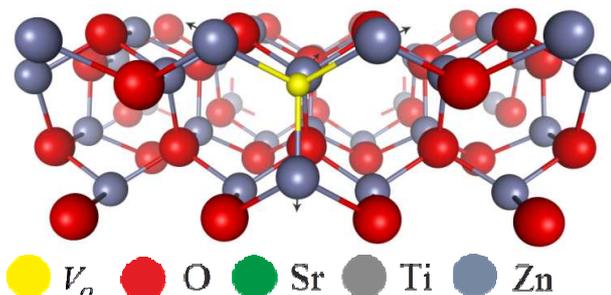


Figure 1. The atomic structure of wurtzite-type ZnO containing a single oxygen vacancy. O and Zn atoms as well as V_O are shown as large red, middle gray-blue and small yellow balls. The arrows show the relaxation pattern around V_O .

good agreement with experimental results. The additional “ghost” basis set centered at the vacancy site considerably affects the defect formation energies and leads to the pattern of almost singly ionized oxygen vacancies (one electron trapped in/around the vacancy). The corresponding defect formation energy in *w*-ZnO at 0 K (4.20 eV) is well converged with respect to the supercell size and its value is consistent with the experiments. The temperature dependences of the Gibbs free energies for formation of O vacancies in *w*-ZnO depending on their concentration were calculated taking into account the phonon contribution (Fig. 2). The temperature dependence of the soft modes as calculated for a

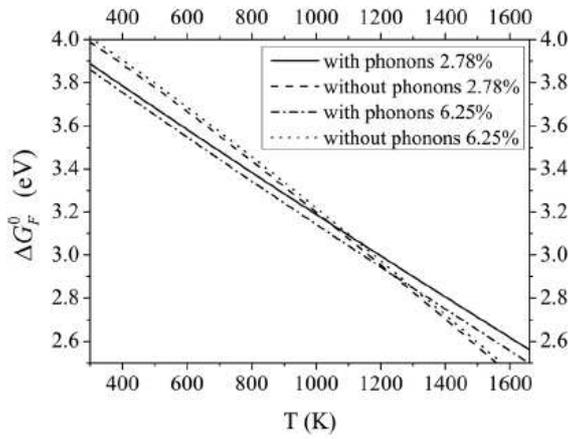


Figure 2. The calculated Gibbs free energy (*per* vacancy) of formation of oxygen vacancy (ΔG_F^0) with and without phonon contribution in the solid phase as a function of temperature in *w*-ZnO. The inset shows different defect concentrations for both cases. The distances between V_O vacancies in ZnO are 6.52 and 9.78 Å for 6.25% and 2.78%, respectively.

defect-free *w*-ZnO within the polarizability model is of key importance for the correct calculation of the defect formation energy. Supercell finite-size effects on values of ΔG_F^0 are caused by a considerable localization of electronic density around V_O vacancy in *w*-ZnO.

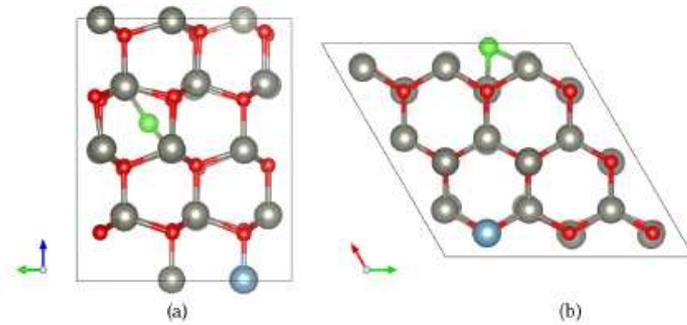


Figure 3. Images of *w*-ZnO:Al structure containing O_i impurity atom along $[\bar{1}00]$ (a) and $[00\bar{1}]$ (b) axes: 73-atom supercell containing 35 Zn_{Zn} (large grey), 36 O_O (small red), 1 Al_{Zn} (large blue) and 1 O_i (middle green) atoms.

In absence of interstitial O_i atoms, group IIIA metal- (especially Al-) doped ZnO (ZA) exhibits a low resistivity while retaining a high optical transparency, thus, being a prominent material for optoelectronics. However, these properties may be destroyed even with small concentrations of oxygen-related defects (*e.g.*, O_i atoms, such a structure is designated as ZAO). This difference can be illustrated by comparison of band structures and DOS for ZA and ZAO (Fig. 4).

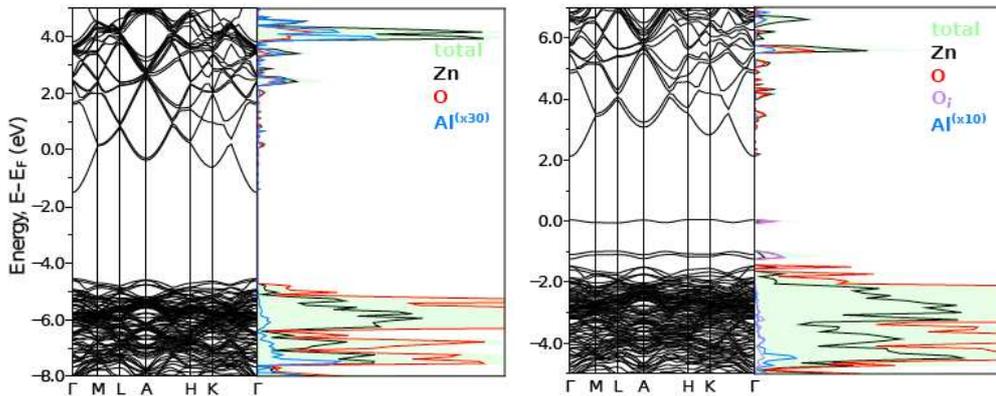


Figure 4. The band structure and DOS of ZA and ZAO (left/right panels, resp.) for 72-atom supercells.

Obviously, for ZA there is no distinct defect level as Al states are mixed with ZnO bands. However, the Fermi level crosses conduction bands, therefore, introducing Al substitute into *w*-ZnO induces the insulator-to-metal transition. On the contrary, in the case of ZAO, there are three distinct defect levels appear in the band structure and DOS, all of which consist mainly from O_i contributions. Al states, on the contrary, are delocalized over valence and conductivity bands as in ZnO:Al. Positions of O_i levels make defective ZAO structure an electron acceptor.

FIRST PRINCIPLES SIMULATIONS OF HYDROGEN IMPURITIES IN ZnO BULK AND ON ZnO(10 $\bar{1}$ 0) SURFACE

E.A. Kotomin, Yu.F. Zhukovskii, A. Sorokin, J. Purans

A. Usseinov, A.T. Akilbekov

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Hydrogen atoms unavoidably incorporated from plasma during growth of ZnO considerably affect their electrical conductivity. Supercell models of single hydrogen atom incorporated in the bulk and upon the non-polar ZnO (10 $\bar{1}$ 0) surface were calculated using hybrid LCAO method. The incorporation energy, the atomic relaxation, the electronic density redistribution and the electronic structure modifications were compared for both bulk interstitial H position (Fig. 5) and the surface adsorption (Fig. 6). It has been shown that hydrogen has a strong binding with the nearest bulk and surface O ions characterized by incorporation energy of the former *per* 2 \times 2 \times 2 supercell (1.8 eV) and adsorption energy of the latter *per* 2 \times 2 surface supercell. Obviously, incorporation of H_i atom into the bulk is energetically unfavorable.

The energetically most favorable position of H_i atom in *w*-ZnO bulk has been found to be the interstitial site near the oxygen atom in a regular lattice, the so-called anti-bonding (AB) configuration perpendicular to *c* axis (Fig. 5). Analogously, the most preferable

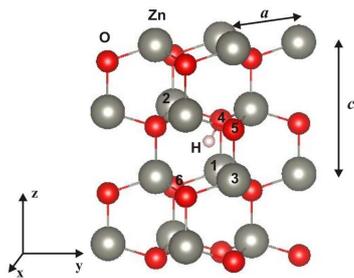


Figure 5. Structural model of the *w*-ZnO (2 \times 2 \times 2) supercell containing the hydrogen impurity atom (H_i). Enumerated Zn and O atoms are the nearest neighbors of H_i being relaxed around it.

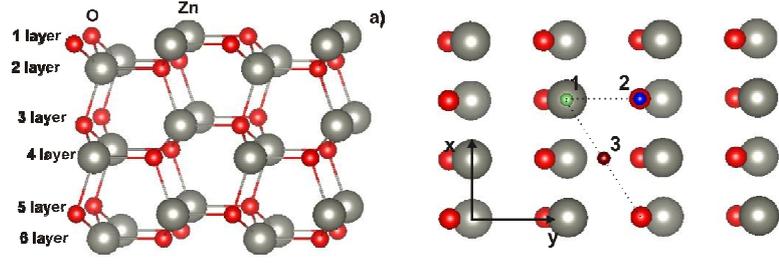


Figure 6. Unrelaxed 6-layer slab model of the ZnO(10 $\bar{1}$ 0) surface (a) and top view of the three possible different positions for the adsorption of hydrogen atom upon it (b): 1 – atop surface Zn atom, 2 – atop surface O atom, 3 – hollow position for H adatom. In the case of the lowest H adatom concentration, ZnO (2 \times 2) surface supercell has been constructed.

adsorption position of H atom upon ZnO(10 $\bar{1}$ 0) surface has been found to be site 2 atop the surface O atom (Fig. 6). Comparative analysis of the electronic structure of ZnO:H bulk and H/ZnO(10 $\bar{1}$ 0) interface confirms that hydrogen atom in both cases is anti-bonding, moreover, it is a shallow donor. Therefore, we would expect a high concentration H nearby ZnO surfaces could make a considerable contribution to the electronic conductivity (surface metallization).

AB INITIO CALCULATIONS OF POINT DEFECTS IN INORGANIC NANOTUBES (BN, SrTiO₃, TiO₂ NANOTUBES CONTAINING SUBSTITUTE DEFECTS)

S. Piskunov, Yu.F. Zhukovskii, S. Lisovski, J. Kazerovskis, J. Begens

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Inorganic nanotubes (NTs) are important and widespread materials in modern nanotechnology. Moreover, imperfect NTs with reproducible distribution of point defects attract enhanced interest, due to potential production of novel innovative nanomaterials and devices. A variety of experimental conditions accompanying their synthesis can certainly promote the appearance of point defects: native vacancies or antisites as well as substitutional impurities. These and other types of irregularities may occur in inorganic NTs as a result of the growth process or intentionally induced to modify their properties. Point defects also play the role of chemically active sites for NT-wall functionalization. This study analyzes a series of results obtained using *ab initio* simulations on both perfect and defective BN NTs, TiO₂ NTs as well as SrTiO₃ NTs.

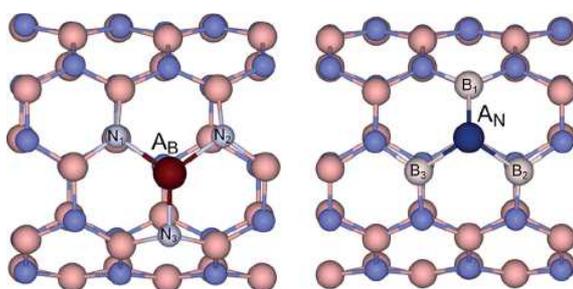


Figure 7. Schematic representation of substitutional defect-containing BN NT (A_h /BN NT) unit cells as calculated using the PBE0-LCAO method with the total geometry optimization: A_B /BN NT (left panel) where A_h are Al, Ga and In; A_N /BN NT (right panel) where A_h are P, As and Sb. N atoms are shown as blue (dark) balls, while B atoms are shown as pink ones.

Using hybrid exchange–correlation functionals applied within the density functional theory (DFT), the following extrinsic isoelectronic substitutional impurities in BN NTs (Fig.7) have been calculated: Al_B , P_N , Ga_B , As_N , In_B , and Sb_N as they may produce a strong effect in the luminescence spectra of nanostructured BN.

Extrinsic substitutional impurities in the TiO₂ NTS and SrTiO₃ NTs (Fig. 8) for further *ab initio* calculations have been chosen C_O , N_O , S_O , and Fe_{Ti} since they essentially enhance photocatalytic activity of both nanotube types. The calculated variations in the formation energies

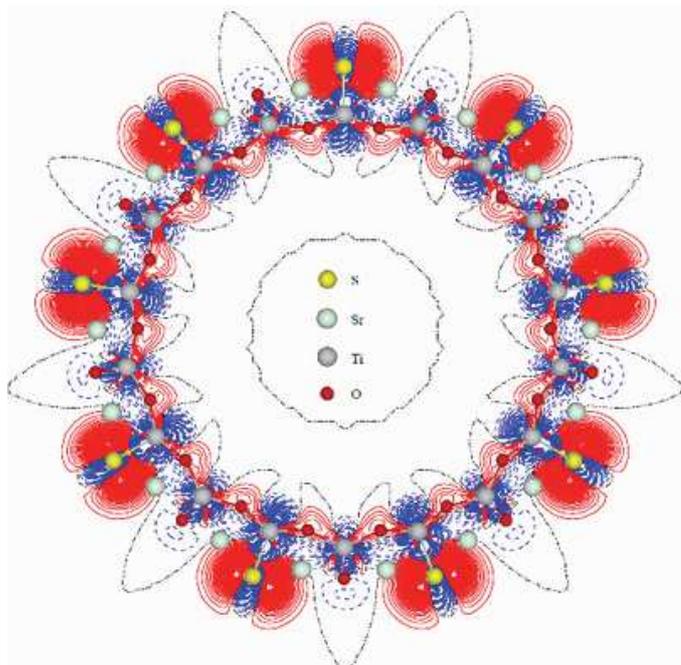


Figure 8. 2D difference electron-density plots projected onto the section planes across SrTiO_3 nanotube containing an impurity defect $\text{C}_0/\text{SrTiO}_3$ NT. Ti are shown as gray balls, O as red (dark gray) balls, Sr as green (gray), substitution impurity atoms (Ah) are shown in yellow (light gray). Atoms that are positioned outside the crossing plane are shown in dimmed colors. Dash-dotted (black online) isolines correspond to the zero level. Solid (red) and dashed (blue) isolines describe positive and negative values of the difference in electron density, respectively.

obtained for equilibrium defective nanostructures allow one to predict the most stable compositions, irrespective of the changes in growth conditions. Calculated charge-density maps (Fig. 8) of the different tubular nanostructures containing extrinsic substitutional impurity atoms highlighted changes in the charge distribution caused by doping. This means that the increased covalency in defect-host atom bonds may lead to an enhancement of adsorption properties. This would imply that defective NTs can be used in gas-sensing devices. On the basis of the performed first-principles calculations, one may conclude that the presence of isoelectronic impurities significantly affects the band structure of the NTs under study, which must be taken into account when constructing nanoelectronic devices based on these NTs. All the mentioned effects can be observed by optical and photoelectron spectroscopy methods, as well as by measuring the electrical properties of the NTs. Midgap levels positioned inside the optical bandgap of defective NTs make them attractive for band gap engineering in, for example, photocatalytic applications.

FORMATION OF Ni NANOCHAINS INSIDE CARBON NANOTUBES: FIRST PRINCIPLES SIMULATIONS

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P.N. D'yachkov

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Moscow, Russia*

S. Bellucci

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Carbon nanotubes with encapsulated monoatomic nanochains of magnetic metals (*e.g.*, Ni) are technologically important one-dimensional (1D) Me@CNT nanostructures fabricated and studied during recent years. Their mechanical, physical and chemical properties can be applied in various nanodevices as well as magnetic data storage and drug delivery platforms. In addition, the CNT walls can provide an effective barrier against oxidation and, thus, ensure long-term stability of the encapsulated metals. Nevertheless, the nanotubes filled with magnetic metals do not always display designed properties because the amount and location of magnetic particles inside the tubes are

difficult to be controlled. To guide reliable fabrication of Me@CNT, it is important to understand the formation mechanism of metal nanochains or separated nanoparticles in nanotubes. Monoatomic chains of nickel atoms encapsulated into single-walled (SW) CNTs of armchair-type (n,n) , $n = 3; 4; 5; 6; 7$ (Fig. 9a) and zigzag-type $(n,0)$, $n = 7; 8; 9; 10; 11$ (Fig. 9b) chiralities have been considered in this study.

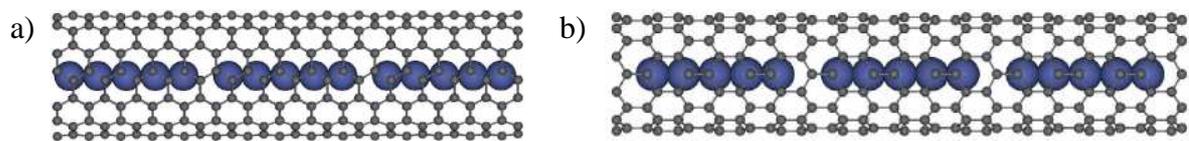


Figure 9. Schematic representation of selected equilibrium structures of Ni nanofilament inside (a) *ac*-CNT (7,7) and (b) *zz*-CNT (10,0) as calculated using PBE functional within the DFT-LCAO formalism. Small gray balls stand for carbon atoms, while large blue (dark gray) ones for nickel atoms.

Nanofilament encapsulation inside CNTs with diameter less than 6 Å (*i.e.*, (5,5) and (7,0) nanotubes of *ac*- and *zz*-chiralities) has been found energetically more favorable, due to stronger interatomic Ni–C bonding, while weakening of Ni–C bond of Ni@CNTs with diameter larger than 6 Å yields an additional freedom for formation of stronger Ni–Ni bonds leading to clusterization of Ni nanofilament (Fig. 9). In all the cases, monoatomic Ni nanochain preserves a ferromagnetic ground state with magnetic moment on Ni as twice as larger than in the Ni bulk (0.62 μB). Enhanced magnetic properties arise mainly from geometry dependent unfilled *d* band and *sp*–*d* hybridization effects typical for transition metal nanofilaments encapsulated inside nanotubes. Carbon nanotubes containing monoatomic Ni nanochains exhibit metallic behavior, even if pristine nanotube is semiconductor (*i.e.*, $(n,0)$ CNTs). Therefore, encapsulation of Ni nanofilament in CNTs is a way to create the highly conductive 1D hybrid nanostructures suitable as interconnects for future nanoelectronic circuits.

ELECTROMAGNETIC PROPERTIES OF CARBON NANOTUBES AND GRAPHENE NANOLAYERS BASED NANOSTRUCTURES FOR NANOSENSOR SYSTEMS

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Fundamental electromagnetic properties of carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) with the essential concentration of ‘dangling bonds’ as well as point defects and functionalized atomic groups of various concentrations are very sensitive to local external perturbations. The induced changes of local electronic density of states lead

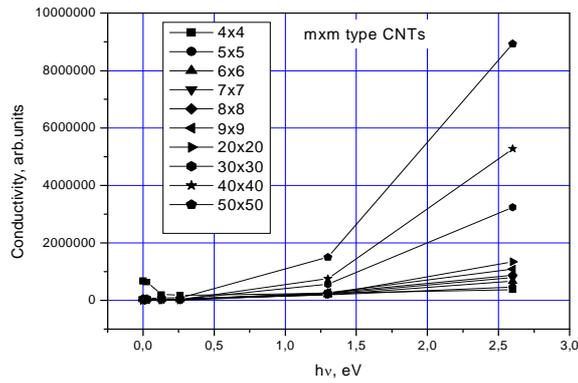


Figure 10. Conductivities of perfect *armchair* SW CNTs of various morphologies. *Note:* The critical frequency of about 0.25 eV corresponds to 60 THz

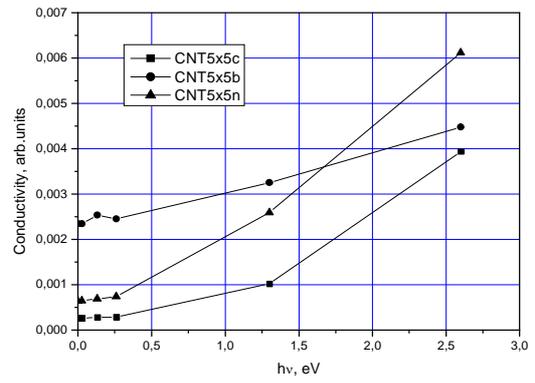


Figure 11. Conductivities of pure perfect and doped (B or N) CNTs in the limit of non-interacting defects.

to the correlated changes of current and spin states. The cluster approach based on the multiple scattering theory combined with effective medium approximation were used to the corresponding model including the dispersion law, electronic density of states, conductivity, *etc.* Multiple scattering problems were solved for nanostructures with radial and axial symmetry. Parametrical numerical simulations of conductivity using the formalism of Kubo-Greenwood were carried out for *zig-zag* ($m,0$), *arm-chair* (m,m) and *chiral* (m,n) CNTs and GNRs. The sensitivity of their conductivity to the local electronic density of states with local impurities (N and B atoms) was demonstrated (Figs. 10 and 11). Both pure CNTs as well as 1D interconnects (CNT-Me and GNR-Me based nanostructures) were found to be fitting for applications in prospective nanosensor devices.

CNT-Fe-Pt INTERCONNECT ELECTROMAGNETIC SIMULATIONS OF MAGNETICALLY STIMULATED CNT GROWTH AS APPLIED FOR NOVEL MEMORY NANODEVICES

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The parametrically controlled production of carbon nanotubes (CNTs) with predefined morphologies is a topical technological problem for modern nanoelectronics. The chemical vapor deposition (CVD) technique for single walled carbon nanotubes (SW CNTs) in the presence of various metal nanoparticle catalysts is generally used now. The application of a magnetically stimulated CVD process scheme and catalyst nanoparticles with a strong magnetism promises additional possibilities for the CVD process management and allows expecting a predictable growth of CNTs with set chiralities and diameters. The main attention is focused on the Pt-Fe nanoparticles effect research. The developed cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as effective medium approximation (EMA-CPA), can be effectively used for modeling of nanosized systems. It allows us to calculate the dispersion law $E(\mathbf{k})$, electronic density of states, conductivity, *etc.* This theoretical approach is used

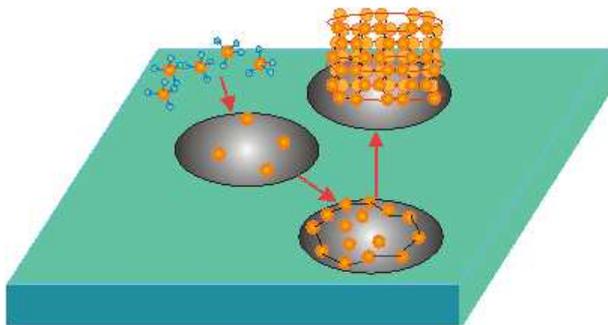


Figure 12. A model of the CVD process of CNT growth upon the catalytic nanoparticle surfaces

in simulations of fundamental electromagnetic properties in Pt-Fe-CNT interconnects, which are responsible for developing CNTs morphologies. The developed model of ‘effective bonds’ and the model of magnetic stimulation for growing CNTs morphologies generated on the Pt-Fe nanoparticle surface are applied for the evaluation of the expected CNT chiralities distribution. The model and conditions controlled magnetically, which stimulate CNT growth in the CVD process, aimed at the predictable SW CNT diameter and chirality and based on Pt-Fe catalyst are discussed. The possibilities of CNT bundle growth upon Fe-Pt nanoparticles for magnetic nanomemory devices are also evaluated.

The formation of the initial optimal perimeter for C-Metal (Fe-Pt) bonds is a synergetic process with a minimal free energy (Fig. 12). The nanoparticle diameter determines with a certain error the diameter of a CNT. The number of effective bonds defines the morphology of the future CNT in terms of growing nanotube chirality. Obviously, there is a considerable uncertainty in CNT morphology, owing to sporadic thermal dynamics of the deposited carbon atoms.

QUANTUM CHEMISTRY CALCULATIONS ON ScF_3 ELECTRONIC STRUCTURE AND LATTICE DYNAMICS

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ScF_3 is a perovskite-type material with a cubic ReO_3 -type structure (space group Pm-3m). Recently it was found that ScF_3 undergoes strong negative thermal expansion (NTE) over a wide range of temperatures from 10 to 1100 K. In the current activity ScF_3 electronic structure, lattice dynamics, and phonon anharmonicity were studied within the framework of quantum chemistry approaches (LCAO, HF-DFT) using Crystal09 program.

Electronic structure of ScF_3 (band structure, DOS, Mulliken analysis) are calculated for the first time. This study predicts that Sc-F bond has considerable covalent nature, F $2p$ and Sc $3d$ states are hybridized. The band gap obtained in HF-DFT calculations is equal to 8-10 eV and is in excellent agreement with those experimentally observed.

It has been found, that Sc position in the middle of regular ScF_6 octahedron is stable. Grüneisen parameters are calculated and phonon mode anharmonicity are studied in the Γ , X , M , R points of the Brillouin zone. It has been found that all modes investigated are harmonic except soft modes in R and M points. Grüneisen parameters of soft modes and coefficients describing mode’s anharmonic potentials are found to be strongly dependent upon calculation technique used. Simple model that accounts static lattice energy and contribution of oscillator (R soft mode) is capable to describe NTE at low temperatures. This suggests that NTE occurs due to R and M mode softness.

**THEORETICAL AND EXPERIMENTAL MODELING OF MATERIALS
FOR RESISTIVE SWITCHING MEMORIES**

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Fe-doped SrTiO₃ became a model material for a wide class of mixed electronic-ionic conductors. Oxygen vacancies (V_O) and iron impurities in SrTiO₃, as well as their complexes, play a key role in electro-optical applications and non-volatile resistive random access switching memories. For example, the understanding of the relative spatial distribution of Fe ions and V_O is important to explain the formation of the conductive filaments. Recently Fe impurities (substituting B-type cations) and V_O in SrTiO₃ — separated and associated — have been addressed by a number of approaches. We performed detailed study of these defect complexes in a close collaboration with the two German partners: Juelich Research center and Max Planck Institute for Solid State research in Stuttgart.

The combined use of *ab initio* quantum mechanical and x-ray absorption near edge structure (XANES) methods confirms that the oxygen vacancies are located in the first coordination shell of Fe³⁺ ions in the cathod region of electro-colored Fe³⁺-doped SrTiO₃. The binding energy of such a complex is estimated as ~0.4 eV. The lattice distortions obtained in *ab initio* modeling and extended x-ray absorption fine structure (EXAFS) experiments are in a very good agreement (Fig.13). The predicted distortions make a minor effect on a simulated XANES signal, and its shape mainly depends on the presence of V_O in the Fe³⁺ first coordination shell. Additionally, formation of the Fe³⁺ V_O complex leads to disappearance of the phonon frequencies in the range 620—760 cm⁻¹ of the calculated phonon spectrum which could be used for its identification.

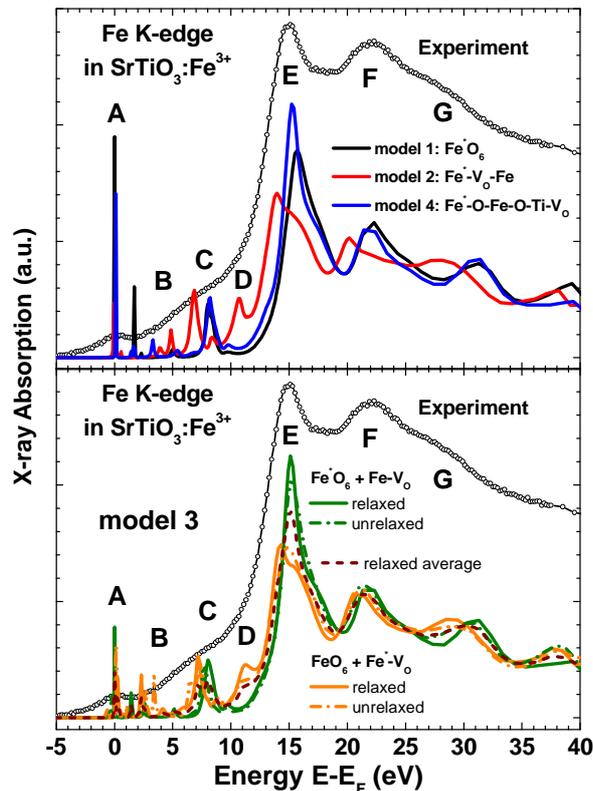


Figure 13. Comparison of the experimental and calculated Fe K-edge XANES spectra. For the model 3 the XANES spectra for the two relaxed (unrelaxed) Fe sites are shown by solid (dash-dotted) lines, and the average XANES spectrum for relaxed structure is shown by dashed line. The zero of energy scale corresponds to the theoretical Fermi level E_F .

MATERIALS FOR SOLID OXIDE FUEL CELLS: *ab initio* STUDY OF OXYGEN DEFECTS IN COMPLEX PEROVSKITES

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(La,Sr)(Co,Fe)O₃ (LSCF) -type perovskite solid solutions are used as mixed conducting SOFC cathode materials and oxygen permeation membranes. In a close collaboration with Max Planck Institute for Solid State Research in Germany and University of Maryland, USA, the formation and migration of oxygen vacancies was studied in detail by means of first principles density functional calculations. Structure distortions, charge redistributions and transition state energies during the oxygen ion migration were obtained and analyzed. Both the overall chemical composition and vacancy formation energy are found to have only small impact on the migration barrier; it is rather the local cation configuration which affects the barrier. The electron charge transfer from the migrating O ion towards the transition metal ion in the transition state is much smaller in LSCF compared to BSCF perovskites where such a charge transfer makes a significant contribution to the low migration barriers observed (in particular for high Ba and Co content).

The oxygen migration occurs via the vacancy mechanism. The oxygen ion passage through the "critical triangle" formed by one B site cation and two A site cations (Fig 14) is the bottleneck; the trajectory is slightly curved away from the B site cation.

In LSCF perovskites, the oxygen vacancy diffusion coefficients were experimentally found to be almost independent upon the cation composition, with a typical migration barrier of 0.8 eV. In contrast, BSCF perovskites exhibit a higher diffusivity with migration barriers as low as 0.5 eV, in particular, for samples with high Ba and Co content. In our calculations we explain how this is related to the peculiarities of the atomic and electronic structure of these two compounds.

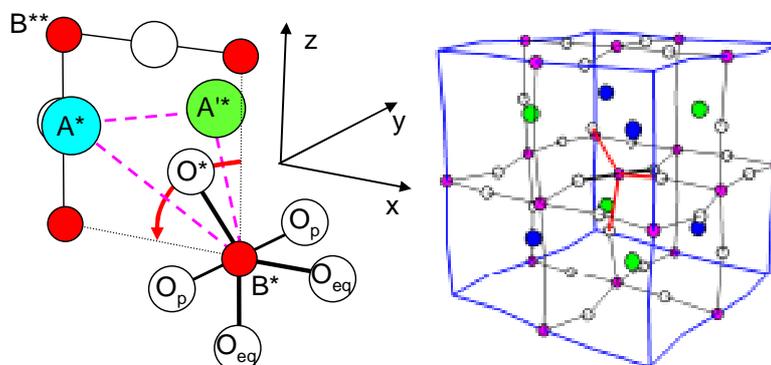


Figure 14. (left) Sketch of the oxygen ion migration path in ABO₃ perovskites through the "critical triangle" formed by one B-site cation B* and two A-site cations A*, A*. (right) The transition state structure distortion for the oxygen migration in LSCF.

Ab initio THERMODYNAMIC STUDY OF PEROVSKITE SOLID SOLUTIONS

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ABO₃-type perovskite solid solutions, e.g. Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-δ} (BSCF), are considered to be promising materials for applications as cathodes of solid oxide fuel cells (SOFC), oxygen permeation membranes and oxygen evolution catalysis. The small oxygen vacancy formation energy characteristic for BSCF leads to high oxygen vacancy concentration, whilst a low oxygen vacancy migration barrier causes the high ionic mobility. These are two key factors leading to fast oxygen exchange of these materials and hence to their potential role in the context of energy conversion. However, a serious disadvantage of BSCF is its intrinsic instability at intermediate temperatures which leads to a slow transformation into a mixture of several phases, including a hexagonal phase with strongly reduced oxygen diffusivity as well as surface exchange rate.

The OSFC cathode performance could strongly depend on the morphology of these materials, remaining a single phase or two-phase mixture. Combining *ab initio* calculations of the atomic and electronic structure of different supercells with thermodynamics of solid solutions, we have constructed and discussed phase diagrams of several important BSCF chemical compositions. It was demonstrated (Fig. 15) that in BSC cobaltite solid solution the spinodal decomposition may occur already at relatively low temperatures, while ferrite (BSF and SCF) solid solutions decompose at relatively high temperatures forming a two-phase system where the coexisting hexagonal and cubic phases significantly differ in fractions of constituents.

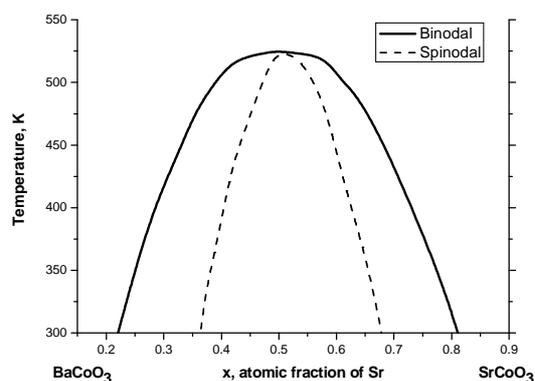


Figure 15. Quasi-binary phase diagram for $\text{Ba}_{1-x}\text{Sr}_x\text{CoO}_3$ solid solution. The solid line is the solubility (binodal) curve, dashed line shows the region of the spinodal decomposition.

AB INITIO CALCULATIONS OF THE ATOMIC AND ELECTRONIC STRUCTURE OF BaZrO_3 AND BaTiO_3 (111) SURFACES AND DEFECTS IN SrF_2

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We performed the calculations of surface relaxations and energetics for the polar (111) surface of BaZrO_3 using a hybrid B3LYP description of exchange and correlation. On the (111) surface, both Zr- and BaO_3 -terminations were analyzed. For both Zr and BaO_3 -terminated BaZrO_3 (111) surfaces upper layer atoms, with the sole exception of BaO_3 -terminated surface Ba atom, relax inwards. The Zr-terminated BaZrO_3 (111) surface second layer Ba atom exhibits the strongest relaxation between all Zr and BaO_3 -terminated BaZrO_3 (111) surface atoms. The calculated surface relaxation energy for Zr-terminated BaZrO_3 (111) surface is almost fifteen times larger than the surface relaxation energy for BaO_3 -terminated BaZrO_3 (111) surface. The surface energy for Zr-terminated BaZrO_3 (111) surface (7.94 eV/cell) is smaller, than the surface energy for BaO_3 -terminated (111) surface (9.33 eV/cell). The calculated BaZrO_3 optical bulk band gap, 4.79 eV is in an excellent agreement with the experimental value, 5.00 eV. The calculated optical band gap for the Zr- and BaO_3 -terminated BaZrO_3 (111) surfaces becomes smaller with respect to the bulk optical band gap [1].

Using a hybrid B3LYP approach, the surface relaxation has been also calculated for the two possible Ti and BaO_3 terminations of BaTiO_3 (111) surface. For both Ti and BaO_3 -terminations of (111) surface, the upper layer atoms relax inwards. The second layer atoms, with the sole exception of Ti-terminated BaTiO_3 (111) surface Ba atom, relax outwards. The calculated surface relaxation energy for Ti-terminated BaTiO_3 (111) surface is more than two times larger than the surface relaxation energy for BaO_3 -terminated BaTiO_3 (111) surface. The surface energy for Ti-terminated BaTiO_3 (111) surface (7.28 eV/cell) is smaller, than the surface energy for BaO_3 -terminated (111) surface (8.40 eV/cell)

AB INITIO SIMULATIONS OF POINT DEFECTS (VACANCIES) AND ATOM SUBSTITUTES (O AND Y) IN fcc-Fe LATTICE

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V.A. Borodin

To understand the mechanism of ODS particle formation in EUROFER steels, we simulated various equilibrium configurations of Y, O impurity atoms and Fe vacancies in steel matrix as well as their interactions and internal migration trajectories. At the first stage of this modeling, *ab initio* spin-frozen calculations using DFT-PW method with PW91 non-local Hamiltonian (as implemented in VASP code) have been performed on the lattice of high-temperature paramagnetic *fcc*-Fe phase.

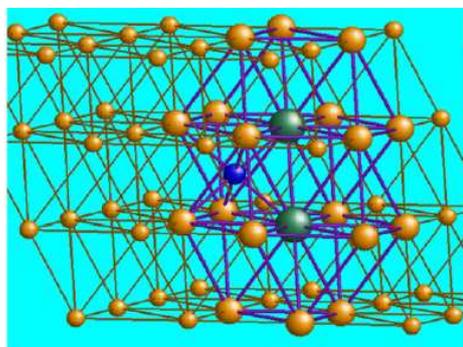


Figure 16. Supercell (SC) of γ -Fe crystal with two Y substitute and one O impurity atoms in the 1st nearest neighbor positions.

Fig. 16 shows its $3 \times 3 \times 3$ supercell with 2 Y substitute atoms located in the adjacent regular lattice sites and one O atom positioned in the nearest octahedral interstitial site. Our main interest was focused on: (i) interaction energies between the defects and (ii) defect migration energies as these data are then used as calculation parameters at the second stage of modeling when performing the lattice kinetic Monte-Carlo (LKMC) simulations of Y_2O_3 nanocluster growth in *fcc*-Fe crystal with various cluster configurations.

Our previous calculations showed an important role of the vacancies in the formation of the Y_2O_3 nanoclusters. To reduce both the defect concentration and interactions between periodic images of defects it has been necessary to increase the supercell size. Since $3 \times 3 \times 3$ supercell did not provide yet satisfactory results of calculations on point defects, majority of previous calculations were performed for $4 \times 4 \times 4$ *fcc*-Fe supercells. The last test calculations have been performed on perfect *fcc*-Fe lattice, to assess the minimum *k*-point mesh and cut-off energies required in order to achieve plausible results. To calculate the dependence of the results on the *k*-points mesh, the latter has been varied from $4 \times 4 \times 4$ up to $9 \times 9 \times 9$ and the cut-off energy has been fixed at 800 eV.

Our calculations clearly show that at least $7 \times 7 \times 7$ *k*-point mesh is required to perform the calculations on the lattice composed from $5 \times 5 \times 5$ supercells, application of which for point defect calculations provides more realistic results as compared to those obtained for $4 \times 4 \times 4$ supercells as calculated previously. Due to dependence of a number of obtained results on the cut-off energy parameter as established in previous calculations, $7 \times 7 \times 7$ *k*-point mesh has been chosen and the cut-off energy has been varied from 700 to 800 eV.

As the results of $5 \times 5 \times 5$ SC calculations reproduced both qualitatively and semi-quantitatively the results received for $4 \times 4 \times 4$ SC, further variation of cut-off energy has not been required and the cut-off energy value of 800 eV has been used in further calculations since it was found to be optimal previously. It has been also necessary to

perform the calculations of point defects in *fcc*-Fe lattice, in order to check if those results received in the calculations of $4 \times 4 \times 4$ supercell are reproducible within $5 \times 5 \times 5$ SC. In order to do this, the binding energies received within the calculations of $4 \times 4 \times 4$ and $5 \times 5 \times 5$ SCs between Y and vacancy have been compared. The corresponding results are present in Table 1 which clearly shows that the absolute values of E_{bind} between defects slightly decrease with SC increase which could be explained by the decreased influence of defect periodic images.

Table 1. Bonding in Y_{Fe} - V_{Fe} pairs in γ -Fe

Supercell	$4 \times 4 \times 4$	$5 \times 5 \times 5$
Configuration	E_{bind} , eV*	E_{bind} , eV*
1-NN	1.67	1.42
2-NN	-0.21	-0.07
3-NN	0.30	0.14
4-NN	0.40	0.30

*binding energies

**AB INITIO SIMULATIONS OF POINT DEFECTS (VACANCIES) AND ATOM
SUBSTITUTES (O AND Y) IN *bcc*-Fe LATTICE**

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Due to essential mismatch between the structures of Y_2O_3 (bixbyite phase) and α -Fe, yttrium solute atoms have to be stabilized in the iron matrix by vacancies. Then vacancies could be healed by oxygen atoms, creating the bixbyite type of Y-O bonds. Since *bcc*-phase of iron is stable in a wide interval of temperatures and displays ferromagnetic properties, *ab initio* supercell calculations on pure and defective α -Fe have been performed in spin-polarized regime using the same DFT-PW approach as for γ -Fe and applying the non-local PBE exchange-correlation functional. The first stage of *ab initio* simulations on α -Fe has included possibilities of vacancy cluster creation in the corresponding lattice which stabilizes implementation of impurity atoms in the iron bulk. Atomic radius of Y atom is larger than that of Fe atom (0.18 and 0.14 nm respectively), which creates a strong repulsion between them inside an iron matrix.

On the other hand, impurity Y atom can stably exist in iron lattice as a substitute only (Y_{Fe}). The repulsion between the two Y_{Fe} atoms could be reduced by creation of Fe vacancies. In *bcc* iron lattice, V_{Fe} vacancies can segregate, forming stable clusters (Tables 2, 3). Stabilization of Y impurity atom inside iron lattice could require more than one vacancy *per* solute atom. In such a case, not only substitute Y_{Fe} atom is stable but also yttrium atom located in interstitial sites (Y_i).

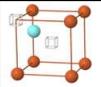
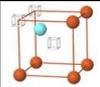
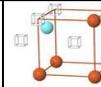
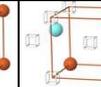
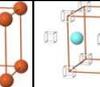
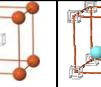
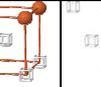
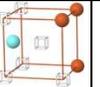
Table 2. Binding energies of multiple vacancies (V_{Fe})_N inside α -Fe lattice (as shown in Table 3).

N	1	2	3	4	5	6	7	8	9
$E_{bind}(N)$, eV	0.	0.23	0.65	1.38	2.19	3.18	2.94	4.23	5.34

Size of vacancy cluster in the *bcc*-Fe lattice has been varied from one to nine vacancies in the $4 \times 4 \times 4$ supercell (Table 3). It has been shown that a growth of vacancy

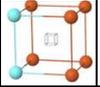
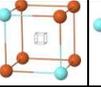
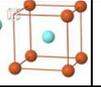
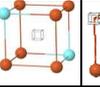
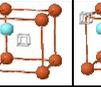
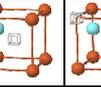
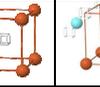
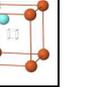
cluster is energetically favorable (Table 2). However, adding one more vacancy to the cluster of six vacancies requires, at least, 0.24 eV. So, clusters of six vacancies could be quite common defects in α -Fe matrix. Analogous calculations have been repeated for a single Y solute atom incorporated in different vacancy clusters (Table 3). As the reference energies, there are used isolated vacancies and isolated Y_{Fe} . In all the configurations, Y atom is positioned in the middle of vacancy cluster and all the corresponding defect complexes have been found energetically stable. As in the case of pure vacancy clusters (Table 2), incorporation of additional vacancy to the cluster containing Y_i atom and six vacancies in octahedral coordination around it (Table 3) is energetically unfavourable. Although the complex of Y_{Fe} atom and eight vacancies in cubic coordination around it has been found to be stable too, the binding energy for this configuration is smaller, than that for clusters containing six and eight vacancies with interstitial Y_i .

Table 3. Binding energy of single solute Y atom in vacancy clusters inside α -Fe lattice.

models								
N	2	3	4	5	6	7	8	8
$E_{bind}(N)$, eV	1.355	2.887	4.893	6.021	7.386	5.579	7.956	7.123

Calculations performed in order to estimate pair-wise Y-Y interaction in different positions of a single vacancy show a weak attraction of ~ 0.1 eV for impurity atoms at 2NN and 3NN distances (Table 4). For 5NN Y-Y distance along the direction [111], the interaction of -0.13 eV is repulsive. Other interactions at close inter-defect distances are

Table 4. Interactions of Y_{Fe} - Y_{Fe} pair with V_{Fe} (NN=1-3), Eq. as well as a single solute Y atom with either a pair of vacancies (NN=4-6), or the V_{Fe} - Y_i - V_{Fe} complex (NN=2) inside α -Fe lattice.

models								
NN distance	1	2	3	3	4	5	6	2
E_{bind} , eV	0.30	1.03	0.27	1.16	0.01	-0.13	-0.04	1.3

negligible small. Interaction of a single solute atom Y_{Fe} with the V_{Fe} - Y_i - V_{Fe} complex at different distances has been calculated (Table 4). At the distances of the 3NN and smaller, Y_{Fe} transforms V_{Fe} - Y_i - V_{Fe} complex into Y_{Fe} - V_{Fe} - Y_{Fe} configuration. The strongest attraction has been observed for the defect aligned along the [111] direction. Starting from the 4NN the interaction becomes weaker and does not exceed 0.15 eV. Interaction between the two V- Y_i -V complexes is attractive too. At three closest distances, without overlapping vacancies, binding energy between the complexes is about 1.3-1.4 eV. Thus, V_{Fe} can segregate, creating stable clusters, while Y impurity atoms can be stabilized by vacancies.

KINETICS OF PROCESSES WITH SELF-ORGANIZATION

THEORY OF NON-EQUILIBRIUM CRITICAL PHENOMENA IN THREE-DIMENSIONAL CONDENSED SYSTEMS OF CHARGED MOBILE NANOPARTICLES

V.N. Kuzovkov, G. Zvejnieks, E.A. Kotomin

A study of 3d electrostatic self-assembly (SA) in systems of charged nanoparticles (NP) is one of the most difficult theoretical problems. In particular, the limiting case of negligible or very low polar media (*e.g.*, salt) concentration, where the long-range NPs interactions cannot be reduced to commonly used effective short-range (Yukawa) potentials, remains unstudied. Moreover, the present study has demonstrated that unlike the Debye-Hückel theory, a complete screening of the charges in SA kinetics is not always possible. Generally speaking, one has to take into account implicitly how each NP interacts

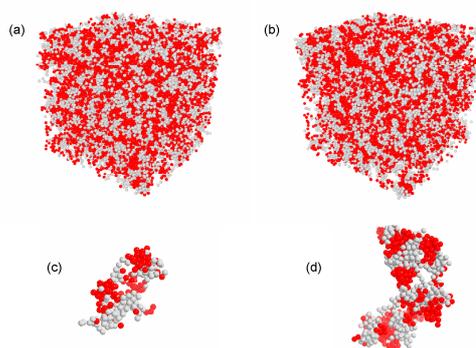


Figure 17. Characteristic 3d structure snapshots obtained using the RMC: (a,b) corresponds to two different times, whereas (c,d) show the maximal domain for snapshots (a,b).

with all other NPs (the true long-range interactions). Traditional theoretical methods allow us to monitor such the electrostatic 3d system kinetics only at very short times, which is far from sufficient for the understanding the dynamic SA. Combining an integrated analytical approach (nonlinear integro-differential kinetic equation for correlation functions) and reverse Monte Carlo in 3d case, we have obtained the self-consistent solution of this challenging problem (Fig. 17). We demonstrate, in particular, the existence of critical points and critical phenomena in the non-equilibrium kinetics in a 3d system of oppositely charged mobile NPs.

KINETIC MONTE CARLO MODELING OF REACTION-INDUCED PHASE SEPARATION IN Au/Ni(111) SURFACE ALLOY

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Kinetic Monte Carlo (KMC) simulations of Au–Ni phase separation in Au/Ni(111) surface alloy during nickel carbonyl formation reaction were performed at room temperature by taking into account realistic rates of Au and Ni adatom diffusion and CO adsorption and desorption, while keeping the rate of nickel carbonyl formation reaction as a free parameter. We also obtained pair and three-body interaction constants

between Au and Ni adatoms using the ab initio calculations and demonstrated that their proper choice is crucial for understanding the Au–Ni separation process.

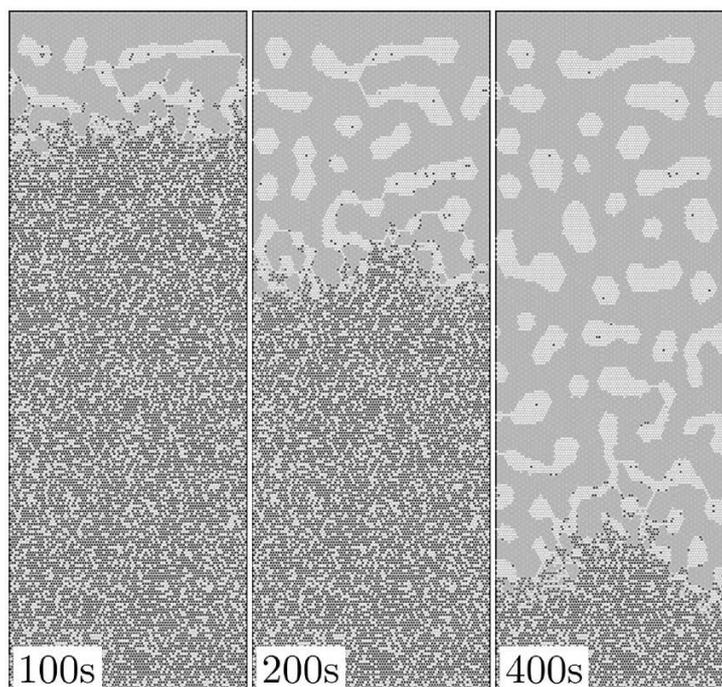


Figure 18. Snapshots of the Au/Ni(111) surface alloy instability kinetics computer simulation. Black, white and gray dots mark top monolayer Ni, Au adatoms and CO molecules, respectively. The reaction front moves from top to bottom.

Three regimes with qualitatively different Ni–CO reaction propagation kinetics in Au/Ni(111) surface alloy were found by varying the constants of trio-triangle interactions within the limits of their accuracy. The sensitivity of the proposed model to interaction parameters leads to the regimes that differ by step flow rate, Au islands formation mechanism(channel-type or homogenous flow), Au island contamination level by Ni impurities and reaction damping tendency at the reaction front. Nucleation of nickel-free Au islands was observed for a homogeneous step flow pattern, and the corresponding step flow rate is in a good quantitative agreement with existing experimental data.

ON PROPERTIES OF ELECTRON-HOLE PAIRS IN DIELECTRICS

E. Klotins

The electron-hole pair is a central concept addressed to problems of advanced materials and, generally, comprising both the fundamental questions and applications in optics. A guiding principle in the theoretical description is to identify a system as an effective vacuum with the electrons and holes as elementary excitations of that vacuum. In these terms the first goal is how to describe the ground state of the system and, then, the excited states playing a central role in determining the measurable quantities of the light-matter interaction.

Two basic approaches are considered with emphasis on their conceptual background and mathematical techniques. The first is the semiconductor-light Hamiltonian (SC) approach, where the system with well separated bands is excited by a classic electromagnetic field in the RWA approximation. This allows a connection of the

creation-annihilation operators for electrons and holes with the exciton operators as the single entities constituting in this way an effective single-particle theory for electron-hole pairs, excitons and their interactions. Restrictions of the SC approach appear in strong field nonlinear and non-adiabatic effects that are fundamental and cannot be abandoned within the existing RWA and the subsequent perturbation approaches. Within the conceptual level the SC approach is based on the Schrödinger's equation with is not Lorentz covariant, and therefore excludes applications where the relativistic effects are essential.

In contrast, the quantum electrodynamics formalism for electron-hole pairs represents a soluble case, i.e. a model resembling the Diracs picture for a two-band dielectric. The excitation of electron-hole pairs is quantified as a Klein-Gordon field, with input entities supported by SC type calculations, namely, dispersion relations for the electron and hole, the band gap between valence and conduction bands as well as symmetry properties of the Brillouin zone.

The rationale find from these prototypic approaches is a kinetic theory based on dynamical foundation. It allows to calculate non-equilibrium distribution function and the relevant physical quantities far from equilibrium. A problem non resolved yet is generalization of this Klein-Gordon formalism to more complicated fermion-fermion interactions and inclusion of electron-phonon interaction as highly motivated subjects in the future work.

PLASMA PHYSICS

RMP ELM SUPPRESSION ANALYSIS BY MEANS OF LOW-DIMENSIONAL MODEL SYSTEM FOR QUASI-PERIODIC PLASMA PERTURBATIONS

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Edge localized modes (ELM) are a significant concern in magnetically confined toroidal fusion plasmas because they can rapidly erode plasma facing material surfaces, cause edge melting and surface cracking. They also reduce the coupling efficiency of rf antennas and trigger other MHD instabilities. The importance of ELM control was realized many years ago and different means of their control were developed. ELM suppression/control is required for a steady state operation of the International Thermonuclear Experimental Reactor (ITER). The natural ELM frequency should be decreased by a factor ~ 30 . Two main control strategies are foreseen for ITER: 1) injection of small deuterium pellets, 2) resonant magnetic perturbations (RMP). We investigate possible mechanisms of RMP ELM suppression in a low-dimensional model system for quasi-periodic plasma perturbations.

EFFECT OF ELECTRON BEAM MISALIGNMENTS ON GIROTRON EFFICIENCY

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The theory describing the operation of gyrotrons with tilted and shifted electron beams has been developed. Effects of the tilt and shift are studied for a 1 MW, 170 GHz gyrotron,

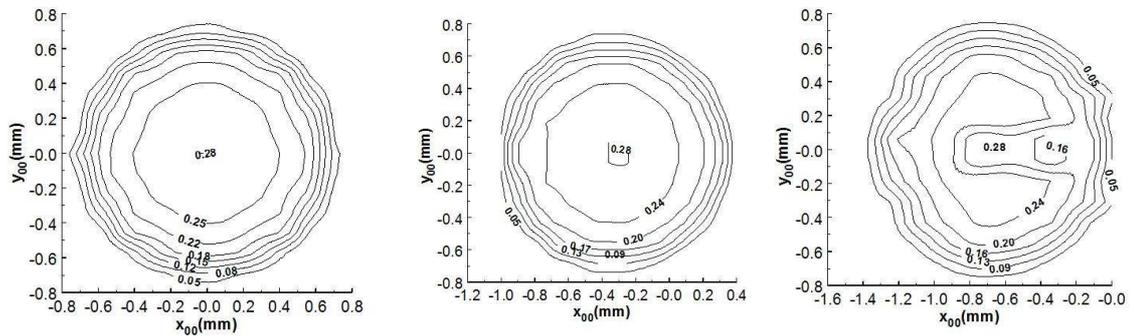


Figure 19. Efficiency as a function of transverse coordinates in the cases of (a) parallel displacement, (b) a tilt angle 0.5° and (c) a tilt angle 1° .

which is presently under development in Europe for electron cyclotron resonance plasma heating and current drive in the ITER. It is shown that one should expect significant deterioration of gyrotron operation in such gyrotrons when the tilt angle exceeds $0.4\text{-}0.5^\circ$ and the parallel shift of the beam axis with respect to the axis of a microwave circuit is larger than $0.4\text{-}0.5$ mm. At the same time, simultaneous tilting and shifting in a proper manner can mitigate this deteriorating effect.

EXPERIMENTAL STUDIES

COMPARATIVE STUDY OF LUMINESCENCE PROPERTIES OF MACRO- AND NANOCRYSTALLINE MgO USING SYNCHROTRON RADIATION

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Wide band-gap MgO ($E_g = 7.8$ eV) continues to attract great attention due to its fundamental interest and applications. The goal of the present study was to compare the luminescent properties of nanocrystalline MgO which was prepared by the extractive-pyrolytic method with macrocrystalline powder analogues and a single crystal. Special attention was paid to VUV spectral range, which is not reachable with commonly lamp and laser sources used. The SUPERLUMI facility of HASYLAB at DESY was used for the measurements of emission and excitation spectra.

Fig. 20 shows the excitation luminescence spectra for all these three samples measured at 2.95 eV (420 nm) in spectral range 4.5–10.0 eV. Two definite conclusions can be drawn here, namely: (a) In both macropowder and single crystal sample, the well-known 5.7 eV excitation band caused by deformation-induced defects/vacancy complexes is revealed. The appropriate peak for nanoparticle samples reveals blue shift

at about 0.3 eV, which could be connected with the nano-size of particles. (b) The excitation spectra for both macro- and nano-particle samples show the clear shoulder at about 5.0 eV, where the both F and F^+ centers have their optical absorption with peak essentially at the same energy of ~ 5.0 eV, while such feature is absent at all in the case of single crystals. (c) in the case of MgO single crystal, the exciton peak is quite well resolved, while in the case of macro and nano powder materials, its exact position is not easy to determine.

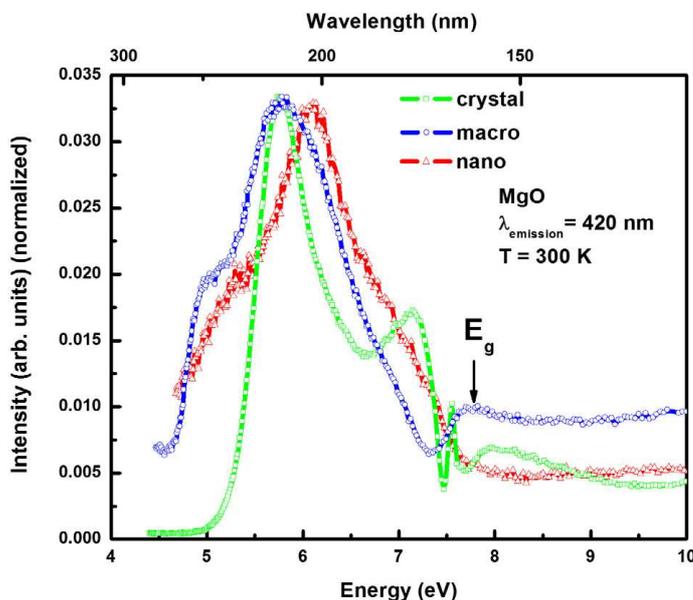


Figure 20. MgO excitation spectra for nano- and macro-samples.

BiI₃ NANOCCLUSERS IN MELT-GROWN CdI₂ CRYSTALS STUDIED BY OPTICAL ABSORPTION SPECTROSCOPY

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Cadmium iodide (CdI₂) is a well known layered-structure compound. Both pure and doped CdI₂ crystals have demonstrated several potentially attractive applications as scintillator and photochromic materials, candidate materials for memory elements, electroplating and lithography.

We studied optical absorption of CdI₂ crystals doped by BiI₃ (1 mol %) in the temperature range of 77–300 K. Complex structure of the optical absorption spectra of these crystals was discussed with the particular focus on clusters contribution to the optical properties of the investigated material.

The main absorption, observed in these crystals at 2.59 eV is related to quantum confined exciton absorption of bimolecular BiI₃ cluster. BiI₃ centers that are formed by substitution of three Cd²⁺ ions for two Bi³⁺ ions. Considering the spectral shift of this peak in CdI₂–BiI₃ with respect to the bulk BiI₃, the radius of the bimolecular cluster of BiI₃ ($R \approx 14$ Å) has been roughly estimated. Bands peaked at higher energies (found in thin samples) are attributed to higher energy states of an exciton confined within the BiI₃ cluster. The possible origin of long-wavelength absorption peaks could be attributed to larger clusters, as shown in the following Table:

Peak position, eV	Width (eV)	Origin
1.94	0.11	6- (or more) molecules BiI ₃ clusters
2.06	0.19	4-molecules BiI ₃ clusters and
2.38	0.38	4-molecules BiI ₃ clusters
2.59	0.44	Bimolecular BiI ₃ clusters
2.84	0.18	?
3.03	0.20	?
3.27	0.22	?

LUMINESCENCE AND ULTRAVIOLET EXCITATION SPECTROSCOPY SrI₂ AND SrI₂:Eu²⁺

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In the renewed search for high resolution γ -ray scintillators within the last decade, improved SrI₂ crystals grown by the Bridgeman technique were found to have exceptional light yield of about 90,000 photons/MeV.

We report measurements of luminescence and its ultraviolet excitation spectra in SrI₂ and SrI₂:Eu²⁺ at temperatures of 10 and 300 K. Excitation spectroscopy technique using synchrotron radiation (SUPERLUMI facility of HASYLAB at DESY) was applied.

Excitonic properties in nominally pure and europium doped crystals have been studied. Special attention is focused on determining the exciton energy ($5.12 \text{ eV} \pm 0.1 \text{ eV}$ at RT) and its temperature shift (namely, thermal peak shift of the 1s exciton in SrI₂ from 10 K to 300 to be about 0.35 eV) from features of the excitation spectra, on observation of a broadened Eu emission band attributed to trace Eu associated with oxygen in nominally undoped crystals, and on adding observations concerning the 3.4 eV band at low temperature attributed to the self-trapped exciton.

Defence of Master Science Thesis

MSc Thesis-- A. Sorokin „First principles thermodynamic calculations on Al-doped ZnO“ was successfully defended in the end of May, 2013, at the University of Latvia.

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1. D. Fuks, **Yu. Mastrikov**, **E.A. Kotomin**, and J. Maier, *Ab initio* thermodynamic study of (Ba,Sr)(Co,Fe)O₃ perovskite solid solutions for fuel cell applications. - J. Mater. Chem. A, 2013, **1**, p. 14320–14328.
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3. **D. Gryaznov**, E. Blokhin, **A. Sorokin**, **E.A. Kotomin**, R.A. Evarestov, A. Bussmann-Holder, and J. Maier, A comparative *ab initio* thermodynamic study of oxygen vacancies in ZnO and SrTiO₃: emphasis on phonon contribution. - J. Phys. Chem. C, 2013, **117**, p. 13776–13784.
4. M.M. Kuklja, **E.A. Kotomin**, R. Merkle, **Yu.A. Mastrikov**, and J. Maier, Combined theoretical and experimental analysis of processes determining cathode performance in solid oxide fuel cells. - Phys. Chem. Chem. Phys., 2013, **15**, p. 5443-5471.
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8. A. Weizman, D. Fuks, **E.A. Kotomin**, and **D. Gryaznov**, *Ab initio* study of phase competition in (La_{1-c},Sr_c)CoO₃ solid solutions. - Solid State Ionics, 2013, **230**, p. 32–36.
9. M.M. Kuklja, **Yu.A. Mastrikov**, B. Jansang, and **E.A. Kotomin**, First principles calculations of (Ba,Sr)(Co,Fe)O_{3-δ} structural stability. - Solid State Ionics, 2013, **230**, p. 21–26.
10. **R.I. Eglitis**, *Ab initio* calculations of the atomic and electronic structure of BaZrO₃(111) surfaces. - Solid State Ionics, 2013, **230**, p. 43-47.
11. H. Shi, L. Chang, R. Jia, and **R.I. Eglitis**, *Ab initio* calculations for the *F*-center transfer and *R* centers in SrF₂. - Comput. Mater. Sci., 2013, **79**, p. 527-533.
12. R. Jia, Z. Yi, C. Liu, H. Shi, H. Zhang, and **R.I. Eglitis**, First principles studies of the self trapped hole and the fluorine adsorption on the SrF₂ (111) surface. - Comput. Mater. Sci., 2013, **73**, p. 9-14.
13. R.A. Evarestov and **Yu.F. Zhukovskii**, Four-faceted nanowires generated from densely-packed TiO₂ rutile surfaces: *Ab initio* calculations. - Surf. Sci., 2013, **608**, p. 226–240.
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17. **A.I. Popov**, L. Shirmane, V. Pankratov, A. Lushchik, A. Kotlov, V.E. Serga, L.D. Kulikova, G. Chikvaidze, and J. Zimmermann, Comparative study of the luminescence properties of macro- and nanocrystalline MgO using synchrotron radiation. - Nucl. Instr. Meth. B, 2013, **310**, p. 23-26.
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19. **R.I. Eglitis**, *Ab initio* calculations of BaTiO₃(111) surfaces. - Phase Transitions, 2013, **86**, p. 1115 - 1120.
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25. **O. Dumbrajs** and G.S. Nusinovich Effect of electron beam misalignments on the gyrotron efficiency.-- Phys. Plasmas **20**, 073105 (2013).

Non-SCI papers

1. O. Dumbrajs, Žirotrons - megavatu mikroviļņu avots kodolplazmas uzkaršēšanai. - Enerģija un pasaule, 2013, 2, p. 74-78.
2. S. Piskunov, J. Kazerovskis, Yu.F. Zhukovskii, P.N. Dyachkov, and S. Bellucci, Incorporation of Ni nanofilament inside carbon nanotubes: DFT calculations. - Proc. Intern. Conf. „Physics, Chemistry and Application of Nanostructures (Nanomeeting-2013, Minsk, Belarus)” (Eds. V.E. Borisenko, S.V. Gaponenko, V.S. Gurin, and C.H. Kam; World Scientific, New Jersey, London, Singapore), 2013, p. 139-142.

3. Yu.N. Shunin, V.I. Gopeyenko, N. Burlutskaya, T. Lobanova-Shunina, and S. Bellucci, Electromagnetic properties of CNTs and GNRs based nanostructures for nanosensor systems. - Proc. Intern. Conf. „Physics, Chemistry and Application of Nanostructures (Nanomeeting-2013, Minsk, Belarus)” (Eds. V.E. Borisenko, S.V. Gaponenko, V.S. Gurin, and C.H. Kam; World Scientific, New Jersey, London, Singapore), 2013, p. 250-253.
4. Yu.F. Zhukovskii, S. Piskunov, O. Lisovski, and J. Begens, First principles simulations on doped TiO₂ and SrTiO₃ nanotubular photocatalysts for water-splitting hydrogen generation. - Proc. Intern. Conf. „Physics, Chemistry and Application of Nanostructures (Nanomeeting-2013, Minsk, Belarus)” (Eds. V.E. Borisenko, S.V. Gaponenko, V.S. Gurin, and C.H. Kam; World Scientific, New Jersey, London, Singapore), 2013, p. 513-516

Chapters in Scientific Books

E.A. Kotomin, R. Merkle, **Yu.A. Mastrikov**, M.M. Kuklja, and J. Maier, Energy Conversion: Solid Oxide Fuel Cells. First-Principles Modeling of Elementary Processes. - Chapter 6 in book: *Computational Approaches to Energy Materials* (eds. A.Walsch, A. Sokol, C.R.A. Catlow, Wiley), 2013, p. 149-186.

PRESENTATIONS AT SCIENTIFIC CONFERENCES, CONGRESSES, MEETINGS, SCHOOLS AND WORKSHOPS

I. 29th ISSP Conference (Riga, Latvia, February, 2013).

1. D. Constantinescu, **O. Dumbrajs**, V. Igochine, K. Lackner, H. Zohm, and ASDEX Upgrade team, "Edge localized mode suppression by means of resonant magnetic perturbations". Abstracts: p. 23.
2. **J. Begens**, **S. Piskunov**, and **Yu.F. Zhukovskii**, "Quantum chemical simulations of doped SrTiO₃ nanotubes for application in photocatalytic reactions". Abstracts: p. 25.
3. A. Anspoks, **D. Bocharov**, J. Purans, F. Rocca, and V.A. Trepakov, "Local structure analysis of SrTiO₃ and SrTi¹⁸O₃ by X-ray absorption spectroscopy". Abstracts: p. 34.
4. **A. Sorokin**, **Yu.F. Zhukovskii**, **D. Gryaznov**, J. Purans, and **E.A. Kotomin**, "Temperature dependence of thermodynamic properties of oxygen vacancies in ZnO: first-principle calculations". Abstracts: p. 35.
5. **J. Kazerovskis**, **S. Piskunov**, and **Yu.F. Zhukovskii**, "Atomic and electronic properties of Ni nanofilament encapsulated inside single-walled nanotubes of different chiralities". Abstracts: p. 36.
6. **R.I. Eglitis**, H. Shi, R. Jia, and L. Chang, "First-principles calculations of hydroxyl impurities in CaF₂ and BaF₂ crystals". Abstracts: p. 55.
7. **A. Gopejenko**, **Yu.F. Zhukovskii**, P.V. Vladimirov, **E.A. Kotomin**, **Yu..A. Mastrikov**, and A. Möslang, "Ab initio calculations of Y and vacancies interactions in fcc Fe lattice". Abstracts: p. 61.
8. A. Anspoks, **D. Bocharov**, J. Purans, F. Rocca, A. Sharakovskis, and V.A. Trepakov, "X-ray absorption spectroscopy and second harmonic generation analysis of SrTi¹⁸O₃". Abstracts: p. 85.
9. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V. Gopeyenko, T. Lobanova-Shunina, N. Burlutskaya, and S.Bellucci, "GNRs and CNTs based nanosensor systems modelling". Abstracts: p. 103.

II. 47th Russian School on Condensed State Physics (St. Petersburg, Russia, March, 2013).

10. P. Zhgun, **D. Bocharov**, **S. Piskunov**, A. Kuzmin, and J. Purans, "Quantum chemistry calculations on ScF₃ electronic structure and lattice dynamics". Abstracts: p. 65.

III. 10th Symposium on Fuel Cell as well as Battery Modelling and Experimental Validation (ModVal-10) (Bad Boll, Germany, March, 2013).

11. R. Merkle, L. Wang, **Yu.A. Mastrikov**, **E.A. Kotomin**, M.M. Kuklja, and J. Maier, "Oxygen exchange mechanism on mixed conducting perovskites: insight from experiment and theory." - Abstracts: p. 37.

IV. 11th International Conference "Information Technologies and Management", IT&M'2013 (Riga, Latvia, April, 2013).

12. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V.I. Gopeyenko, T. Lobanova-Shunina, N. Burlutskaya, and S. Bellucci, "Carbon-based nanosensor systems: modelling and technology". Abstracts: p. 17-18.

13. **J. Kazerovskis**, **S. Piskunov**, and **Yu.F. Zhukovskii**, "First principles simulations on Ni nanofilaments incorporated in carbon nanotubes". Abstracts: p. 53.

14. **Yu.F. Zhukovskii**, **S. Piskunov**, **O. Lisovski**, and **J. Begens**, "Doped TiO₂ and SrTiO₃ nanotubular photocatalysts for water-splitting hydrogen generation: First principles simulations". Abstracts: p. 80-82.

15. **S. Piskunov** and **Yu.F. Zhukovskii**, "BN nanotubes doped by Al, P, Ga, As, In, and Sb: Predictions from first principles". Abstracts: p. 110-111.

16. **A. Gopejenko**, **Yu.F. Zhukovskii**, P.V. Vladimirov, **E.A. Kotomin**, **Yu.A. Mastrikov**, and A. Möslang, "First principles modeling of interactions between Y, O and vacancies in fcc-Fe lattice". Abstracts: p. 112-114.

V. 9th International Conference "Functional Materials and Nanotechnologies" FM&NT-2013 (Tartu, Estonia, April, 2013).

17. **A.I. Popov** and G.J. McIntyre, "Photostimulable storage phosphors and image-plate development for neutron imaging". – Abstract: OR-11.

18. A. Anspoks, **D. Bocharov**, J. Purans, F. Rocca, A. Sarakovskis, V.A. Trepakov, A. Dejneka, and M. Itoh, "Local structure studies of SrTi¹⁶O₃ and SrTi¹⁸O₃." – Abstract: OR-15.

19. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V.I. Gopeyenko, N. Burlutskaya, T. Lobanova-Shunina, and S. Bellucci, "Electromagnetic properties of interconnects in nanodevices based on CNT, GNR and graphene aerogels." – Abstract: OR-28.

20. **G. Zvejnieks**, **P. Merzlyakov**, **V.N. Kuzovkov**, and **E.A. Kotomin**, "Cellular automata modeling of void lattice self-organization in CaF₂ under irradiation." – Abstract: OR-29.

21. **Yu.F. Zhukovskii**, **A. Gopejenko**, **Yu.A. Mastrikov**, **E.A. Kotomin**, P.V. Vladimirov, and A. Möslang, "Modeling of Y-O precipitation in bcc-Fe and fcc-Fe lattices." – Abstract: OR-35.

22. **E.A. Kotomin**, M.M. Kuklja, **Yu.A. Mastrikov**, O. Sharia, D. Fuks, and J. Maier, "Prediction of structural stability of complex perovskites for solid oxide fuel cells from first principles." – Abstract: OR-36.

23. **E. Klotins** and **G. Zvejnieks**, "Electron-phonon interactions: spatial localization." – Abstract: OR-44.
24. **P. Merzlyakov**, **G. Zvejnieks**, **V.N. Kuzovkov**, and **E.A. Kotomin**, "Statistical analysis of void lattice formation in CaF_2 ." – Abstract: PO-30.
25. **A.I. Popov**, V. Savchyn, J. Purans, A. Dabrowska, A. Huczko, B. Pathak, and D.P. Subedi, "Cathodoluminescence study of Al-doped ZnO nanofilms." – Abstract: PO-78.
26. F.U. Abuova, A.T. Akilbekov, **E.A. Kotomin**, and **S. Piskunov**, "First-principles calculations of defects in MgF_2 ." – Abstract: PO-146.
27. A. Usseinov, **E.A. Kotomin**, **Yu.F. Zhukovskii**, J. Purans, **A. Sorokin**, and A.T. Akilbekov, "First-principles calculations of ZnO crystals doped with hydrogen." – Abstract: PO-168.
28. **A. Sorokin**, **D. Gryaznov**, **E.A. Kotomin**, and J. Purans, "First-principles calculations of electronic structure and phonon properties of Al- and H-doped ZnO." – Abstract: PO-169.
29. **A.I. Popov**, L. Shirmane, V. Pankratov, V. Dimza, M. Antonova, M. Livinsh, A. Kotlov, and J. Zimmermann, "VUV synchrotron radiation of PLZT ceramics." – Abstract: PO-176.

VI. 2013 MRS Spring Meeting (San Francisco, USA, April, 2013).

30. **E.A. Kotomin**, R. Merkle, **Yu.A. Mastrikov**, M.M. Kuklja, D. Fuks, and J. Maier, "Ab initio modeling of oxygen transport in mixed conducting perovskites for SOFC applications." - Abstract: G6.02.
31. **E.A. Kotomin**, E. Blokhin, **D. Gryaznov**, R.A. Evarestov, and J. Maier, "Ab initio study of confinement effects for ionic carriers in perovskite ultrathin films." - Abstract: XX1.05.

VII. International Conference NANOMEETING-2013 (Minsk, Belarus, May, 2013).

32. **S. Piskunov**, **J. Kazerovskis**, **Yu.F. Zhukovskii**, P.N. Dyachkov, and S. Bellucci, "Incorporation of Ni nanofilament inside carbon nanotubes: DFT calculations."
33. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V.I. Gopeyenko, N. Burlutskaya, T. Lobanova-Shunina, and S. Bellucci, "Electromagnetic properties of CNTs and GNRs based nanostructures for nanosensor systems."
34. **Yu.F. Zhukovskii**, **S. Piskunov**, **O. Lisovski**, and **J. Begens**, "First principles simulations on doped TiO_2 and SrTiO_3 nanotubular photocatalysts for water-splitting hydrogen generation."

VIII. E-MRS 2013 Spring Meeting (Strasbourg, France, May, 2013).

35. **E.A. Kotomin**, M.M. Kuklja, D. Fuks, **Yu.A. Mastrikov**, O. Sharia, and J. Maier, "Understanding structural stability of complex perovskites for solid oxide fuel cells: First principles calculations." - Abstract: F.P2-1.
36. **E.A. Kotomin**, **D. Bocharov**, **D. Gryaznov**, and **Yu.F. Zhukovskii**, "Ab initio simulations of oxygen interaction with surfaces, interfaces and grain boundaries in uranium mononitride nuclear fuels." - Abstract: M.7-2.
37. **G. Zvejnieks**, **V.N. Kuzovkov**, and **E.A. Kotomin**, "Characterization of self-assembled charged nanoparticle structures." - Abstract: N.P1-9.

38. **V.N. Kuzovkov, G. Zvejnieks, and E.A. Kotomin**, "Non-equilibrium charge screening in pattern formation kinetics for oppositely charged nanoparticles." - Abstract: N.P1-10.
39. **D. Gryaznov, E.A. Kotomin, E. Blokhin, R.A. Evarestov, J. Maier, and J. Purans**, "A comparative ab initio thermodynamic study of oxygen vacancies in oxides." - Abstract: O.P2-5.
40. **A. Usseinov, E.A. Kotomin, Yu.F. Zhukovskii, J. Purans, A. Sorokin, and A.T. Akilbekov**, "Atomic and electronic structure of hydrogen-doped ZnO: Ab initio hybrid calculations." - Abstract: O.P2-6.

IX. Work Package Meeting of the EC COST project CM 1104 "Reducible oxides" (London, UK, May, 2013).

41. **E.A. Kotomin and Yu.A. Mastrikov**, "Ab initio modelling of oxygen transport in (Ba,Sr)(Co,Fe)O₃ perovskite solid solutions for solid oxide fuel cells." - Abstract: p. 1.
42. **Yu.A. Mastrikov and E.A. Kotomin**, "Ab initio modeling of oxygen reduction and diffusion in perovskite solid solutions for SOFC and permeation membranes." - Abstract: p. 3.

X. Bunsentagung 2013 Meeting [Annual meeting of German Physical Chemistry Society] (Karlsruhe, Germany, May, 2013).

43. **R. Merkle, Yu.A. Mastrikov, E.A. Kotomin, M.M. Kuklja, and J. Maier**, "Comparative analysis of oxygen mobility in (La,Sr)(Co,Fe)O₃ perovskites based on ab initio modeling."

XI. International Symposium on Recent Electronic-Structure Theories and Related Experiments (Stuttgart, Germany, June, 2013).

44. **D. Gryaznov, E.A. Kotomin, A. Bussmann-Holder, and J. Maier**, "A comparative ab initio thermodynamic study of oxygen vacancies in oxide perovskites: role of phonons."
45. **E.A. Kotomin, Yu.A. Mastrikov, R. Merkle, and J. Maier**, "A comparative analysis of oxygen vacancy diffusion in LSCF and BSCF perovskite solid solutions: ab initio modeling."

XII. International Symposium on Solid State Ionics (SSI-19) (Kyoto, Japan, June, 2013)

46. **M.M. Kuklja, Yu.A. Mastrikov, R. Merkle, E.A. Kotomin, and J. Maier**, "Comparative analysis of oxygen mobility in LSCF." - Abstracts: A2-08.
47. **R. Merkle, L. Wang, A. Wedig, Yu.A. Mastrikov, E.A. Kotomin, and J. Maier**, "Oxygen exchange kinetics on SOFC cathode materials - reaction mechanism and importance of defects." - Abstract: C1-12.

XIII. Annual Monitory Meeting of European Fusion Development Agreement, EFDA - 2013 (Bucharest, Romania, June, 2013).

48. **Yu.A. Mastrikov, P.V. Vladimirov, V.A. Borodin, Yu.F. Zhukovskii, E.A. Kotomin, and A. Möslang**, "Ab initio modeling of nY/nV_{Fe} complexes diffusion in the α -Fe lattice."

XIV. 25th Joint Russian-German Workshop on ECRH and Gyrotrons (Karlsruhe, Germany, June, 2013).

49. O. Dumbrajs, "Effect of electron beam misalignments on the gyrotron efficiency".

XV. 17th International Conference on Radiation Effects in Insulators, REI'17 (Helsinki, Finland, July, 2013).

50. M.M. Kuklja, **E.A. Kotomin**, O. Sharia, **Yu.A. Mastrikov**, and J. Maier, "Radiation defects in complex solid solutions." - Abstract: O-33.

51. F.U. Abuova, A.T. Akilbekov, **E.A. Kotomin**, **S. Piskunov**, and V.M. Lisitsyn, "Ab initio modelling of radiation damage in MgF₂." - Abstract: PB-13.

52. **D. Gryaznov**, **E.A. Kotomin**, E. Blokhin, R.A. Evarestov, J. Maier, and J. Purans, "A comparative ab initio thermodynamic study of oxygen vacancies in oxides." - Abstract: PB-18.

XVI. European Physical Society Plasma Physics conference (Espoo, Finland, July, 2013).

53. **O. Dumbrajs**, "RMP ELM suppression analysis by means of a low-dimensional model system for quasi-periodic plasma perturbations".

XVII. Workshop on New Horizons in Electrochemistry- at the Boundary to Physics and Materials Science (Capri, Italy, August, 2013).

54. **E.A. Kotomin**, **Yu.A. Mastrikov**, R. Merkle, and J. Maier, "Ab initio modelling of oxygen reduction and transport in perovskites for solid oxide fuel cells." - Abstract: p. 24.

XVIII. Advances in the Chemistry of Disordered Solids: Workshop Honouring the Contributions of Professor Patrick Jacobs to Solid State Chemistry (London, UK, September, 2013).

55. **E.A. Kotomin**, "First principles modelling of strongly non-stoichiometric perovskite solid solutions."

XIX. 246th American Chemical Society National Meeting & Exposition (Indianapolis, USA, September, 2013).

56. M. Kuklja, **E.A. Kotomin**, D. Fuks, **Yu.A. Mastrikov**, O. Sharia, R. Merkle, and J. Maier, "First principles modeling of complex perovskites for energy applications." Abstracts: p. 416.

XX. European Congress on Advanced Materials and Processes, EUROMAT 2013 (Sevilla, Spain, September, 2013).

57. D. Fuks, M.M. Kuklja, **Yu.A. Mastrikov**, and **E.A. Kotomin**, "Phase stability versus decomposition in complex perovskite solid solutions from DFT study." Symposium E1.III. Materials for Fuel Cells.

XXI. 38th International Conference on Infrared, Millimeter and Terahertz Waves, IRMMW-THz 2013 (Mainz, Germany, September, 2013).

58. **O. Dumbrajs**, "Effect of the tilt on the gyrotron operation". Abstracts: We5-5.

XXII. Ab initio Modelling in Solid State Chemistry, MSSC2013 (London, UK, September, 2013).

59. P. Zhgun, **D. Bocharov**, **S. Piskunov**, A. Kuzmin, and J. Purans, "Quantum chemistry calculations on negative thermal expansion in scandium fluoride".

XXIII. 14th International Workshop on Nanoscience and Nanotechnology, n&n-2013 (Frascati, Italy, September-October, 2013).

60. **S. Piskunov**, **Yu.F. Zhukovskii**, **O. Lisovski**, **J. Begens**, E. Spohr, and S. Bellucci, "C-, N-, S-, and Fe-doped TiO₂ and SrTiO₃ nanotubes for photocatalytical water-splitting: Prediction from first principles." - Abstracts: p. 15-17.

61. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V.I. Gopeyenko, N. Burlutskaya, T. Lobanova-Shunina, and S. Bellucci, "Nanocarbon electromagnetics in CNT-, GNR - and aerogel-based nanodevices." - Abstracts: p. 22-24.

62. **Yu.F. Zhukovskii** and R.A. Evarestov, "Theoretical description of TiO₂ nanowires modeled from densely-packed rutile surfaces." - Abstracts: p. 88-91.

XXIV. 6th International Conference "Physics of Disordered Systems" (Lviv, Ukraine, October, 2013).

63. A. Usseinov, **E.A. Kotomin**, **Yu.F. Zhukovskii**, J. Purans, A.T. Akilbekov, and A.K. Dauletbekova, "Hydrogen adsorption on non-polar surfaces of ZnO: Ab initio calculations." - Abstracts: p. 91.

XXV. 2nd General COST Meeting, Action CM 1104 "Reducible Oxide Chemistry" (Uppsala, Sweden, November, 2013).

64. **Yu.A. Mastrikov** and **E.A. Kotomin**, "First principles modeling of processes in complex perovskites for solid oxide fuel cells". - Abstracts, p. 67.

XXVI. 6th International Conference on Innovative Information Technologies, IIT-2013 (Vilnius, Lithuania, November, 2013).

65. **Yu.N. Shunin**, **Yu.F. Zhukovskii**, V.I. Gopeyenko, T. Lobanova-Shunina, N. Burlutskaya, and S. Bellucci, "Carbon based nanosensor systems for intelligent systems: Modeling and technology."

DEPARTMENT OF PHOTONICS MATERIALS PHYSICS

Head of department Dr.habil.phys. D.Millers

LABORATORY OF SOLID STATE RADIATION PHYSICS

Head of laboratory Dr.habil.phys.L.Grigorjeva

RESEARCH AREA AND EXPERIMENTAL SETUPS

The electronic properties of single crystals, ceramics, nanostructured materials were studied by time-resolved luminescence and absorption methods. Excitation sources: a pulsed electron beam accelerator (10 ns, 270 keV, 10^{12} electrons/pulse), YAG:Nd and nitrogen lasers (266 nm, 337 nm, 532 nm). X ray source and 980 nm laser diode was used for steady state luminescence spectra and radiation defect creation. TSL methods were developed.

VIS-UV absorption spectrometer LABOMED for measurements within 190-1100 nm range. FTIR absorption spectroscopy: EQUINOX 55 (10000-400 cm^{-1} and 22000-7000 cm^{-1} spectral regions) was developed for dispersed materials in wide temperature range.

Scientific Staff

1. Dr.habil.phys. D.Millers
2. Dr.habil.phys. L.Grigorjeva
3. Dr.phys. K.Smits

Students

1. V.Liepina
2. M.Vanks
3. L.Puķina
4. A.Zolotarjevs

MAIN RESULTS

The electron beam induced short-lived absorption in PZLT optical ceramic.

D.Millers, V.Dimza, L.Grigorjeva, M.Antonova, K.Smits, M.Livins.

The short lived absorption induced by a pulsed electron beam in the lead-lanthanum-zirconate-titanate (PLZT) optical ceramics was studied. The measured absorption spectrum covers 1.1–2.9 eV energy range and consists of several strongly overlapping peaks. The rise of the absorption is delayed with respect to the excitation pulse, due to charge carrier migration before trapping at centers responsible for the absorption. The formation rate of absorption centers and decay rate of absorption depend on the photon energy. The kinetics of short lived absorption varies over spectrum and can be approximated with a stretched exponent. The stretched exponent parameters indicate that the local disorder of a matrix is similar around all absorption centers.

TSL and tractional glow study of Ge-doped α -quartz.

A.Zolotarjevs, A.Trukhin, K.Smits., D.Millers

Crystalline α -quartz doped with 0.1 wt% and 0.9 wt% germanium was studied using TSL and FGT equipments. It is known that Ge in quartz is effective trap for electrons, therefore it could be used for detection of hypothetical self-trapped hole in quartz. The activation energies for two TSL peaks are found by fraction glow and

Hoogenstraaten methods. The TSL distribution changes depending on Ge concentration and also on irradiation type. The TSL peaks below 70K in quartz doped with Ge could belong to hole trapped on Ge.

Photocatalytic Properties of TiO₂ and ZnO Nanopowders

L. Grigorjeva, J. Rikveilis, J. Grabis, Dz. Jankoviča, C. Monty, D. Millers, K. Smits

Photocatalytic activity of TiO₂ and ZnO nanopowders is studied depending on the morphology, grain sizes and method of synthesizing. Photocatalysis of the prepared powders was evaluated by degradation of the methylene blue aqueous solution. Absorbance spectra (190-100 nm) were measured during exposure of the solution to UV light. The relationships between the photocatalytic activity and the particle size, crystal polymorph phases and grain morphology were analyzed. The photocatalytic activity of prepared TiO₂ nanopowders has been found to depend of the anatase-to-rutile phase ratio. Comparison is given for the photocatalytic activity of ZnO nanopowders prepared by sol-gel and solar physical vapor deposition (SPVD) methods.

Up-conversion luminescence dependence on structure in zirconia nanocrystals.

K.Smits, Dz.Jankoviča, A.Sarakovskis, D.Millers.

The zirconia samples containing two different concentrations of Er and Yb dopants were prepared using the Sol–Gel method and up-conversion luminescence was studied using the time-resolved techniques. The up-conversion luminescence depends on the oxygen content in surrounding gasses during annealing as well as on the annealing temperature. These dependencies indicate that ZrO₂ intrinsic defects annealing and generation, phase transition as well as dopant redistribution take place. The possible role of these processes on up-conversion luminescence is discussed. The results of experiments confirmed that the annealing temperature has a crucial influence on up-conversion luminescence for samples containing small concentrations of Er and Yb; whereas for samples containing large concentrations of Er and Yb, the primary change of up-conversion luminescence is due to the grain size growth during annealing. The optimal annealing temperature depends upon the Er and Yb ion concentration. It is crucial to obtain up-conversion zirconia material with high quantum efficiency.

SCIENTIFIC VISITS ABROAD

1. Dr.habil.phys.L.Grigorjeva, Estonia (10 days)
2. Dr.K.Smits, Estonia (7 days)
3. Dr.Habil.phys. L.Grigorjeva, Poland (4 days)
4. Dr.Habil.phys. D.Millers, Poland (4 days)
5. A.Zolotarjovs, Estonia (3 days)
6. A.Zolotarjovs, Lithonia (5days)
7. Dr.K.Smits. Germany (5 days)
8. Dr.K.Smits. Pland 6 days.

COOPERATION

Latvia

Riga Technical University, Institute of Inorganic Chemistry (Dr.habil.sc.ing. J.Grabis).

ZRF RITEC SIA (Dr.V.Ivanov).

LU Institute of Microbiology (M.Gavare, J.Liepiņš)

Estonia

Institute of Physics, Tartu (Dr.S.Zazubovich, Dr. I.Sildos))

Russia

GOI, St.Peterburg (Dr.L.Maksimov)

GIREDMET, Moscow (Pr. I.S Lisitskii)

Poland

Institute of High Pressure Physics, PAN, Warszawa, Poland (Prof.W.Lojkowski,)

France

CNRS Processes, Material and Solar Energy Laboratory, (PROMES), Odeillo

(Dr.C.Monty)

China

Shanghai Institute of Technology (SIT), Dr. Jiayue Xu.

SCIENTIFIC PUBLICATIONS

1. **L.Grigorjeva, D.Millers, K.Smits, Dz.Jankoviča, L.Puķina.** Characterization of hydroxyapatite by time-resolved luminescence and FTIR spectroscopy. IOP Conference Series: Material Science and Engineering. 2013, 49(1), 012005.
2. **L.Grigorjeva, J.Rikveilis, J.Grabis, D.Millers, K.Smits.** Photocatalytic properties of TiO₂ and ZnO nanopowders. Latvian Journal of Physics and Technical Sciences. 2013, 50(4), 48-55.
3. **D.Millers, V.Dimza, L.Grigorjeva, M.Antonova, K.Smits, M.Livins.** The electron beam induced short-lived absorption in PZLT optical ceramic. Optical Materials, 2013, 35(5), 1090-1094.
4. U.Rogulis, E.Elsts, J.Jansons, A.Sarakovskis, G.Doke, A.Stunda, **K.Smits.** Cathodoluminescence of oxyfluoride glass-ceramics. Radiation Measurements, 2013, 56, 120-123.
5. **K.Smits, Dz.Jankoviča, A.Sarakovskis, D.Millers.** Up-conversion luminescence dependence on structure in zirconia nanocrystals. Optical materiāls. 2013, 35(30), 462-466.
6. A.Zolotarjevs, A.Trukhin, **K.Smits, D.Millers,** TSL and tractional glow study of Ge-doped α -quartz. IOP Conference Series: Material Science and Engineering. 2013,49, 012056.

LECTURES IN CONFERENCES

International Baltic Sea Region Conference "Functional materials and nanotechnologies 2013 (FM&NT)", April, 21-24, Tartu, Estonia.

L.Grigorjeva, D.Millers, K.Smits, Dz.Jankoviča, L.Puķina. Characterization of hydroxylapatite by time-resolved luminescence and FTIR spectroscopy. Book of Abstracts, PO41.

V.Liepiņa, K.Smits, Dz.Jankoviča, J.Grabis, L.Grigorjeva, D.Millers. Investigation of Luminescence mechanism of persistent strontium aluminates phosphor. Book of Abstracts, PO84.

K.Smits, D.Millers, L.Grigorjeva, Dz.Jankovia, C.Monty. Rare earth doped zirconia nanostructured transparent ceramics. Book of Abstracts, PO43.

A.Zolotarjovs, A.Trukhin, **K.Smits**, **D.Millers**, TSL equipment development and application for crystalline silicon dioxide study. Book of Abstracts, PO164.

LU CFI 29th Scientific Conference, 2013, 20-22 Febr., Riga, Latvia

V.Liepina, **K.Smits**, Dz.Jankoviča, **L.Grigorjeva**, **D.Millers**. The luminescent properties of long-lasting strontium aluminate phosphor. Thesis, p.49.

A.Zolotarjovs, **K.Smits**, **D.Millers**. Modification of TSL equipment and software development. Thesis, p.51.

L.Puķina, **L.Grigorjeva**, **D.Millers**, Dz.Jankoviča, **K.Smits**. Eu and Ce doped hydroxilapatite luminescence. Thesis, p.50.

M.Vanks, **D.Millers**, **L.Grigorjeva**, **K.Smits**. The luminescence and induced absorption of ZnO single crystals. Thesis, p.48.

17th International Conference on Crystal Growth and epitaxy. University of Warsaw, Poland, 11-16 August, 2013.

K.Smits, J. Xu, J.Grabis, **D.Millers**, **L.Grigorjeva**. Comparison of RE ion luminescence in zirconia nanocrystals and single crystals. Book of Abstracts, p.458.

2013 E-MRS Fall Meeting, Warsaw University of Technology, 16-20th September, Warsaw, Poland.

L.Grigorjeva, D.Millers, A.Sarakovski, K.Smits. Subnanosecond luminescence of single crystals and ceramics. P.208.

D.Millers, **L.Grigorjeva**, **K.Smits**, P.A.Rodnyi, **M.Vanks**. Short-lived absorption in ZnO single crystals., p208.

Bachelor Thesis

L.Pukina. Ar retzemju joniem aktivētu hidroksilapatītu spektāli-kinētiskie pētījumi. LU, Rīga, 2013.

M.Vanks. ZnO monokristālu luminiscence un inducētā absorbcija. LU, Rīga, 2013.

LABORATORY OF AMORPHOUS MATERIALS SPECTROSCOPY

Head of laboratory Dr.habil.phys. L.Skuja

RESEARCH AREA AND MAIN PROBLEMS

The optical and electronic properties of advanced wide-band gap materials for applications in optical elements for high power laser optics, optical fibers, for deep-ultraviolet and vacuum-ultraviolet spectral ranges, for radiation environments and for nanoscience.

Scientific Staff

1. Dr.habil.phys. L.Skuja
2. Dr.habil.phys. A. Trukhin
3. Dr.habil.phys. A.Siliņš

EXPERIMENTAL METHODS AND EQUIPMENT

The research is performed mainly by spectroscopic methods, including optical absorption and luminescence spectroscopy, magnetic resonance spectroscopy (electron paramagnetic resonance), infrared absorption and Raman scattering, energy-dispersive X-ray microanalysis, thermal desorption mass-spectrometry.

Several of these experimental techniques are available by collaboration with other laboratories of ISSP or with our research partners in other institutions in Latvia or abroad. The equipment, available directly in the laboratory is listed here below:

Optical absorption spectroscopy.

Absorption measurements in the NIR-VIS-UV range by double monochromator (AMKO-LTI) or CCD-based spectrometers (Andor/Shamrock 303-i) and Hamamatsu TM-UV/VIS C10082CAH portable spectrograph. Configurations for NIR-VIS-UV measurements of attenuation in optical fibers are available (using OceanOptics DH-2000-S-TTL D₂-halogen light source).

Luminescence spectroscopy.

Luminescence excitation by the following sources is available : YAG:Nd laser (266 nm, 532 nm), nitrogen laser (337 nm), excimer lasers (248, 193 and 157 nm), semiconductor lasers (650, 765 nm), deuterium and xenon lamps. Luminescence detection is performed using photomultipliers/monochromators and cooled CCD camera coupled with spectrograph. Time-resolved luminescence is detected by digital oscilloscopes, multichannel photon counters or time-correlated single-photon counting.

Vacuum ultraviolet spectroscopy:

McPherson 234/302 200 mm monochromator with D₂ lamp with MgF₂-window serving as light source (120-250 nm) is used in configurations for optical absorption and photoluminescence excitation measurements.

Raman spectroscopy:

Andor Shamrock303i spectrometer with Newton DU971N electron multiplying cooled CCD , NIR to UV spectral range.

Energy-dispersive X-ray fluorescence microanalysis

(EDAX Eagle III spectrometer, Rhodium X-ray source with micro-capillary focusing lens, detected elements from Na to U, spatial resolution ~50 μm).

Mass spectrometry:

Dycor LCD-300 quadrupole mass-spectrometer, 1-300 a.m.u. with oil-free vacuum station.

MAIN RESULTS

IMPACT OF FLUORINE ADMIXTURE, HYDROGEN LOADING, AND EXPOSURE TO ARF EXCIMER LASER ON PHOTOLUMINESCENCE OF BISMUTH DEFECTS IN AMORPHOUS SILICA

AnatolyTrukhin¹,JanisTeteris¹,AleksyBazakutsa²,KonstantinGolant^{2 1}

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Photoluminescence (PL) excited by ArF (193 nm), KrF (248 nm) and N₂ (337 nm) pulsed lasers is studied in bismuth doped unfused silicon dioxide synthesized on silica substrates by surface-plasma chemical vapor deposition (SPCVD). Additive free and fluorinated (F content ~0.4 wt.%) amorphous silica are examined as host materials for bismuth. Three typical PL bands peaking at wavelengths of 650 nm (orange), 800 nm and 1400 nm (near infrared, NIR) were observed. It is found that fluorine additive weakly affects PL detail of as deposited samples. However, hydrogen loading completely deactivates NIR PL in the case of fluorine free sample, but only slightly suppresses the NIR band in fluorinated silicon dioxide. In fluorine free sample quenching of orange PL band caused by hydrogen loading is not as great as for the NIR band. By contrast, the NIR band intensity only slightly goes down in fluorinated silica sample, whereas the orange PL band becomes even more intense as a result of hydrogen loading. Exposure of the hydrogen loaded fluorine free sample to photons of ArF excimer laser renews NIR PL. Storage of fluorine free hydrogen loaded sample in oxygen ambience leads to significant increase of the NIR PL band intensity. The effect of hydrogen loading is explained by collisional deactivation of the excited NIR PL centers. Subsequent outcome of H₂ molecules accelerated by UV irradiation and/or storing the sample in oxygen ambience leads to PL recovery. Presence of fluorine in silica network somehow prevents NIR PL centers from collisions with interstitial hydrogen molecules. These molecules at the same time considerably neutralize the negative effect of fluorine on the intensity of the orange PL band. No impact of fluorine on either effectiveness of the orange PL band excitation via electron-hole recombination or inactivity of this process for the NIR PL band excitation is observed.

INTRA-CENTER AND RECOMBINATION LUMINESCENCE OF BISMUTH DEFECTS IN FUSED AND UNFUSED AMORPHOUS SILICA FABRICATED BY SPCVD

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Photoluminescence (PL) of bismuth doped silicon dioxide excited by UV excimer lasers (ArF — 193 nm, KrF — 248 nm) and a green light laser diode (532 nm) is studied in a wide spectral band at temperatures ranging from 12 to 750 K. Two types of samples are investigated: unfused, 100 μm in thickness amorphous layer immediately deposited on the inner surface of silica substrate tube, and the same material after profusion resulted from tube collapsing to a rod by external heating. PL bands centered at 620–650 nm, 820 nm and 1400 nm wavelengths are observed in both fused and unfused samples. Under excitation by the green laser diode decay time constants for 650

nm (orange) and 1400 nm (NIR) PL bands measured at room temperature amount 3 μ s and 600 μ s respectively. These rather long decay times point to partly forbidden intra-center electron transitions. PL intensities of the orange and NIR bands are not temperature dependent within 12–450 K range. At higher temperatures the orange band manifests an intra-center thermal quenching, activation energy and frequency factor being 0.42 ± 0.04 eV and $5 \cdot 10^9 \text{s}^{-1}$ respectively, while intensity of the NIR band weakly depends on temperature up to 700 K. Electron-hole recombination excitation mechanism is found to contribute to the orange, but not to the NIR PL band under UV laser pumping. The specific feature of orange PL excited by recombination is the magnitude of decay time constant being about milliseconds at temperature of 12 K and decreasing with the temperature increase. Localized state ionization and two-photon absorption of intense UV light excite electron-hole pairs in silica host. Some bismuth defects serve as traps for the electrons, while holes transmute into self-trapped state thus generating self-trapped holes (STHs). Thermally activated escape of the STHs followed by their subsequent recombination with trapped electrons forms the mechanism to transfer the excitation to particular bismuth defects responsible for orange PL. At the same time no signature of the impact of such recombination process on the excitation of NIR PL is observed. This permits one to conclude that the nature of bismuth defects responsible for these two PL bands varies, and these two types of defects are available in both fused and infused silicon dioxide.

LUMINESCENCE OF UNFUSED 95%SiO₂–5%GeO₂ AMORPHOUS FILMS WITH FLUORINE ADDITIVE: NO EVIDENCE FOR PRESENCE OF GEODC(I) DEFECTS FOUND

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Photoluminescence (PL) of unfused amorphous germanosilicate films with fluorine additive is studied in 2–8.5 eV spectral range. Experiments are based on films deposited on silica substrates by means of the surface-plasma chemical vapor deposition (SPCVD). Films of about 100 μ m in thickness with “high F” (~ 4.2 wt.%) and “low F” (~ 0.5 wt.%) fluorine content have been fabricated for the experiments. KrF (248 nm), ArF (193 nm) and F₂ (157 nm) excimer lasers are used to pump PL. It is found that absorption and luminescence associated with germanium oxygen deficient centers (GeODCs) in “high F” and “low F” films differ. In the “high F” unfused film absorption coefficient of the band at 5 eV as well as intensity of the blue PL band at 3.1 eV are significantly greater. This film proves features of the so called GeODCs(II), which symbolize twofold coordinated germanium defects in silica network. In the “low F” unfused film absorption band at 5 eV is feebly marked. Poorly resolved PL intrinsic to GeODCs(II) can be detected in this film under the KrF laser pump. The most significant PL features are revealed under deeper UV pump by ArF and F₂ lasers. Spectral positions of PL bands excited by these lasers correspond to GeODCs(II). However PL decay kinetics dramatically differs from that one intrinsic to GeODCs(II). Noticeable growth of PL intensity caused by permanent (half an hour and more) exposure to ArF and/or F₂ lasers takes place, indicating GeODC(II) formation. It is found that considerable body of fluorine additive has the same effect as profusion for “low F” and/or fluorine free germanosilicate amorphous material synthesized by SPCVD. In the “high F” film yield of GeODC(II) PL pumped by the F₂ laser remains high. This speaks for the suppression of the competitive 7.6 eV absorption band associated with SiODCs(I) by fluorine additive indicating a decrease in the content of this type of defects in the material. High

yield of GeODC(II) luminescence pumped by deep UV photons as well as hypothetical similarity of SiODC(I) and GeODC(I) permit one to conclude that GeODCs(II) are the only defects dominating in the materials under study.

ULTRAVIOLET LUMINESCENCE OF SCPO₄, ALPO₄ AND GAPO₄ CRYSTALS

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The luminescence of self-trapped excitons (STEs) was previously observed and described for the case of tetragonal-symmetry ScPO₄ single crystals. The subject band in this material is situated in the UV spectral range of ~210 nm or ~5.8 eV. In the present work, we are both expanding this earlier luminescence study and seeking to identify similar luminescence phenomena in other orthophosphate crystals, i.e., AlPO₄ and GaPO₄. These efforts have proven to be successful—in spite of the structural differences between these materials and ScPO₄. Specifically we have found that for AlPO₄ and GaPO₄, in addition to an α -quartz-like STE, there is a UV luminescence band that is similar in position and decay properties to that of ScPO₄ crystals. Potentially this represents an STE in AlPO₄ and GaPO₄ crystals that is analogous to the STE of ScPO₄ and other orthophosphates. The decay kinetics of the UV luminescence of ScPO₄ was studied over a wide temperature range from 8 to 300 K, and they exhibited some unusual decay characteristics when subjected to pulses from an F₂ excimer laser (157 nm). These features could be ascribed to a triplet state of the STE that is split in a zero magnetic field. A fast decay of the STE was detected as well, and therefore, we conclude that, in addition to the slow luminescence corresponding to a transition from the triplet state, there are singlet–singlet transitions of the STE. Time-resolved spectra of the slow and fast decay exhibit a small shift (~0.15 eV) indicating that the singlet–triplet splitting is small and the corresponding wavefunction of the STE is widely distributed over the atoms of the ScPO₄ crystal where the STE is created.

FORMATION AND ANNIHILATION OF INTRINSIC DEFECTS INDUCED BY ELECTRONIC EXCITATION IN HIGH-PURITY CRYSTALLINE SiO₂

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Formation of oxygen vacancies (Si-Si bonds) due to the decomposition of regular Si-O-Si bonds (Frenkel process) is the dominant intrinsic defect process in high-purity α -quartz subjected to electronic excitation with ⁶⁰Co γ -rays. Compared to amorphous SiO₂, in α -quartz the yield of Si-Si bonds is an order of magnitude smaller, their 7.6 eV optical absorption band is less broadened, their thermal annihilation completes at a lower temperature around the α - β transition of quartz, and, in contrast, the radiation-induced interstitial oxygen atoms practically do not form interstitial oxygen molecules.

FRENKEL DEFECT PROCESS IN SILICON DIOXIDE

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Optical properties of high-purity silicon dioxide (SiO₂), including amorphous SiO₂ (*a*-SiO₂) and α -quartz (a crystalline polymorph of SiO₂), are significantly influenced by the presence of intrinsic defects. Both *a*-SiO₂ and α -quartz consist of Si-O-Si network extending into three dimensions, and the detachment of an oxygen atom from a regular Si-O-Si bond can be regarded as the Frenkel defect process in SiO₂. It is an intrinsic defect process in SiO₂ and is universally observed both in *a*-SiO₂ and α -quartz. It is the most important in high-purity SiO₂, where the defect formation associated with impurities and local non-stoichiometry is considerably suppressed. The main difference of intrinsic defect generation mechanisms between *a*-SiO₂ and α -quartz is the absence in α -quartz of the formation of dangling bond pairs, which is an additional defect process in SiO₂. The most probable source of the dangling bond pairs in *a*-SiO₂ is “strained” Si-O-Si bonds, arising from the wide distribution in the Si-O-Si bond angle in *a*-SiO₂. However, the presence of the strained Si-O-Si bonds promotes the Frenkel mechanism as well. Fluorine doping at moderate concentration is effective in improving the radiation hardness of *a*-SiO₂ by decreasing the concentrations of the strained Si-O-Si bonds and of other network modifiers, vulnerable to radiation. The Frenkel defect process in high-purity α -quartz is less efficient as compared both to high-purity fluorine-doped *a*-SiO₂ and to conventional α -quartz containing a certain amount of metallic impurities.

SCIENTIFIC VISITS ABROAD

Anatoly Trukhin, International Conference Functional Materials And Nanotechnologies, Tartu, Estonia, April, 21 – 24, 2013

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2. **A. N.Trukhin**, K.Smits, T. I. Dyuzheva, L. M.Lityagina Luminescence of Stishovite. International Conference Functional Materials And Nanotechnologies, Tartu, Estonia, April, 21 – 24, 2013.

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LABORATORY OF OPTICAL RECORDING

Head of Laboratory Dr. J.Teteris

RESEARCH AREA AND MAIN PROBLEMS

Synthesis and research of amorphous chalcogenide semiconductor (As-S, As-Se and As-S-Se) and azobenzene containing organic polymer thin films for optical recording, nanotechnology and holography have been performed. Photoinduced changes of optical properties, holographic recording and hologram self-enhancement effects, and relaxation processes in amorphous films are studied. The main task was RTD of high sensitive photoresists in the visible region for holography and lithography for production of diffractive optical elements. Rainbow hologram production technology based on chalcogenide semiconductor photoresists was developed. The methods for fabrication of subwavelength-gratings and surface-relief features with nanometer scale have been developed.

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MAIN RESULTS

SUBWAVELENGTH STRUCTURES IN AMORPHOUS CHALCOGENIDE THIN FILMS

Mara Reinfelde and Janis Teteris

Thin films of amorphous chalcogenide semiconductor As_2S_3 , As-Se and As-S-Se systems were used for recording of refractive index and surface-relief modulated gratings. Amorphous chalcogenide semiconductors are high index materials with refractive index in the range 2.2 – 3.5, depending on the film composition and light

wavelength. The photoinduced changes of refractive index down to $\Delta n \approx 0.15 - 0.5$ are observed in these systems.

The photo- and electron-beam stimulated changes of wet etching rate in amorphous As-S, As-Se and As-S-Se films have been studied. Amorphous chalcogenide semiconductor (AChS) resists obtained by thermal deposition in vacuum are characterized by very high resolution capability and they possess a number of peculiarities that make them attractive for application in many photo- and electron-beam lithographic (EBL) processes.

The recording of the subwavelength gratings with a period of $0.15 \mu\text{m} - 1 \mu\text{m}$ was performed by holographic method. The fringe period for two intersecting light beams in a media with high refractive index n can be expressed as $\Lambda = \lambda_0 / 2n \sin\theta$, where λ_0 is the wavelength of laser light in vacuum, n is refractive index of the resist and θ is the half-angle between the laser beams inside the resist. The right angle prisms with $n = 1.8 - 2.6$ were used to increase the value of θ . The grating period and profile after chemical etching was measured by AFM. The transmission, reflection and polarization properties of the obtained gratings were studied.

OPTICAL RECORDING IN AMORPHOUS CHALCOGENIDE THIN FILMS

Janis Teteris

During the past 10 years, research in the field of optical materials based on amorphous chalcogenide semiconductors has made significant advances. Much of this research is driven by applied interest and this field of research is extremely broad and active. The use of amorphous chalcogenide thin films in holography and lithography has probably only just begun, but already produced some promising results.

The main functional principles and practical application of amorphous chalcogenide photoresists for production of the embossed *rainbow* holograms and holographic optical elements are discussed. The laser interference lithography is used as a low-cost method for the exposure of large surfaces with regular patterns like subwavelength-gratings and microsieves. The regular features with the sizes of about 50 nm and less can be fabricated by this method. The Bragg reflection gratings were recorded and studied in amorphous As_2S_3 and As-S-Se films. Amorphous chalcogenide thin films are thought to be one of the potential materials for all-optical integrated circuits for the optical communication systems due to their excellent infrared transparency, large nonlinear refractive index, and low phonon energies. The possibility to use the amorphous chalcogenide films as a media for holographic recording, processing and storage of information with high density is discussed.

HOLOGRAPHIC LITHOGRAPHY IN AMORPHOUS CHALCOGENIDE THIN FILMS

J.Teteris, J.Aleksejeva and M.Reinfelde

The recording of the surface-relief and refractive index modulated gratings with a period of $0.15 - 1.0 \mu\text{m}$ was performed by solid immersion holographic method. The grating period for two intersecting light beams in a coupling prism with refractive index n can be expressed as $\Lambda = \lambda_0 / 2n \sin\theta$, where λ_0 is the wavelength of laser light in vacuum, n is refractive index of the prism and θ is the half-angle between the laser beams inside the prism. The right angle prisms with $n = 1.5 - 2.6$ were used. Amorphous As-S-Se based photoresist with refractive index $n_1 = 3.2$ at $0.488 \mu\text{m}$ was used for the recording of surface-relief gratings. After recording, wet etching of the photoresist was

performed to obtain a surface-relief grating. The grating period and profile were measured by AFM. If the recording was performed in air ($n=1$) and the angle between the beams was equal to 90° , a grating with a period of $0.345 \mu\text{m}$ was obtained. If the intersection of the laser beams is performed in a prism with a refractive index of 1.75, a grating period of $0.197 \mu\text{m}$ was obtained. The application of a prism as an immersion medium decreases the period of the recorded grating n times. The transmission, reflection and polarization properties of the subwavelength transmission gratings in As_2S_3 amorphous films were studied. The angular selectivity of holographic recording in amorphous chalcogenide thin films has been improved significantly by a decrease of grating period.

SURFACE RELIEF FORMATION DURING HOLOGRAPHIC RECORDING

U.Gertners and J.Teteris

The key element for the production of surface-relief holographic optical elements is photoresist or light sensitive material. Changes of the chemical properties induced in resist material by light or e-beam exposure enable the surface relief structuring by *wet* or *dry* etching. Therefore this process includes two steps: recording and development by etching. Recently a number of organic and inorganic materials have been studied for direct surface relief formation during the exposure process by a light or e-beam. It is very promising for practical application enabling the possibility to simplify technology of the surface patterning.

In this research the study of direct holographic recording of the surface-relief gratings on amorphous As-S and As-S-Se films has been presented from the side of light polarization. Because of direct surface relief formation, efficiency of the relief formation also depends on softening temperature of the sample what in this case is about 170°C . Results have shown that the surface relief formation efficiency is many times larger in case of extra softening by additional incoherent light during recording. The mechanism of the direct recording of surface relief on amorphous chalcogenide films based on the photoinduced plasticity has been discussed.

NANOSTUCTURED SURFACES FOR OPTICAL ANTIREFLECTION

J.Aleksejeva and J.Teteris

The demand for optically antireflective layers during last years has increased. Particularly such high demand is in the branches where large surfaces will be covered (greenhouses, solar cells etc.) At present work we show the results obtained for surface patterning consisting of nano-structural elements smaller than incident light wavelength. The decreasing of light reflection for such structures results from light diffraction on above mentioned structures. Nanostructured antireflective elements are formed by holographic recording in chalcogenide photoresist. The next step is electrochemical growing of Ni shim used as a stamp for printing of nanostructures into organic polymer – laminate which can be pasted on glass surface. Nano-relief surface are transferred into transparent polymer films by hot embossing at $100\text{-}120^\circ\text{C}$ or UV curing.

The nanostructures with a sizes less than 100 nm were fabricated by immersion holography in amorphous chalcogenids, organic azobenzol and photopolymer films. For recording UV CW lasers with 325nm wavelength (He-Cd laser) and 266nm (frequency doubler pumped by Verdi-8 laser 532 nm radiation) and visible region lasers (442 and 532 nm) were used. The conventional photoresist technology and as well as direct relief

fabrication method - surface relief formation in amorphous films during the holographic recording were used. For holographic grating forming was used Two-beam holographic setup for 1D, and three- and more beams holographic setup with possibility to change polarization state for each beam for 2D structural element recording were used.

Optical properties of nanostructures as transmission, reflection, diffraction efficiency and their spectral dependences were studied. The form and size of nanostructures were studied by AFM.

OPTICAL RECORDING IN AZOBENZENE CONTAINING POLYMER FILMS

A. Gerbreders and J. Teteris.

Preparation method and optical properties of spiropyran and polymer composite thin films was studied. Polyvinyl acetate, polymethylmetacrylate and copolymer of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) were used as base for composite.

The transmission spectra of composites were measured before and after illumination by laser beams with different wavelengths. Transmission of composite film of merocyanine form was measured by laser beam wavelength 532 nm in dependence on beam intensity.

The holographic recording of diffraction gratings was performed by different laser lines (325, 532 nm). During recording the diffraction efficiency was measured in transmission mode. The profiles of the gratings area were analyzed by AFM microscope.

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14. **J.Aleksejeva**, **J.Teteris**, *Surface relief grating recording in azo polymer films*, IOP CS MSE, **49** (2013) 012024.
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17. **E.Potanina**, **J.Teteris**, *Photo-induced formation of surface relief in amorphous As₂S₃ films*, IOP CS MSE, **49** (2013) 012046.
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2. **U. Gertners**, **J.Teteris**, Gaismas inducētās izmaiņas amorfās As₂S₃kārtniņās (Photo-induced changes in amorphous chalcogenide films), Book of Abstracts, p.18.
3. **I.Rundāne**, **J.Teteris**, Fotoinducētais dichroisms As-S savienojumu plānās kārtniņās (Photoinduced dichroism in thin As-S films), Book of Abstracts, p.47.
4. **A.Kiseļovs**, **J.Teteris**, Hologrāfiskais ieraksts As-S kārtniņās ar 473 nm lāzeri (Holographic recording in As-S layers with 473 nm laser), Book of Abstracts, p.45.
5. **K.Klismeta**, **J.Teteris**, Fotoinducētās masas pārvietošanās virziena atkarība no gaismas polarizācijas organiskos un neorganiskos fotohromos materiālos (The dependence on light polarization of photoinduced mass transfer`s direction in organic and inorganic photochromic materials Book of Abstracts, p.17.
6. **E.Potanina**, **J.Teteris**, Fotoinducētā virsmas reljefa veidošanās As₂S₃ kārtniņās (Photoinduced formation of surface relief in As₂S₃ films), Book of Abstracts, p.16.
7. **A.Gerbreders**, A.Bulanovs, **J.Teteris**, Ag nanodaļiņas veidošanās hologrāfiskā ieraksta procesā (Ag nanoparticles formation in the process of holographic record), Book of Abstracts, p.15.
8. **M.Jirgensons**, **J.Teteris**, Fotoinducētā virsmas reljefa veidošanās masīvā As₂S₃ (Photoinduced surface relief formation in bulk As₂S₃), Book of Abstracts, p.46.

International Conference FM&NT2012 (Functional materials and nanotechnologies 2013) Tartu, Estonia, April 21-24, 2013:

9. **J.Teteris**, Optical Field-Induced Surface Patterning of Soft Materials, Book of Abstracts,.OR-6.
10. **U.Gertners, J.Teteris**, Optical-field induced surface-relief formation phenomenon in thin films of vitreous chalcogenide semiconductors, Book of abstracts,. PO-88.
11. **M.Reinfelde, J.Teteris**, Influence of grating period on surface relief hologram recording efficiency in amorphous As_2S_3 and $As_{40}S_{15}Se_{45}$ films, Book of abstracts,. PO-111.
12. **K.Klismeta, J.Teteris**, Photoinduced mass transport in azo-benzene containing compounds, Book of abstracts,. PO-122.
13. **E.Potanina, J.Teteris**, Photo-induced formation of surface relief in amorphous As_2S_3 films, , Book of abstracts, PO-147.
14. **A.Gerbreders, A.Bulanovs, E.Sledevskis, V.Gerbreders, J.Teteris**, Photosensitive properties of composite films based on copper chloride in polymer matrix, Book of abstracts,PO-161.
15. **J.Aleksejeva, J.Teteris**, Surface relief grating recording in azo polymer films, Book of abstracts,.PO-165.

International Young Scientist Conference “Developments in Optics and Communications 2013”, Riga, Latvia, April 10-12, 2012:

16. **J.Aleksejeva, J.Teteris**, Surface relief formation in azo-dyed polymers, Book of abstracts, p. 70.
17. **V.Kolbjonoks, V.Gerbreders, J.Teteris, A.Bulanovs**, Investigation of As-Se-S thin films as electron beam lithography multilevel resists, Book of abstracts, p. 126.
18. **K.Klismeta, J.Teteris**, The dependence of light polarization of photoinduced mass transport direction in organic and inorganic photochromic materials, Book of abstracts, p. 72.
19. **E.Potanina, J.Teteris**, Photo-induced formation of surface relief in As_2S_3 films, Book of abstracts, p. 68.

3rd International *Advances in Applied Physics and Materials Science* Congress (APMAS2013), Antalya, Turkey, April 24-28, 2013:

20. **J.Teteris**, Optical Field-Induced Surface Patterning of Amorphous Chalcogenide and Azobenzene Containing Organic Polymer Films, Poster 794.

56th Scientific Conference for Young Students of Physics and natural Science – Open Readings 2013, Vilnius, Lithuania, March 20-23:

21. **J.Aleksejeva, J.Teteris**, Holographic recording in azocopolymers, Book of abstracts, p.30.

6th International Conference on Amorphous and Nanostructured Chalcogenides (ANC-6), Brasov, Romania, 24-28 June, 2013:

22. **J.Teteris**, Photoinduced mass transport phenomenon in soft materials, Book of abstracts, p. 12. (Invited).
23. **U.Gertners, J.Teteris**, Optical-field Induced Surface-relief Modification ion Amorphous As_2S_3 Films Book of abstracts, p. 28.
24. **K.Klismeta, J.Teteris**, Mass transport in azo-benzene containing compounds induced by polarized laser light, Book of abstracts, p. 32.
25. **E.Potanina, J.Teteris**, Photo-induced formation of surface relief in amorphous As_2S_3 films, Book of abstracts, p. 39.

26. **J.Aleksejeva, J.Teteris**, Surface relief patterning in azo-dye containing organic polymers, Book of abstracts, p. 23.
27. **A.Gerbreders, A.Bulanovs, E.Sledevskis, V.Gerbreders, J.Teteris**, Optical recording in polymer-copper chloride films, Book of abstracts, p. 15.

The 23rd International Congress on Glass, Prague, Czech Republic, July 1-5, 2013:

28. **M.Reinfelde, M.Jirgensons, J.Teteris**, Light-field induced surface patterning of chalcogenide glasses Book of abstracts, p. 290, (P403).

25th International Conference on Amorphous and Nano-crystalline Semiconductors „ICANS25”, August 18-23, 2013, Toronto, Canada:

29. **J.Aleksejeva, M.Reinfelde, J.Teteris**, Direct Surface Relief Patterning of Azo-polymers Films via Holographic Recording, Book of abstracts, p.116.
30. **J.Teteris**, Relationship between Photo-induced Surface Relief Formation and Birefringence in Soft Materials, Book of abstracts, p.20.
31. **M.Reinfelde, J.Teteris, E.Potanina**, Surface Relief Grating Formation in Amorphous $As_{40}S_{15}Se_{45}$ and As_2S_3 Films under 0.532 μm Illumination, Book of abstracts, p.6.

SPIE 2013 Optics +Photonics, 25-29 August 2013, San Diego, USA:

32. **U.Gertners, Z.Alute, E.Potanina, J.Teteris**, Optical-field induced volume- and surface-relief formation phenomenon in thin films of vitreous chalcogenide semiconductors, P8836-33.

15th International Conference-School „Advanced materials and Technologies”, 27-31 August 2013, Palanga, Lithuania:

33. **U.Gertners, J.Teteris**, Optical-Field Induced Volume- and Surface-Relief Formation in Thin Films of Chalcogenide Semiconductors, P49, p.84.
34. **K.Klismeta, J.Teteris, J.Aleksejeva**, The Direction of Photoinduced Mass Transport in Azobenzene Containing Compounds, P68, p/105.
35. **E.Potanina, J.Teteris**, Photoinduced Formation of Surface Relief Gratings in Amorphous As_2S_3 Films, P65, p.102.

10th International Conference HoloExpo 2013, 17-18 September 2013, Moscow, Russia:

36. **M.Reinfelde, J.Teteris**, Light induced surface relief grating formation in amorphous chalcogenides, Proceedings p.196-204.
37. **J. Aleksejeva and J. Teteris**, Surface relief grating formation in azo-dye containing functional polymers, Proceedings p.292-297.

3rd International Conference on Materials and Applications for Sensors and Transducers IC-MAST, Prague, Czech Republic, 13-17 September 2013:

38. **A.Gerbreders, A.Bulanovs, E.Sledevskis, Vj.Gerbreders, J.Teteris**, Optical properties of composite films based on copper chloride in PMMA matrix, Abstracts book, P3P26.

12th International Conference on Laser Ablation, Ischia, Italy, October 6-11, 2013:

39. **J.Teteris**, Optical Field-induced Surface Patterning of Amorphous Chalcogenide and Azobenzene Containing Polymer films, Book of abstracts, P1-11, p.120.

LABORATORY OF SURFACE PHYSICS

Head of Laboratory Dr.habil. phys. J.Maniks

RESEARCH AREA AND MAIN PROBLEMS

The research interests are focused on problems related to structure, micromechanical and optical properties of surfaces, interfaces and thin films of advanced materials for micro/nanotechnologies (e.g. oxides, halides, metals, alloys, and composite systems). Research area includes development of methods for surface modification of functional materials and studies of surface and interface effects on properties. The research is based on methods of micro- and nanoindentation, AFM, SEM and XRD.

MAIN RESEARCH TOPICS

- Modification processes of structure and micromechanical properties of functional materials, such as wide band-gap oxides (MgO), alkali halides (LiF) and carbon materials (HOPG and polycrystalline graphite) under irradiation with high energy (MeV-GeV) ions.
- Micro- and nano-mechanical characterization of surface layers, thin films and interfaces of advanced materials.

Scientific Staff

6. Dr.habil.phys., emeritus J.Maniks
7. Dr.phys. F.Muktepavela
8. Dr.phys. I.Manika

Students

1. R.Grants
2. L.Brauna

PhD Students

Mg.phys. R.Zabels

Technical Staff

A.Pētersons

Scientific visits abroad

1. Dr.F.Muktepavela, Iib-2013, Halkidiki, Greece (6 days)
2. R.Zabels, REI-17, Helsinki, Finland (6 days)
3. Dr.I.Manika, FM&NT 2013, Tartu, Estonia (6 days).

Visitors from Abroad

1. Prof.K.Schwartz, GSI, Darmstadt, Germany (6 days).

COOPERATION

Latvia

Daugavpils University, Innovative Microscopy Centre
Institute of Physics, University of Latvia (Dr.A.Shisko).

Germany

GSI, Darmstadt, (Prof. K.Schwartz).

Kazakhstan

L. Gumilyov Eurasian National University (Dr.A.Dauletbekova)

Russia

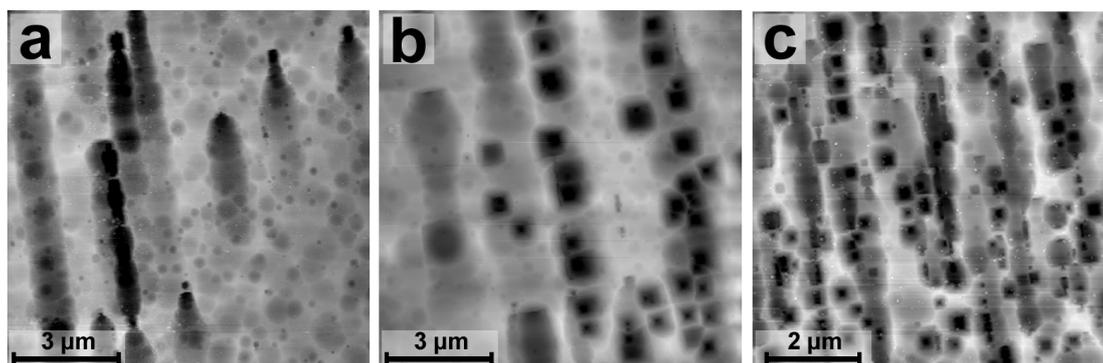
Institute of Solid State Physics RAN, Chernogolovka (Prof.B.Straumal, Dr.V.Sursajeva)

MAIN RESULTS

MeV–GeV ION INDUCED DISLOCATION LOOPS IN LiF CRYSTALS

R. Zabels, I. Manika, K. Schwartz, J. Maniks, R. Grants

Formation of prismatic dislocation loops and evolution of dislocation structure in LiF crystals irradiated with swift ^{238}U and ^{36}S ions of specific energy 11 MeV/u at doses up to 10^{13} ions cm^{-2} has been investigated using nanoindentation, chemical etching, AFM, SEM and X-ray diffraction.



AFM images of dislocation etching pits in far-standing (a) and overlapping tracks ((b) and (c)) of 2.2 GeV uranium ions in LiF crystals, irradiated to fluences 10^8 , 10^9 and 5×10^9 , correspondingly. Dislocations were revealed by selective chemical etching of irradiated samples cleaved along the ion path.

It has been shown that prismatic dislocations are formed in the initial stage of track overlapping (fluences 10^9 U cm^{-2} and 10^{10} S cm^{-2}). The diameter of dislocation loops reaches 600–1000 nm for U ions and 200 nm for S ions. The dislocations induced by heavy ions (U), which create track core damage, are arranged in rows along the direction of ion tracks. Further evolution of dislocation structure with increasing the fluence results in formation of mosaic-type nanostructure with low-angle boundaries between sub-grains. In the case of S ions, the energy loss of which is below the threshold energy loss (10 keV/nm) for track core damage, a structure, consisting of freely distributed dislocation loops is created. Both the dislocation-rich structure and ion-induced nanostructure, which contain numerous strong obstacles for dislocations, exhibit high hardness. The mechanisms of formation, growth and self-organized ordering of dislocations in the stress field of ion tracks have been discussed.

SCI PUBLICATIONS

1. A.Dauletbekova, K. Schwartz, M.V. Sorokin, **J. Maniks**, A. Rusakova, M.Koloberdin, A. Akilbekov, M. Zdorovets. LiF crystals irradiated with 150 MeV Kr ions: peculiarities of color center creation and thermal annealing Nucl. Instr. and Meth. in Phys. Res. B295 (2013) 89-93.
2. **I. Manika, J. Maniks, R. Zabels**, K. Schwartz, **R. Grants**, A. Dauletbekova, A.Rusakova, M. Zdorovets. Modification of LiF structure by irradiation with swift heavy ions under oblique incidence. IOP Conf.Series:Materials Science and Engineering 49 (2013) 012011
3. **J Maniks, R Zabels**, R Merijs Meri, J Zicans. Structure, micromechanical and magnetic properties of polycarbonate nanocomposites. IOP Conf.Series:Materials Science and Engineering 49 (2013) 012012
4. V.Vinciunaite, A.Grigonis, A.Medvid, **R.Zabels**. Changes in amorphous hydrogenated carbon films by ultraviolet and infrared laser irradiation. Acta Physica Polonica A 123 (5) (2013) 874-876. DOI: 10.12693/APhysPolA.123.874.

LECTURES ON CONFERENCES

International Conference on Functional materials and Nanotechnologies FM&NT 2013, 21–24 April 2013, Tartu, Estonia.

1. **R. Zabels, I. Manika**, K. Schwartz, **J. Maniks, R. Grants**, Structural and micromechanical changes in MgO after high-dose irradiation with swift heavy ions. Abstracts PO- 26
2. **J Maniks, R Zabels**, R Merijs Meri, J Zicans. Structure, micromechanical and magnetic properties of polycarbonate nanocomposites. Abstracts PO-51
3. **I. Manika, J. Maniks, R. Zabels**, K. Schwartz, **R. Grants**, A. Dauletbekova, A.Rusakova, M. Zdorovets. Modification of LiF structure by irradiation with swift heavy ions under oblique incidence..Abstracts PO-52

International Conferece on Radiation Defects in Insulators (REI- 17), 30 June-5 July, 2013, Helsinki, Finland

4. **R.Zabels, I.Manika**, K.Schwartz, **J.Maniks, R.Grants**. MeV-GeV ion induced dislocation loops in LiF crystals, Abstracts PB-11
5. **J.Maniks, L.Grigorjeva, R.Zabels, D.Millers**, I. Bochkov, J. Zicans, T. Ivanova, J. Grabis. Swift heavy ion induced modifications of luminescence and mechanical properties of polypropylene/ZnO nanocomposites, Abstracts PA-13.

XIV Intern. Conf. Intergranular and Interphase Boundaries in Materials. (Iib2013) 23-28 June 2013, Halkidiki Greece

6. **F. Muktepavela, R. Zabels**, V. Sursajeva, L. Grigorjeva, K.Kundzins. Adhesion processes on interfaces and grain boundaries during sintering of ZnO powders with different morphology. Book of Abstracts, p.183.
7. V.Sursajeva, **F.Muktepavela**. Flat grain boundaries migration. . Book of Abstracts, p.177.

**29th Scientific Conference,ISSP, University of Latvia February 20 – 22,
2013, Riga, Latvia**

8. **R.Zabels, R.Grants** Structural changes in MgO crystals under irradiation with swift Au and N ions. Abstracts P.26.
9. L.Brauna, **R.Grants** Fluence effect on dislocation mobility in LiF crystals irradiated with swift ^{36}S ions . Abstracts P.78.
10. A.Shishko, **F.Muktepavela**, A.Klukins, E.Platacis, A Sobolevs. The effect of diverter poloidal magnetic field on the liquid metal flow Abstracts P.62

LABORATORY OF ORGANIC MATERIALS

Head of laboratory Dr. phys. M.Rutkis

RESEARCH AREA AND MAIN PROBLEMS

The fundamental and applied research of organic molecules, materials and their structures are conducted by the laboratory. In most cases the objects of investigations are original organic compounds synthesized by Latvian chemists. The main research goal of laboratory is to develop knowledge about the structure - properties relationship of organic materials for next generation electronics and photonics. Based on concepts derived from these studies, new materials with improved properties are designed in close cooperation with the Latvian chemists. Assessment and demonstration of possible applications of the novel developed materials is an important task of the laboratory. Trained human resources, generated knowledge and technology within the laboratory are a base for development of organic electronics and photonics in Latvia.

Scientific Staff:

Mārtiņš Rutkis	Dr.phys.
Lilīta Gerca	Dr.chem.
Oskars Vilītis	Dr.phys.
Aivars Vembris	Dr.phys.
Andrejs Tokmakovs	MSc.
Andrejs Jurgis	
Jānis Busenbergs	
Mikelis Svilans	

Students:

Mārtiņš Narels	BSc
Santa Popova	
Zane Kalniņa	
Igors Mihailovs	BSc
Arturs Bundulis	

PhD students:

Elīna Laizāne	MSc.
Jānis Latvels	MSc.
Edgars Nitišs	MSc.
Kaspars Pudžs	MSc.
Raitis Gržibovskis	MSc.

Research topics:

- Quantum chemical investigation of structure and properties of chromophores;
- Design of thin films;
- Energy structure of thin films;
- Electrical and photoelectrical properties;
- Nonlinear optical phenomena;
- Stimulated emission;
- Electroluminescence in thin films;
- Optically induced switching;

Research methodology within a laboratory:

- Quantum chemical modelling by Gaussian 09, GaussView 5.0 and HyperChem 8.0 software packages;

- Deposition of organic thin films by thermal evaporation in vacuum, spin coating, blade casting, Langmuir– Blodgett technology, self-assembled monolayers;
- Space charge limited current, time of flight and carrier extraction by linearly increasing voltage methods are used for acquiring electrical properties of thin films;
- Investigation of energetic structure is done by temperature modulated space charge limited current method, Kelvin probe and photoconductivity measurements;
- Determination of linear optical parameters by absorption and reflection spectroscopy and M-line method;
- Investigation of light emission properties by luminescence, stimulated emission and electroluminescence spectral methods;
- Characterisation of nonlinear optical properties by hyper Rayleigh scattering, optical second harmonic generation, Maker fringe, Kurtz powder, Teng-Man ellipsometric, attenuated total reflection and Mach – Zehnder interferometric methods.

Scientific projects of the Latvian Council of Sciences:

10.0032	„Development of research and technology potential for elaboration of new and nanostructured materials and related applications.” subproject „Supramolecular nanostructuring of photonic materials – theoretical modeling and experimental investigations” (2010-2013)
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National Research Program in Materials Science and Information Technologies IMIS (2010-2014):

Project No.1 “Multifunctional materials for high-tech applications in conversion of radiation energy, information recording, storage, transfer and processing”

Project No.6 “Graphene, modified graphene and graphene containing composites for surface coatings, nanodevices, sensors and energy conversion.”

ERAF projects of the activity 2.1.1.1.”Support of science and research”:

No.2010/0308/2DP/2.1.1.1.0/10/APIA/VIAA/051, “Development of Polymer EO modulator prototype device”

No. 2010/0252/2DP/2.1.1.1.0/10/APIA/VIAA/009, “Materials and its tandem structure for solar cells” (2010-2013)

ESF project of the activity 1.1.1.2 “Attraction of Human Resources to Science”:

No.2013/0045/1DP/1.1.1.2.0/10/APIA/VIAA/018 “Design and investigation of low molecular weight glass forming organic compounds with use in photonics”

INTERNATIONAL PROJECTS:

1. EC 7F project: „*Waste heat to electrical energy via sustainable organic thermoelectric devices - H2ESOT*”
2. Latvian – Lithuanian – Taiwan partnership program project: „*Synthesis and studies of organic electroactive materials for effective and reliable optoelectronic devices*”

3. “Osmoze” – cooperation programme between France and Latvia for the development of science and technology: Project „*Phthalocyanine architectures for sensor application*” (2012-2013)

COLLABORATION:

Latvia:

- Riga Technical University;
- Institute of Organic Synthesis;
- Institute of Physical Energetics;
- Daugavpils University.

Lithuania:

- Vilnius University (Prof. S. Jursenas);
- Kaunas University (Prof. J. V. Grazulevicius);
- Center for Physical Sciences and Technology (Prof. L. Valkunas un Prof. V. Gulbinas).

Taiwan: National Sun Yat-sen University (Dr. Li-Yin Chen).

France: Institut des Nanosciences de Paris (Prof. N. Witkowski).

England: Nottingham University (Prof. S. Woodward).

Germany: Julius-Maximilians Universität Würzburg (Prof. J. Pflaum).

Bulgaria: Institute of Organic Chemistry, Bulgarian Academy of Sciences (Prof. V. Dimitrov).

Moldova: Universitatea Tehnică a Moldovei (Prof. A. Casian).

AVARDS:

Latvian Academy of Science award for Latvian science major breakthrough in practical applications of the year 2013:

Synthesized and studied the original structure organic glasses for use in photonic devices

MAIN RESULTS

Light emitting and electrical properties of pure amorphous thin films of organic compounds containing 2-tert-butyl-6-methyl-4H-pyran-4-ylidene

Santa Popova, Kaspars Pudzs, Janis Latvels, Aivars Vembris

Low molecular weight organic compounds which make thin films from organic solutions would be a great benefit in future organic light emitting systems. Two most important advantages should be mentioned. First – repeatability of synthesis of small molecules is better than of polymers. Second – wet casting methods can be applied.

In this paper we present optical and opto-electrical properties of three glassy forming compounds containing 2-tert-butyl-6-methyl-4H-pyran-4-ylidene fragment as a backbone. They have the same N,N-dialkylamino electron donating group with attached bulky trityloxyethyl groups. The difference between these compounds is in an electron acceptor group. One has indandione group, second has barbituric acid and third has malononitrile group.

Absorption maximum of the compounds is between 470 and 500 nm and photoluminescence maximum is between 620 and 670 nm. Spectra are red shifted from the weakest acceptor group to the strongest one. Attached bulky trityloxyethyl groups and tert-butyl group decrease interaction between the molecules. This allows obtaining amplified spontaneous emission in pure thin films. The lowest obtained threshold energy was 95 J/cm^2 .

Electroluminescence efficiency for the system ITO/PEDOT:PSS/Organic compound/BaF/Al was low. For the best compound with malononitrile group it was 0.13 cd/A and 0.036 lm/W. These compounds most probably could be more suitable as a light emitting dopant in electroluminescence layer.

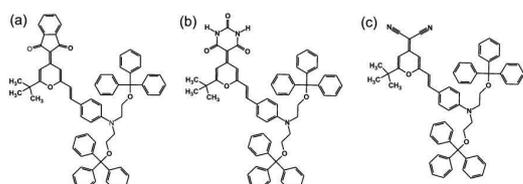


Fig. 1. Chemical structure of the compounds: (a) ZWK-1TB, (b) JWK-1TB and (c) DWK-1TB.

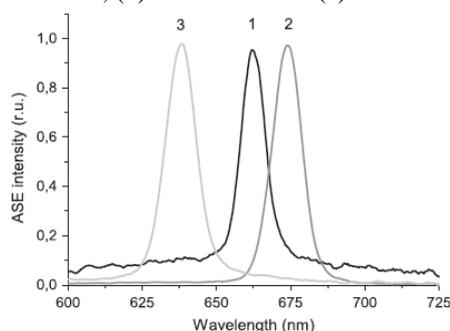


Fig. 3. Amplified Spontaneous Emission spectra of (1) ZWK-1TB, (2) JWK-1TB and (3) DWK-1TB.

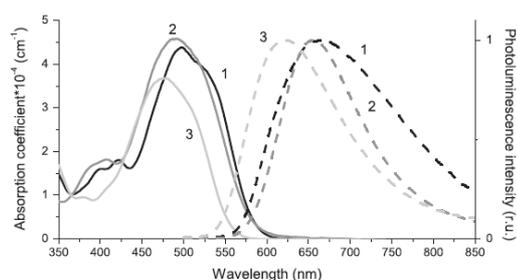


Fig. 2. Absorption (solid line) and photoluminescence (dashed line) spectra of (1) ZWK-1TB, (2) JWK-1TB and (3) DWK-1TB.

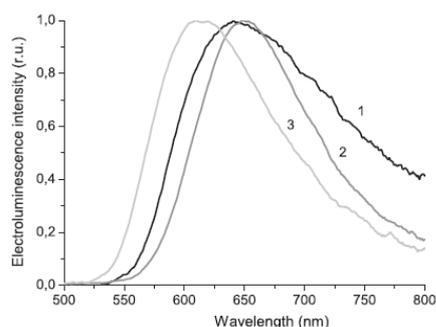


Fig. 4. Electroluminescence spectra of (1) ZWK-1TB, (2) JWK-1TB and (3) DWK-1TB.

The red shift of the absorption maximum in thin films of the investigated molecules corresponds sequentially to ZWK-1TB, JWK-1TB, DWK-1TB as the stronger acceptor group induces a larger red shift. Stokes shift is similar for ZWK-1TB, JWK-1TB and it is larger than for DWK-1TB compound. It could be explained by the longer conjugation length due to the spatially larger acceptor group for ZWK-1TB and JWK-1TB.

Amplified spontaneous emission was observed in pure thin films of the all investigated compounds. The lowest threshold value of 95 J/cm^2 was obtained for DWK-1TB. It is higher in comparison to several micro joules per square centimetre reported for some other materials. Nevertheless to the best of our knowledge till now there are no papers about observation of amplified spontaneous emission in pure films made from DCM derivatives. We succeed it from DWK-1TB compound which is the same DCM compound with the attached bulky trityloxyethyl group. This group increases the distance between the molecules wherewith decreasing intermolecular interaction and photoluminescence quenching.

Electroluminescence efficiency was low for prepared systems where the active layer was made only from investigated compounds. One of the reasons could be unbalanced charge carrier injection which could be improved by adding hole or electron

blocking layer. Another reason could be small photoluminescence quantum yield. Previous experiments with similar compounds showed only a few percent of it. The quantum yield could be increased by doping these compounds in a matrix which give the possibility to use investigated compounds as light emitting dopants in electroluminescence layer.

Electrooptic coefficient measurements by Mach Zehnder interferometric method: application of Abelès matrix formalism for thin film polymeric sample description

E. Nitiss, M. Rutkis, M. Svilans,

Nonlinear optical (NLO) polymers have drawn considerable attention in the last couple of decades due their potential for applications in electrooptic (EO) devices. Such organic EO materials are likely substitutes for the traditional inorganic ones, since they possess the advantages of easier processability, lower costs and higher nonlinearity coefficients. High NLO activity is a most important material prerequisite for further successful application in EO devices. Therefore evaluation of this property is an important task for new material development. The most popular techniques used for measurement of EO coefficients are Teng – Mann reflection ellipsometry, attenuated total reflection (ATR) and Mach Zehnder interferometry (MZI) [3]. All of them possess some significant drawbacks. The widely used Teng – Mann technique can provide good measurement results of effective EO coefficient r_{ef} . However, this technique is limited when it comes to determining both r_{13} and r_{33} independently. As r_{ef} is a function of r_{13} and r_{33} , the r_{33}/r_{13} ratio also needs to be known. In contrast, with ATR r_{13} and r_{33} can be determined independently, however this method is quite complex and must be performed with high precision. In spite of high sensitivity to acoustic and mechanical vibrations MZI techniques – both in transmission or in reflection mode – are being applied more and more often. However researchers using the MZI technique in transmission mode have mostly excluded from their considerations multiple internal reflections and sample thickness change by electrostriction and piezoelectric effects. According to our observations, these effects can greatly contribute to the EO modulated AC signal maximal amplitude and location of that maximum in MZI phase shift scan (see Fig. 1). These effects become crucial when one would like to obtain both EO coefficients r_{13} and r_{33} from the EO modulated signal amplitude dependence on light propagation angle in the poled sample. The light intensity and phase transmitted by the multilayer EO sample can be described by Abelès matrix formalism. An explicit analytical solution to EO modulations for a simple system in which only one layer is of thickness comparable to light wavelength has been shown earlier. However, when expanding the system by adding glass and air layers and including thickness modulation in polymer layer, the explicit analytical solution becomes too complicated.

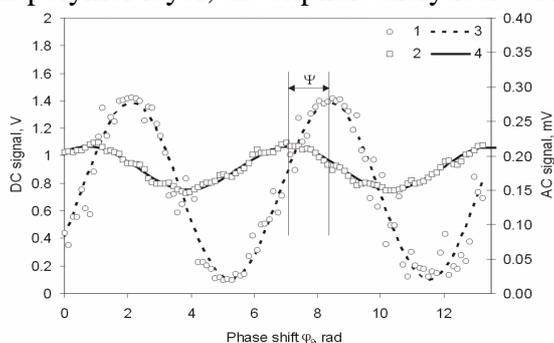


Fig. 1. Typical EO measurement performed at 8° incidence angle with s polarized light: 1 – I_{DC} signal

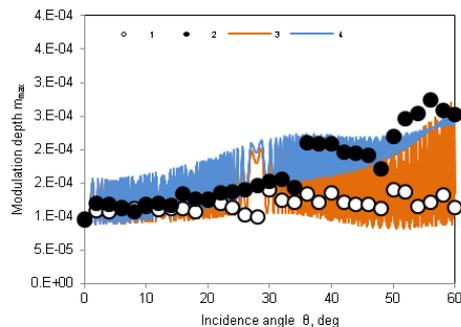


Fig. 2. Modulation depth dependence on incidence angle in MZI in transmission

experimental data, 2 – I_{AC} signal experimental data, 3
- I_{DC} signal sine fit, 3 - I_{AC} signal sine fit, Ψ – AC and
DC signal maxima phase difference

configuration for sample 2: 1, 2 – experimental
data for s and p polarization, respectively 3, 4 –
MatLab fit to functions based on Abelès matrix
formalism for s and p polarization,
respectively.

With this work we have demonstrated that both EO coefficients (r_{13} and r_{33}) of poled polymer films can be determined by applying Abelès matrix formalism to the interpretation of experimental MZI data of a sandwich sample structure at different incidence angles (see Fig. 2 for data fit). Using a simple MZI reflection technique we have shown that for PMMA+DMABI 10wt% polymer films, thickness changes due to an applied electric field influence the detected modulation depth and therefore must be taken into account. Moreover, if an air gap is formed in the sample, the modulated signal in the MZI is usually dominated by the air gap thickness modulation. Experimental data fits show that thickness modulations of an air gap result in beam intensity modulations which are at least one order larger in amplitude than those of the polymer layer. In this case, the thickness modulations of the air gap also override the EO modulations of polymer layer, so that the EO coefficients for such a system cannot be reliably determined. For a sample structure that has no air gap the modulated signal in the MZI is mainly caused by EO modulations. The proposed experimental procedure and data treatment for determining the EO coefficients resulted in values of $r_{13}=0.19\pm 0.02$ pm/V and $r_{33}=0.55\pm 0.06$ pm/V for a poled PMMA+DMABI 10wt% polymer film.

Poling Induced Mass Transport in Thin Polymer Films

Edgars Nitiss, Eduards Titavs, Karlis Kundzins, Andrej Dementjev, Vidmantas Gulbinas, Martins Rutkis

In this study we report investigation of the polymer film morphology modifications during their corona poling for fabrication of nonlinear optically (NLO) active materials. We demonstrate that at certain poling conditions surface and spatial inhomogeneities in the poled area of the sample appear (see Fig. 1. And 2.).

Formation of surface irregularities was observed by reaching threshold poling temperatures at high poling fields for all used host polymers. Appearance of irregularities may be controlled by prepoling and poling conditions. A certain prepoling procedure helps to avoid formation of irregularities. It involves the film heating to temperatures higher than the poling temperature for a short period of time with no poling field applied. This approach helps to suppress formation of inhomogeneities for PMMA, PS and PSU thin films doped with DMABI and increases the effective NLO efficiency. Optimal poling parameters are demonstrated in Fig. 3. We also demonstrate that greater grid to sample distances additionally help to avoid irregularities, while keeping the poling efficiency unaffected.

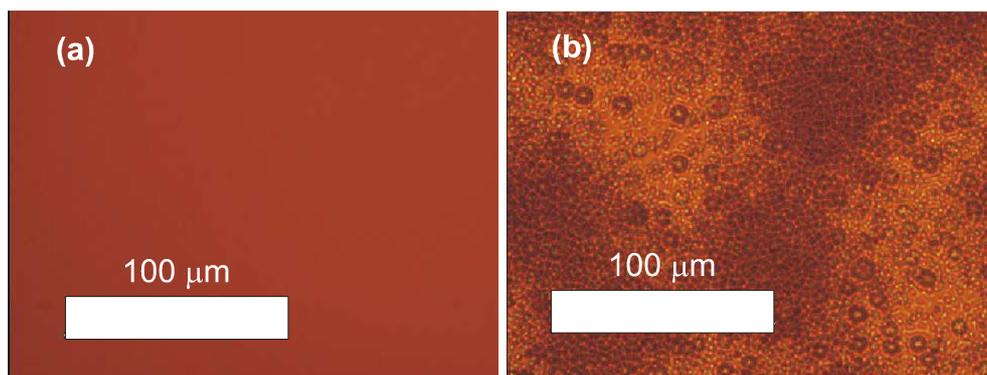


Fig. 1. Optical images of the unpoled (a) and poled (b) regions of PMMA+DMABI (10wt%) thin film

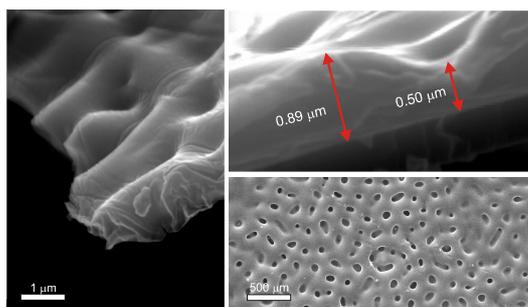


Fig. 2. Electron microscope image of poled part of PMMA+DMABI (10wt%) thin film.

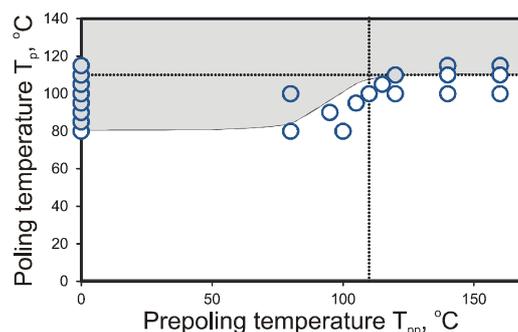


Fig. 3. The “inhomogeneity” chart: surface condition at respective prepoling T_{pp} and poling T_p temperatures. The filled circles represent the samples, which have changed their surface morphology, and the empty circles represent the samples which maintained their optical properties. Black dotted lines represent the coordinates of glass transition temperature.

We propose three hypotheses that could explain the effect of surface and morphology changes in the sample during the corona poling. The inhomogeneities in the form of hollows could be formed due to high energy ion bombardment. We have shown that the density of scattering elements or hollows grows if we increase the kinetic energy of the ions which can be done either by increasing grid voltage or decreasing the distance between the grid and sample surface. However, we were not able to observe any changes in the sample morphology in case nonpolar chromophores are dissolved in the host. This suggests that polar molecules are required in the thin film in order to observe formation of inhomogeneities. Thus possibly the changes in the sample morphology are induced by the poling field and chromophore dipole moment interaction which causes mass transport to take place. The mentioned hollows could also be formed by local electrical breakdown in the film. This hypothesis is encouraged by the fact that we were able to observe correlation between the sample conductivity and probability for the changes in sample morphology to take place during the poling. Unfortunately, the mechanism of formation of these inhomogeneities is still unclear.

SCIENTIFIC PUBLICATIONS

1. **E. Nitiss, M. Rutkis, M. Svilans**, Electrooptic coefficient measurements by Mach Zehnder interferometric method: application of Abeles matrix formalism for thin film polymeric sample description, *Optics Communications*, 286, (2013), 357–362, <http://dx.doi.org/10.1016/j.optcom.2012.09.020>
2. **O.Vilitis, E. Titavs, E. Nitiss, M.Rutkis**, Chromophore poling in thin films of organic glasses. 3. Setup for corona triode discharge, *Latvian Journal of Physics and Technical Sciences*, 2013, No. 1, pp. 66-75; DOI: 10.2478/lpts-2013-0004
3. **E. Nitiss, E. Titavs, K. Kundzins, A. Dementjev, V. Gulbinas, and M. Rutkis**, Poling Induced Mass Transport in Thin Polymer Films, *J. Phys. Chem. B*, 2013, 117 (9), pp 2812–2819, DOI: 10.1021/jp310961a
4. **E. Zarins, A. Tokmakovs, Z. Kalnina, V. Kokars, M. Rutkis, A. Ozols, P. Augustovs, K. Lazdovica, V. Kampars**, Thermal, glass-forming, nonlinear optical and holographic properties of "push-pull" type azochromophores with triphenyl

- moieties containing isophorene and pyranilidene fragments, Proc. SPIE 8622, (2013), 86221H doi:10.1117/12.2003085
5. **M. Rutkis, A. Jurgis**, Inspirations for EO polymer design gained from modeling of chromophore poling by Langevin dynamics, Proc. SPIE 8622, (2013), 86220R, doi:10.1117/12.2001361
 6. **E. Nitiss, J. Busenbergs, M. Rutkis**, Optical propagation loss measurements in electro optical host – guest waveguides, Proc. of SPIE Vol. 8772, (2013), 87721L, doi:10.1117/12.2017226
 7. J. Hierrezuelo, R. Rico, M. Valpuesta, A. Díaz, J. M. López–Romero, **M. Rutkis**, J. Kreigberga, V. Kampars, M. Algarra, Synthesis of Azobenzene Substituted Tripod-Shaped Bi(p-phenylene)s. Adsorption on Gold and CdS Quantum-Dots Surfaces, Tetrahedron, 69, 16, 2013, 3465–3474, <http://dx.doi.org/10.1016/j.tet.2013.02.054>
 8. K. Traskovskis, K. Lazdovica, **A. Tokmakovs**, V. Kokars, **M. Rutkis**, Modular approach to obtaining organic glasses from low-molecular weight dyes using 1,1,1-triphenylpentane auxiliary groups: Nonlinear optical properties, Dyes and Pigments 99 (2013) 1044 – 1050 <http://dx.doi.org/10.1016/j.dyepig.2013.08.020>
 9. **S. Popova, K. Pudzs, J. Latvels, A. Vembris**, Light emitting and electrical properties of pure amorphous thin films of organic compounds containing 2-tert-butyl-6-methyl-4H-pyran-4-5 ylidene, Optical Materials 36, 2, 2013, 529-534 <http://dx.doi.org/10.1016/j.optmat.2013.10.025>
 10. **R. Grzibovskis, A. Vembris, J. Latvels**, Photovoltaic properties of glass forming pyraniliden derivatives in thin films, IOP Conference Series: Materials Science and Engineering 49, 2013 012055 doi:10.1088/1757-899X/49/1/012055
 11. **J. Latvels, R. Grzibovskis, A. Vembris, D. Blumberga**, Improvement of Solar PV Efficiency. Potential Materials for Organic Photovoltaic Cells. Environmental and Climate Technologies. Nr.12, 2013, 28.-33.lpp. ISSN 16915208.

LECTURES AT CONFERENCES

SPIE Photonics West, February 2-7, 2013, San Francisco, USA:

1. **M. Rutkis, A. Jurgis**, Inspirations for EO polymer design gained from modeling of chromophore poling by Langevin dynamics, Technical summaries, p. 265
2. E. Zarins, **A. Tokmakovs**, Z. Kalnina, V. Kokars, **M. Rutkis**, A. Ozols, P. Augustovs, A. Belajevs, K. Lazdovica, V. Kampars, Thermal, glass-forming, nonlinear optical and holographic properties of triphenyl group containing molecular glasses of indene-1,3-dione, isophorene and pyranilidene, Technical summaries, p. 266

29th Scientific Conference of the Institute of Solid State Physics, University of Latvia, February 20-22, 2013:

1. **K. Pudzs, A. Vembris**, Determination of charge carrier mobility in thin films of pyraniliden fragment containing compound, Abstracts p.39
2. **S. Popova, A. Vembris**, Optical and electroluminescence properties of molecular glasses modified with tert butyl group and a pyraniliden fragment as a backbone, Abstracts p.41
3. **R. Grzibovskis, K. Pudžs, B. Turovska, M. Rutkis, A. Vembris**, Energetical levels of glass forming pyraniliden derivatives, Abstracts p.42
4. **M. Narels, E. Laizane, A. Vembris**, Influence of temperature on photoinduced properties of azobenzene molecules doped in polymer thin film Abstracts p.40

5. **M. Rutkis, L. Gerca, K. Kundziņš**, Assessment of Langmuir – Blodgett technology capabilities for production of conductive graphene coatings, Abstracts p.100
6. Z. Kalniņa, **A.Tokmakovs, M.Rutkis**, V. Kokars, E.Zariņš, K. Traskovskis, Azobenzene based fragment glassy state forming nonlinear optical material properties research, Abstracts p.38
7. A. Bundulis, **E. Nitišs, M. Rutkis**, Determination of polymer electro optical coefficient by interferometric method using light source phase noise, Abstracts p.87.

9th International Young Scientist Conference „Developments in Optics and Communications” Riga, April 10-12, 2013:

1. **R.Grzibovskis, A.Vembris** Photoelectrical properties of pyraniliden fragment containing compounds in thin films, Book of Abstracts, p.62
2. **K.Pudzs, A.Vembris**, Charge carrier mobility in thin films of glass forming pyraniliden derivatives, Book of Abstracts, p.64
3. **S.Popova, A.Vembris**, Optical and electroluminiscent properties of organic compounds containing barbituric acid, Book of Abstracts, p.138
4. **M.Narels, E.Laizane, A.Vembris**, Impact of temperature on optical switching effect of azobenzene molecules doped in polymer thin films, Book of Abstracts, p.134
5. **E. Nitišs, A. Tokmakovs, M. Rutkis**, Assessment of material refractive index near absorption band using kramers-kronig relations, Abstracts, p. 52
6. Z.Kalnina, **A.Tokmakovs, M.Rutkis**, J.V. Grazulevicius, V. Zilinskaite, D. Gudeika, Tryphey lamino indandione type structures research as nonlinear active materials, Book of Abstracts, p.124

SPIE Optics+Optoelectronics, April 15-18, 2014. Prague, Czech Republic

1. **E. Nitiss, J. Busenbergs, M. Rutkis**, Optical propagation loss measurements in electro optical host - guest waveguides, 8772-59

International Conference on Functional materials and Nanotechnologies FM&NT 2013, April 21 – 24, 2013, Tartu, Estonia:

1. A. Sternberg, L. Grīnberga and **M. Rutkis**, Latvian national instruments for material science and nanotechnologies within a framework of Baltic cooperation, Book of Abstracts, INV-1
2. **K.Pudzs, A Vembris**, Charge carrier mobility in thin films of glass forming low molecular organic compounds, Book of Abstracts, p 227
3. **M.Narels, E.Laizane, A Vembris**, Influence of temperature on photoisomerisation process of polymer films doped by azobenzene derivatives, Book of Abstracts, p 209
4. **S.Popova, A.Vembris**, Optical and electroluminescence properties of terc-butyl group containing piraniliden derivatives, Book of Abstracts, p 196
5. **A.Vembris, R.Grzibovskis, K.Pudzs**, B.Turovska, Energy structure and photoelectrical properties of glass forming pyraniliden derivatives in thin films, Book of Abstracts, p 267
6. **J.Latvels, R.Grzibovskis**, D.Blumberga, I.Maderniece, Photoelectrical properties of DMABI derivatives as materials for solar cells, Book of Abstracts, p 236

9th International Conference on Organic Electronics ICOE 2013, June 17-20, 2013, Grenoble, France:

1. **A.Vembris, R.Grzibovskis, K.Pudzs**, B.Turovska, Photoelectrical properties of amorphous thin films with pyraniliden derivatives, CD, p PC55

2. **K.Pudzis, A.Vembris**, , Determination of charge carrier mobility in amorphous thin films of low molecular weight organic derivatives, CD, p PC40

Gaussian Workshop, Wroclaw, Poland, June 24-28, 2013:

1. **M. Rutkis, A. Jurgis, A. Tokmakovs, I. Mihailovs, A. Ernstsons, L. Skuja**, Comparison of Second-Order Nonlinear Properties of Some 1,3-Indandione Derivatives

Advanced Study Institute NATO (ASI NATO) "Nanomaterials and Nanoarchitectures" and 13th European Conference on Organised Films (ECOF13), 30th June - 7th July and 8th - 12th July, 2013, Cork, Ireland:

1. **R.Grzibovskis, A.Vembris, K.Pudzis**, Photoelectrical properties of pyraniliden fragment containing compounds, Book of Abstracts, P18

15th International Conference–School "Advanced Materials and Technologies", August 27-31, 2013, Palanga, Lithuania

1. **K. Pudzis, A. Vembris, E.Zarins, V.Kokars**, Determination of charge carrier mobility in thin films of indandione group containing azobenzene compounds, Abstracts, p. 94
2. **R.Grzibovskis, A.Vembris**, Photovoltaic effect of pyraniliden fragment containing compounds in bulk heterojunction thin films, Abstracts, p. 170
3. **M. Narels, A. Vembris, E. Laizane**, Polymer Free Volume Model as an Explanation of Photoisomerisation Process in Azobenzene-Doped Polymer Films, Abstracts, p. 99
4. **S. Popova, A.Vembris**, Luminescence Properties of Glassy Forming Organic Compounds Containing Modified Barbituric Acid Group as Electron Acceptor, Abstracts, p. 96
5. **Z. Kalnina, A. Tokmakovs, I. Mihailovs, K.Traskovskis, L. Laipniece, M. Rutkis**, Thermo-induced non-centrosymmetric crystal growth in glassy thin films of azobenzene chromophore, Abstracts, p. 117

Baltic Polymer Symposium, 2013, September 18-21, 2013, Trakai, Lithuania:

1. **M. Rutkis, V. Kokars, V. Kampars**, Low molecular glasses as a promising class of materials for photonic applications, Programme and Abstracts, p. 30

DEPARTMENT OF SEMICONDUCTOR MATERIALS

SEMICONDUCTOR MATERIALS AND SOLID STATE IONICS

Head of Division Dr.phys. A.Lusis

RESEARCH AREAS AND EXPERTISE

- Electrophysics and electrochemistry of specific semiconductor materials, mixed conductors, ion conductors (transition metal oxides, bronzes, metal hydrates, solid electrolytes, nanostructured and porous materials, composites etc.)
- Material preparation methods: thin and thick film technologies, sol-gel process, leaching, sonochemical processes, pyrolysis spray coating, electrochemical deposition
- Material characterization by spectroscopic methods (Raman scattering, Fourier IR, optical and X-ray absorption, EXAFS), electrical and electrochemical impedances, AFM, TGA/DTA, etc
- Solid state ionics:
 - electro-, photo-, thermo-, chemo- or gaso-chromic phenomena in transition metal oxides
 - structural changes due to ion intercalation
 - lattice dynamics and structural and electronic phase transitions
 - solid state reactions at interfaces electrode – solid electrolyte
 - gases and ions sensing phenomena and detection technologies
- Functional coatings and multi layer electrochemical systems
- Hydrogen absorption phenomena in metals, semiconductors and insulators
- Development of hydrogen generation equipment and new nano structured materials for hydrogen storage
- New measurement technologies and instruments with artificial intellect (encl., eNose)
- Development methods and techniques for quality and reliability testing for lead – free joints of PCB
- Hydrogen technologies (production, storage, transportation, application); renewable energy technologies (solar, wind, static electricity, water, microbial fuel cells);
- Development of cathode materials for Lithium thin film batteries;
- Gas sensors and sensor arrays; odour removal with adsorbent and low temperature plasma discharge technologies.
- Tritium analysis

RESEARCH TOPICS

- Ion transfer in solids, over two phase interfaces and composites as well as structural changes due to ion intercalation, lattice dynamics and structural and electronic phase transitions.
- Ion transfer problems related to electro-, photo-, chemo-, thermo-chromic phenomena in transition metal oxides as well as to solid state reactions at interfaces electrode – solid electrolyte.

- Application of electrical and electrochemical impedances for characterization of ionic systems, nanostructured and porous materials, composites.
- Development of nanostructuring methods for functionalization of plate glass and fiber glass surfaces as well investigation influence of ultrasound on leaching processes, pores structure and ion exchange of glass fibers.
- Application of thermal analyses (TGA/DTA) and sorptometry for investigation of porous materials and absorbing capacity of functional species.
- Investigation of stability of materials for electrochemical multi layer systems and electrochromic coatings as well as intergrain activity in solid electrolyte layers based on polymer composites.
- Development methods and techniques for functionalization
- Thin films preparation by magnetron sputtering techniques.
- Development methods and techniques for quality and reliability testing for lead-free joints of printed circuit boards.
- Servicing of common research facilities: thin film vacuum coating machines, TGA/DTA equipment and powerful ultrasound bath-reactor.
- Membranes and membrane/electrode systems for fuel cells and gas filtration.
- The technologies for hydrogen production, storage, transportation, applications in transport and stationary applications; for energy storage and electricity/heat generation; synthesis and research of new materials for hydrogen technologies (electrodes in electrolyzers and microbial fuel cells, structured nanomaterials for photoelectrolysis, hydrogen storage media, polymer membranes and membrane-electrode assemblies for fuel cells);
- Lithium intercalation materials and their application for thin film rechargeable battery; the technologies for electricity generation from renewables (solar, wind, static electricity, water, algae and microorganisms);
- Gas sensors and sensor arrays for gas and odour monitoring; odour removal with adsorbents and corona discharge technologies;
- X-ray Absorption Spectroscopy of functional materials and development of advanced EXAFS data analysis methodologies, based on Molecular Dynamics and Reverse Monte Carlo methods.
- Confocal laser spectromicroscopy.
- The use of high performance computing for functional materials simulations.
- The magnetic ions exchange interaction in the antiferromagnetic oxides MeO-MgO solid solutions were studied using of optical absorption, luminescence, EPR and Raman spectroscopies: exchange interaction between radiation defects and transition metals ions in the dielectric crystals doped with the transition metals ions
- EPR, FTIR, Raman and optical spectroscopies study of human blood after irradiation
- The use of high performance computing for functional materials first principles and Molecular Dynamics simulations.
- Investigations of tritium release properties of neutron multiplier beryllium materials for fusion reactor development. Analysis of tritium distribution in plasma-facing carbon-based components.

Laboratories of Semiconductor Material Department

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Laboratory of EXAFS Spectroscopy –	Head of Laboratory Dr. hab. phys.J.Purans
Laboratory of Hydrogen Energy Materials –	Head of Laboratory Dr.J.Kleperis

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17. IC „Plazma PL”,
18. SIA “Adviser Union”
19. Housing and Environment Department of Riga City Council, Riga,
20. Riga Energy Agency, Riga City Council

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PARTICIPATION IN RESEARCH PROJECTS

Latvian:

1. National Research Program “Innovative multifunctional materials, signal processing and informatic technologies -IMIS”
2. Cooperation project of. Latvian Council of Science SP 10.0032 “Development of research and technology potential for elaboration of new and nanostructured materials and related applications” -1.4. “Functional coatings, processes and technologies for modification physicochemical properties of materials”
3. Cooperation project of. Latvian Council of Science SP 10.0040 “Investigation of Latvian renewable raw materials – flax and hemp products for development of innovative technologies and new functional materials”.
4. National Research Program “Energy and Environment”, Project No.4 “Research of methods for hydrogen production, storage and energy release, and development of prototypes for application in national economy”

5. Grant from Latvian Council of Science No. 09.1195 "Research and development of proton conducting PEEK polymer and composite membranes and catalysts for use in direct methanol and hydrogen fuel cells"
6. Grant from Latvian Council of Science No. 09.1192 "Research of properties and structure of nanosize composite materials for hydrogen storage and electrodes for water electrolysis"
7. "Structure of nano-oxide materials and self-organization in stochastic media "Latvian Government Grant Nr.09.1580 (2010-2012).
- 8.ESF project "Innovative materials for transparent electronics and photonics", No. 2013/0015/1DP/1.1.1.2.0/13/APIA/VIAA/010.
9. ERDF project "Innovative glass coatings", No. 2010/0272/2DP/2.1.1.1.0/10/APIA/VIAA/088.
11. Partners in ERDF Project Nr.2010/0243/2DP/2.1.1.1.0/10/APIA/VIAA/156, RTU PVS ID1524 „Solar thermal energy storage material development using sol-gel and vacuum coating technology” (Head A.Lusis)

International

1. Mutual fundsTaiwan – Latvia – Lithuania cooperation project “Materials and processing development for advanced li ion batteries” (Head G.Bajars)
2. Materials, Physical and Nanosciences COST Action MP0804: "Highly Ionised Pulse Plasma Processes", 2010 - 06.2013 (Head: J. Purans).
3. "OSMOSE" project "Nano-structured test samples for a combined near-field and X-ray microscopy" within the bilateral collaboration programme between France and Latvia.
4. EURATOM project "Production and characterization of laboratory-scale batches of nano-structured ODSFS", No. WP13-MAT-ODSFS-01-01.
5. EURATOM project "Experimental validation of models", No. WP13-MAT-IREMEV-05-01.
Materials, Physical and Nanosciences COST Action MP0804 "Highly Ionised Pulse Plasma Processes".
6. The European joint undertaking “Fusion for Energy” (F4E) work programme 2009 “Test Blanket Modules”. Contract reference: F4E-2009-GRT-030 Action 3. Contract title: “Action 3 - Post Irradiation Examination of Be materials irradiated in HIDOBE-01 campaign”. Project Manager: J.B.J. (Hans) Hegeman (NRG, Petten, the Netherlands). Coordinator at the University of Latvia: Gunta Kizan (Principal investigator: Dr.chem. A. Vitins).

Didactic work at the University of Latvia

1. Master degree course "Solid State Ionics" at Faculty of Chemistry, UL – 4 credit points (G. Vaivars)
2. Course Fizi5028 "Structure and Description of Nanomaterials" at the Latvian University (A.Kuzmin).
4. Course Fizi7009 „Solid State Structure” at the Latvian University (A.Kuzmin).

LABORATORY OF SOLID STATE IONICS

MAIN RESULTS

Lattice dynamics of CdWO₄

J.Gabrusenoks

The first-principle calculations are employed to study lattice dynamics of cadmium tungstate. The equilibrium structure of wolframite-type crystal and lattice vibrations were calculated within the density functional theory using CRYSTAL09 program. The hybrid B3LYP exchange-correlation functional was used.

Cadmium tungstate has wolframite-type structure with monoclinic crystal lattice. The space group of CdWO₄ is P2/c (C_{2h}⁴). In this structure each W atom is surrounded by 6 near O atoms in approximately octahedral coordination [1]. Group-theoretical analysis of the wolframite structures with C_{2h}⁴(P2/c) space group gives the irreducible representations of vibrations as

$$\Gamma=8A_g+10B_g+7A_u+8B_u$$

where A_g and B_g are Raman active, while A_u and B_u are infrared active.

The vibrational modes were calculated theoretically and determined experimentally by Raman and IR reflection spectroscopy.

Calculated and experimentally observed Raman and IR vibrations.

Raman modes

Modes	Calculated, cm ⁻¹	Observed, cm ⁻¹
B _g	83	78
A _g	99	100
B _g	126	118
B _g	145	135
B _g	161	150
A _g	170	179
A _g	244	231
B _g	260	249
B _g	291	271
A _g	328	308
B _g	364	354
A _g	403	390
B _g	519	518
A _g	555	551
B _g	693	691
A _g	718	711
B _g	782	778
A _g	912	902

Infrared modes

Modes	Calculated, cm ⁻¹		Observed, cm ⁻¹	
	LO	TO	LO	TO
A _u		118		
B _u		119	120	106
B _u		153	180	161
B _u		247	245	233
B _u		282		
B _u		291	372	308
A _u		293		
A _u		359		
A _u		415		
B _u		450	468	461
A _u		500		
B _u		569	761	577
A _u		662		
B _u		788	909	786
A _u		877		

The number of A_g and B_g Raman active vibrations exactly corresponds to the number determined on the basis of group-theoretical calculations.

[1] M.Daturi, G.Basca, M.M.Borel, A.Leclaire, P.Paiggio, J.Phys.Chem. B101 4358(1997).

INVESTIGATION OF CARBONIZED LAYER ON SURFACE OF NAALSI GLASS FIBERS

Evalds Pentjuss, Andrejs Lusion, Gunars Bajars and Jevgenijs Gabrusenoks

Glass fiber fabrics are used in dry and wet atmosphere and in water at elevated and changeable temperatures. The changes in environment can initiate processes in the

glass fabric that lead to a new its equilibrium state and changed physical properties. Some of them may be irreversible. It is accepted that interaction of alkali silicate glasses with water or mineral acids proceeds by ionic exchange by diffusion of Na^+ ions to glass surface and H^+ or H_3O^+ from water into the bulk of glass to fill the vacancies of Na^+ ions. It looks that Na^+ ions and H_2O and CO_2 from atmosphere during months form the shell of $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ or its mixture with $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ on the surface of glass fibres. Such shell can be dissolved in water and acids. The heating leads to weight loss associated with decomposition by reaction of $2(\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}) \rightarrow 3\text{Na}_2\text{CO}_3 + \text{CO}_2\uparrow + 5\text{H}_2\text{O}\uparrow$ at temperature over $55\text{-}57^\circ\text{C}$, and dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ over 100°C . There are studied the weight uptake after different thermal treatment of unleached and leached fabrics for K-glass fabric (initial composition of (18-22) Na_2O (3-5) Al_2O_3 (73-79) SiO_2) and powder of leached by water carbonates. The experimental weight-time curves were analyzed using regression technique. There are observed fast uptake of weight during the first tenths of minutes after heating for both types of samples and much slower (hundreds of hours) uptake up to equilibrium weight for unleached samples.

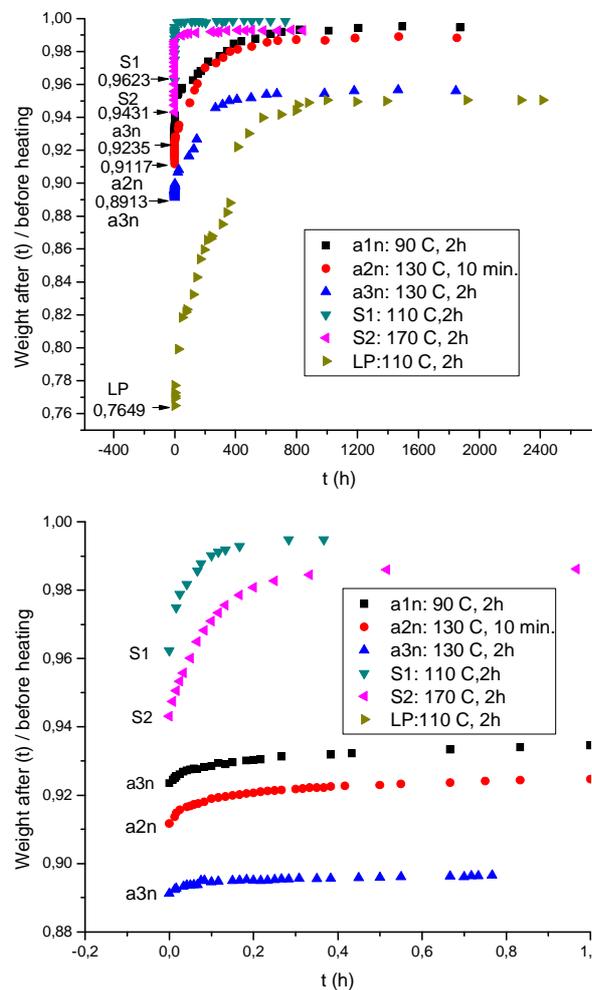


Fig.1. Ratio of fabric weight after and before heating procedure for unleached (a1n-a3n) and leached fabrics (S1, S2), and leached powder (LP) versus time (t)

Analysis indicated that fast weight uptake consist of two simultaneously going processes on surface of shell. One of them should be associated with water absorption, and second, with water diffusion from surface inside the shell. The late uptake should be associated with hydration of bulk of shell. The irreversible weight loss should be associated with loss of Na atoms in evolving process of vapour of H_2O and CO_2 during heating of samples. In a case of leached samples the surface process are much faster.

An increased temperature (170 °C) treatment leads to increase of weight losses and decrease of absorption rate that should be caused by increase of roughness of glass surface. The late slow uptake of weight of leached samples is negligible.

BAST FIBRE FABRICS FUNCTIONALIZATION STUDIES

A. Lusiš, U.Sidaroviča, E. Pentjuss, J. Balodis

Sustainable development of technical textiles is associated with natural (bast) fibers to replace the oil-producing fibers. In this context, it is necessary to carry out studies on the bast fiber fabric (BFF) functionalization technologies for technical applications. The natural fibers as well as fabrics themselves are hydrophobic and porous media. They absorb moisture from environment. It is important for BFF functionalization process and characterization of properties.

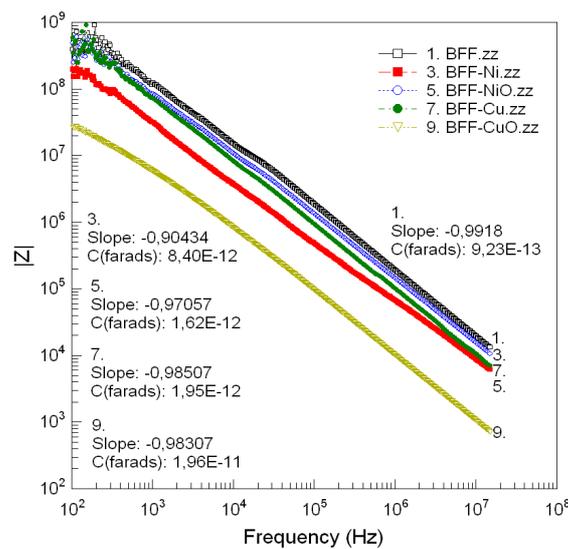


Fig.1. Impedance spectra for dry samples

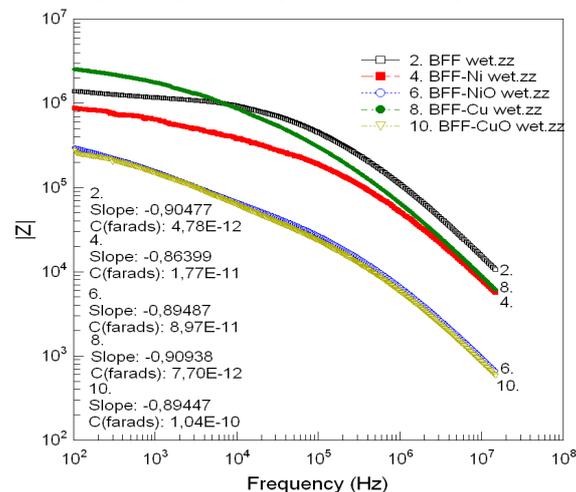


Fig.2. Impedance spectra for wet samples

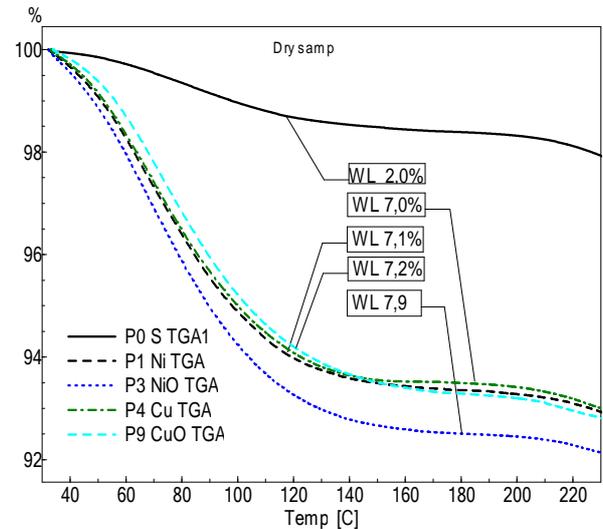


Fig.3. Weight loss for dry samples

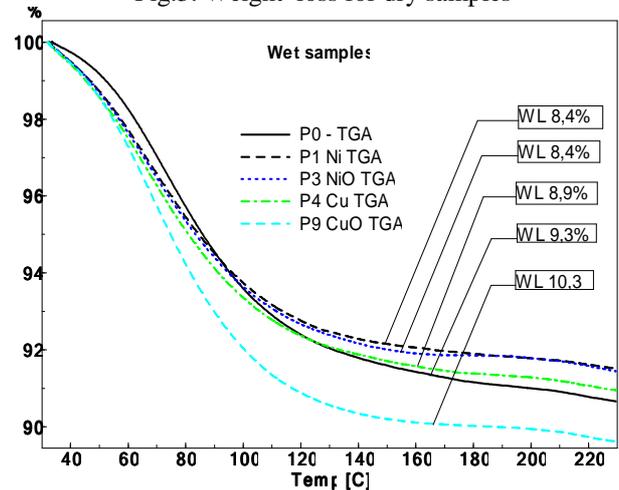


Fig.4. Weight loss for wet samples

Metal and metal oxide coatings are widely used for functionalization of fabrics for different technical applications. To characterize the metal coating is a problem in itself. First of all, to functionalize fibers or fabrics is to examine the content of moisture and its role on physical properties. The impedance spectroscopy (IS) has been used to study moisture in BFF and coated fabrics. The impedance spectra of such samples are complicated due to heterogeneous and nonhomogeneous constitution.

The moisture content has strong influence on impedance modulus $|Z|$ spectra (Fig.1 & 2) and has been measured by weight loss with TGA method (Fig.3 & 4). For dry samples humidity and coating shifts the $|Z|$ to the smaller side resistances (Fig.1). For wet samples (Fig.2) have a significant impact of moisture on the $|Z|$ from 100 Hz to 2 MHz, and $|Z|$ values from 2 MHz to 15 MHz are similar to dry samples. The metal oxide coated BFF have higher water absorption capability then metal coated.

STRUCTURE AND PHOTOCATALYTIC PROPERTIES OF TiO₂-WO₃ COMPOSITES PREPARED BY ELECTROPHORETIC DEPOSITION

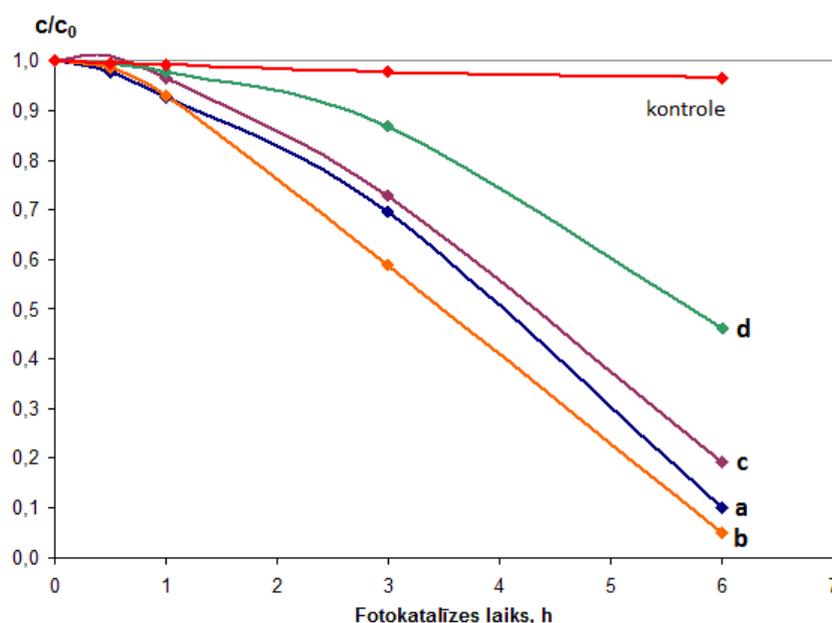
Ineta Liepina, Gunars Bajars, Marcis Rublans, Andrejs Lulis, Evalds Pentjuss,
Janis Balodis, Jevgenijs Gabrusenoks

Due to its photocatalytic capability, low cost and chemically inert properties, TiO₂ is a promising material for water and air contamination treatment technologies. In this work bi-component WO₃ is used as a photo-electron storing material, since the electrophoretic deposition was carried out on steel substrates that might suffer from corrosion. Among other traditional deposition methods (physical vapour deposition, electrochemical vapour deposition, plasma technologies etc.), EPD doesn't require vacuum environment and has the advantages of obtaining coatings with homogenous surface.

TiO₂-WO₃ coatings were prepared by electrophoretic deposition (EPD) on 3x3 cm steel substrates (316 mark) using working electric field ranges from 50 to 100 V/cm. Dispersion medium was prepared from either HCl or charging additive (benzoic acid) solution in isopropanol. After the metal oxides were added, the dispersion was ultrasonificated for 30 min. Deposition was carried out for 5 to 20 min.

EPD suspensions containing different compositions of TiO₂/WO₃ (molar ratios a - 1:1, b - 2:1, c - 3:1, d - 1:2) were used to obtain composite films.

As-deposited films were heated in 60 °C for 2 h and then annealed at 500 °C for 2 h. The phases and crystalline sizes of obtained TiO₂ thin films were determinate by X-ray diffraction. X-ray fluorescence was used to establish WO₃ content in thin films. Surface morphologies were analysed by scanning electron microscopy. Photoacatalytic properties of obtained coatings were assessed in dependence on TiO₂/WO₃ content ratio. UV photocatalytic degradation of methylene blue on the surface of TiO₂/WO₃ films has been investigated. By comparing absorption-time curves it was found that most efficient photocatalysis occurs on TiO₂/WO₃ composite film obtained from the suspension b with the molar ratio 2:1.



STUDY OF ELECTROPHORETICALLY DEPOSITED GRAPHENE FILMS AS ELECTRODE FOR LITHIUM ION BATTERIES

G. Bajars, K. Kaprans, G. Kucinskis, A. Dorondo, J. Mateuss J. Kleperis and A. Lusis

Graphene, two-dimensional graphite, is a rapidly rising star in material science. It has atomic thickness, high aspect ratio (the ratio of lateral size to thickness), excellent electrical conductivity and good mechanical properties, which qualify it as an attractive candidate for the use of promising electrode material for lithium ion batteries. Electrophoretic deposition (EPD) is an economical and versatile processing technique that has been applied for deposition of coatings and films. It has many advantages in the preparation of thin films from suspensions, such as high deposition rate and throughput, good uniformity and controlled thickness of the obtained films, no need of binders, and simplicity of scaling up.

A stable ethanol (96 %) suspension of graphene oxide was used for electrophoretic deposition of films under potentiostatic mode. As electrodes for EPD process were 1 mm thick 316 stainless steel with a working area of about 1 cm x 4 cm. The distance between the two electrodes was 10 mm, and the applied electric field was 150 V/cm. Under the applied voltage, the negatively charged graphene oxide particles migrated toward the positive electrode and were subsequently orderly deposited. The thickness of the graphene films was tuned ranging from several nanometers to a few micrometers by varying the deposition conditions, including the concentration of graphene oxide, the applied voltage, and the deposition time. The thickness of the films was evaluated using a Veeco Dektak 150 profilometer. Graphene oxide thermal reduction was performed by heating at 700 °C in argon/hydrogen flow.

Obtained graphene layers were analyzed by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The application of these films as an electrode for lithium ion batteries was tested by various electrochemical methods such a voltammetry, chronopotentiometry, and electrochemical impedance spectroscopy (EIS). The measurements were performed for graphene thin film as a working electrode in two or three-electrode cell with metallic lithium as a reference and a counter electrode, and LiPF₆ in ethylene carbonate and dimethyl carbonate mixture as an electrolyte. The measurements in an open circuit state, charged and discharged states and during charging and discharging processes were carried out.

Results of scanning electron microscopy, X-ray diffraction and Raman spectroscopy confirm the formation of homogeneous graphene sheet films by EPD followed by thermal reduction. The profile of voltammetric curves indicated smooth lithiation and delithiation processes of obtained graphene films. Extended cycling was performed that demonstrated good reversibility of lithium intercalation and deintercalation in graphene sheet films. Results of current research show that obtained ordered graphene films have a high potential for application as electrode material in lithium ion batteries. The use of light-weight graphene and lithium metal provides a high gravimetric capacity and energy density.

Experimental results give the evidence that EPD is highly powerful tool for the ordered deposition of graphene films. Given the great potential of EPD for manipulation of graphene oxide and their assembly into ordered deposits, films and coatings, it is likely that novel applications of EPD based graphene structures will emerge in various fields such as biological engineering, optical electronics, ultrafiltration, photovoltaic cells and energy storage.

PREPARATION AND ELECTROCHEMICAL PROPERTIES OF LiFePO₄/C/GRAPHENE NANOCOMPOSITE CATHODE FOR LITHIUM ION BATTERIES

K. Bikova, G. Kucinskis, G. Bajars, J. Kleperis, A. Lūsis

LiFePO₄/C (LFP/C) composite was synthesized by solid-state reaction. The suspension was mixed by ball-milling for 2 h in ethanol. After drying, the precursor was heated at 350 °C for 5 h in flowing Ar/H₂ (95:5) atmosphere and grinded afterwards. It was then sintered at 700 °C for 5 h in Ar/H₂ (95:5).

Graphene oxide was mixed with LiFePO₄/C either by magnetic stirring or by ball milling. In the first route graphene oxide (GO) powder was added to LFP/C and the mixture was ball milled in N-Methyl-2-pyrrolidone (NMP) for 2 h. In the second case a suspension of GO and LFP/C in NMP was prepared by continuous magnetic stirring of the materials for 48 h at 60 °C.

In both cases graphene oxide was thermally reduced afterwards: samples were then dried in air, followed by heat-treatment in Ar/H₂ (95:5) at 700 °C for 5 h.

Materials were characterised with X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

All the XRD diffraction peaks correspond to well-crystallized single phase LiFePO₄ (figure 1). LFP/C/G (Milling) and LFP/C/G (Stirring) are samples where graphene was added via ball milling in NMP and stirring in NMP respectively. Although peaks at 11 ° and 43 ° were observed for GO, none of the two are visible in any of the LFP/C/G diffractograms, indicating that GO has been mixed and reduced properly.

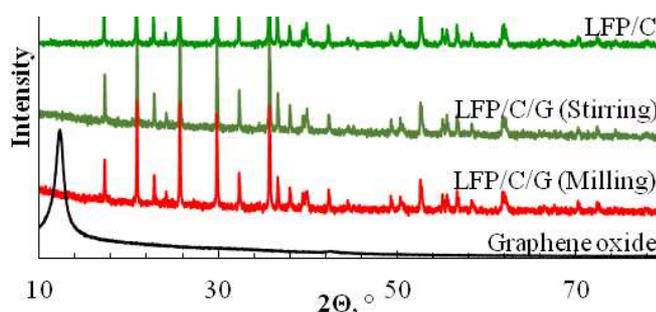


Figure 1. XRD diffractograms of GO, LFP/C/G (Stirring), LFP/C/G (Milling) and LFP/C samples.

SEM shows that the route of preparation does indeed influence the overall structure and morphology of the material with mixing by stirring yielding a better dispersed graphene nanosheets. Overall grain size of LFP particles, in all cases can be evaluated to be 100 – 250 nm.

Discharge capacities of both LFP/C/G composites and LFP/C were determined at various charge and discharge rates. To gain a better understanding of the rate capability improvement provided by graphene, the capacities were plotted to show discharge capacity retention from the highest value measured (figure 2). The initial discharge capacities were 113, 91 and 90 mAh/g for LFP/C/G (Stirring), LFP/C/G (Milling) and LFP/C samples respectively.

The analysis confirms that graphene additive has indeed efficiently improved the rate capability and decreased charge transfer resistance of the cathode. It can be concluded that the excellent electron-conducting properties of graphene have helped to improve the widely researched LiFePO₄ even further, suggesting graphene could be one of the most efficient electron-conducting additives for lithium ion battery cathode materials. Magnetic stirring appears to be a more suitable route for evenly dispersing graphene oxide, and it allows avoiding graphene nanosheet stacking.

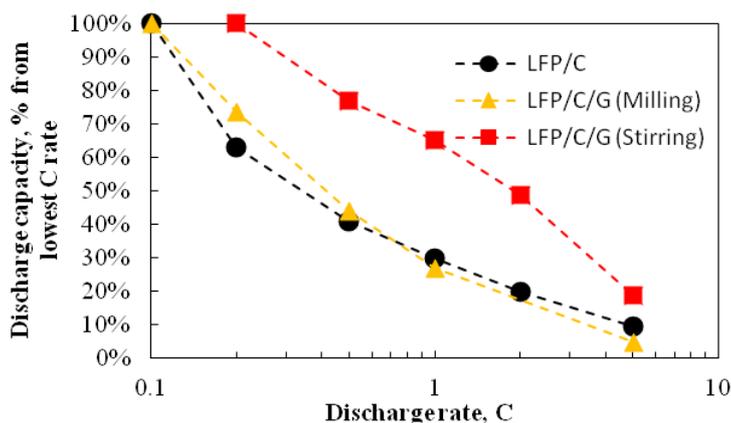


Figure 2. Discharge capacities of LFP/C/G (Stirring) and LFP/C/G (Milling) composites when compared to LFP/C, 1 C = 170 mA/g.

TRITIUM RELEASE FROM HIDOBE-01 (798 K) BERYLLIUM PEBBLES ON ANNEALING WITH SIMULTANEOUS ELECTRON RADIATION AND MAGNETIC FIELD

Aigars Vītiņš (a, b), Gunta Ķizāne (a), Andris Matīss (a), Gennady Ivanov (a),
 Valentīna Kinerte (a), Juris Jansons (a), Milan Zmitko (c)
 (a) *Institute of Chemical Physics, University of Latvia,*
 (b) *Institute of Solid State Physics, University of Latvia,*
 (c) *Fusion for Energy Spain*

Beryllium pebbles are foreseen as a neutron multiplier to ensure sufficient tritium breeding in a ceramic breeder in the European Helium-Cooled Pebble-Bed (HCPB) breeding blanket for a future demonstration fusion power reactor (DEMO). Under the operating conditions, the beryllium pebbles will be under intense fast neutron radiation of about 10^{18} n m⁻² s⁻¹, in a high magnetic field of 7-10 T at 573-923 K temperature. Helium and tritium are produced in beryllium as a result of neutron-induced transmutations, causing swelling and tritium inventory. One of tasks of blanket designs is to reduce tritium inventory in the beryllium pebble beds while maintaining their structural integrity and functional ability for their whole operating period.

The subject of the present study was beryllium pebbles irradiated for 646 full power days from June 2005 to October 2007 to the neutron fluence of 6.94×10^{25} m⁻² ($E > 1.0$ MeV) at temperature 798 K in the HIDOBE-01 experiment in the High Flux Reactor at Petten, The Netherlands. Post irradiation tritium release (PITR) was investigated on annealing a pebble at 773-1079 K for 3 h in a flow of 14-15 L/h of He + 0.1% H₂ purge gas with simultaneous 5 MeV fast electron irradiation of 10-13 MGy/h both without ($B=0$) and in a magnetic field of 1.5-1.7 T ($B=1.7$ T). The tritium activity in the purge gas was continuously monitored using a proportional counter DDH 32 with an operating volume of 300 cm³ and a tritium monitor TEM 2102A using a counting time of 120 s. The counting gas in the proportional counter was Ar + 10% CH₄ (P-10) with the flow rate 42-45 L/h so that the ratio of the counting gas to the purge gas was 3:1.

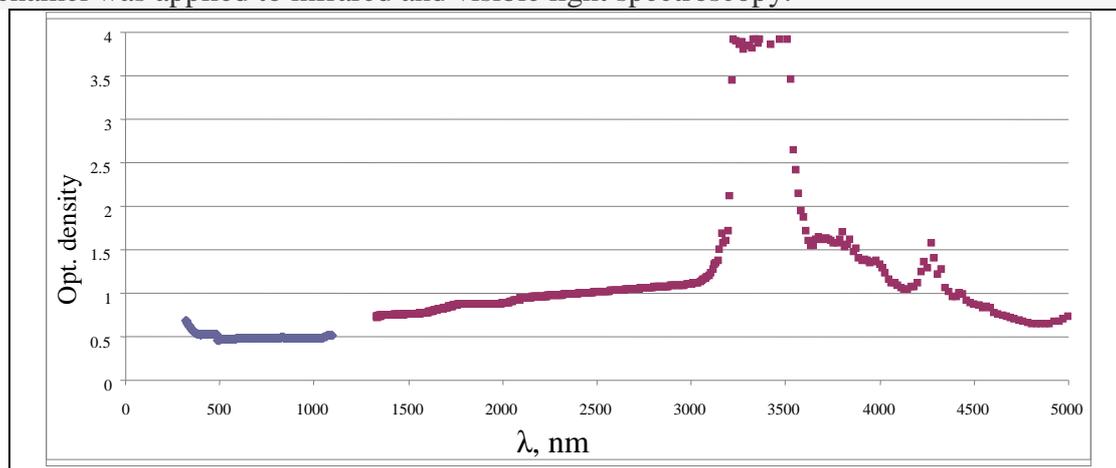
7 successive electron irradiations at 780, 830, 880, 930, 978, 1045 and 1078 K released 16.6 GBq/g (B=1.7 T) and 9.9 GBq/g (B=0) of tritium from the pebbles with $\varnothing \approx 1$ mm. In these PITER experiment series for both B=0 and B=1.7 T, a considerable tritium release (>0.5 GBq/g) was observed only at temperatures above 920 K, but a considerable facilitating effect of a magnetic field of 1.5-1.7 T was observed at temperatures above 1040 K. An electron irradiation at 1070-1079 K released 22.2 GBq/g (B=1.7 T) and 14.3 GBq/g (B=0) of tritium from the pebbles with $\varnothing \approx 0.5$ mm. The tritium release rate, particularly in the case of the pebbles with $\varnothing \approx 1$ mm, had strong irregular oscillations; the sharp peaks were indicative of burst release. After switching off both the electron radiation and the external additional heating, about 30-50% of the cumulative tritium amount was released. That indicates activation of the tritium release possibly by formation of microcrevices, which allow a following appreciable tritium release from a cooling pebble. According to the estimation in [5], the HIDOBE-01 neutron irradiation produced 25.4 GBq/g of tritium in beryllium, which corresponds to 19.2 GBq/g of tritium taking account of tritium decay to the time of these PITER experiments. The results of the PITER experiments indicate a facilitating effect of a magnetic field of 1.5-1.7 T with the simultaneous 5 MeV fast electron radiation at temperatures above 1040 K on the tritium release, but because of the fact that only one pair of pebbles was investigated on the magnetic field effect from each batch, the ability to draw general quantitative conclusions about the magnetic field effect is very limited by possible dissimilarity of the pebbles within the batch with respect to their initial total tritium amount and their tritium release properties.

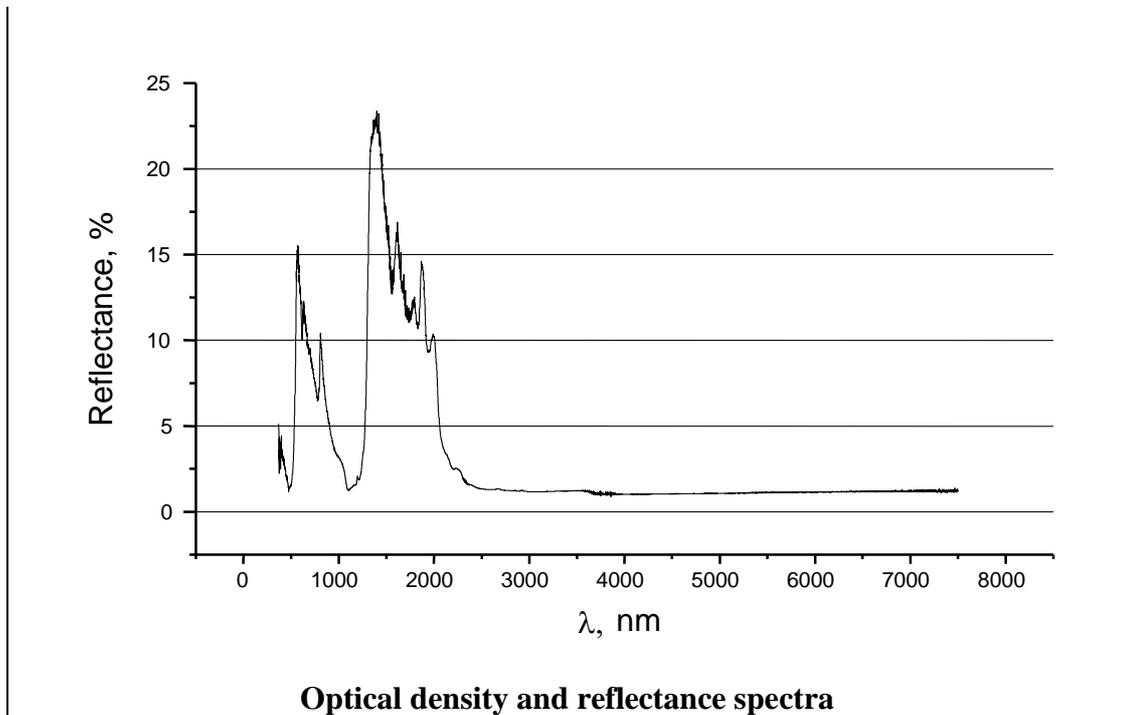
SPECTRAL CHARACTERISTICS OF BLACK ENAMEL

J.Balodis, G.Bajars, J.Gabrusenoks, I.Liepiņa, A.Lūsis, G.Mežinskis*,

**Institute of Silicate Materials, Riga Technical University*

Selective absorption of solar radiation in the development of coatings is used enamel on iron-chromium oxide pigment base. The spectral characterization of the enamel was applied to infrared and visible light spectroscopy.





The resulting black enamel samples show good enough solar radiation absorption properties in the visible spectrum and near-infrared region (300-1000 nm). This reflected radiation is less than 10% of the incident energy. Infrared region will remain the same level of reflection. It's not good enough to create low-emission coating. Such spectral properties does not provide minimal thermal energy emission in the infrared region (<2000 nm).

LABORATORY OF EXAFS SPECTROSCOPY

X-RAY ABSORPTION SPECTROSCOPY OF FUNCTIONAL MATERIALS

A. Anspoks, A. Kalinko, A. Kuzmin, J.Purans, J. Timoshenko

X-ray absorption spectroscopy, combined with advanced simulation techniques as classical Molecular Dynamics and reverse Monte Carlo, has been used to study the local structure and dynamics of several functional materials.

Lattice dynamics of ReO_3 has been efficiently studied using reverse Monte Carlo (RMC) technique. We have demonstrated that reverse Monte Carlo (RMC) method can be successfully used to interpret EXAFS spectra of crystalline materials even in case, when the multiple-scattering effects are very pronounced. The analysis of the Re L_3 -edge EXAFS data from the second and third coordination shells of rhenium in ReO_3 has been carried out for the first time taking into account both thermal disorder and multiple-scattering effects. The obtained results are in agreement with the rigid unit model of lattice dynamics in ReO_3 . We affirm the strong correlation (i) between displacements of oxygen and nearest rhenium atoms and (ii) between oxygen motion in the direction orthogonal to the $\text{Re}_0\text{-Re}_2$ bond and the variation of the average $\text{Re}_0\text{-Re}_2$ distance. Our results reveal also the strong correlation between the motion of two nearest rhenium atoms.

We have also successfully interpret the W L_3 -edge EXAFS spectra in scheelite-type AWO_4 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) compounds using a combination of classical NVT molecular dynamics (MD) and ab initio multiple-scattering (MS) theory. The configuration-averaged EXAFS spectra show good agreement with our room temperature experimental data supporting the reliability of the developed force-field models. The contributions from all coordination shells up to 6 Å are elucidated. The contribution of the MS effects into the total EXAFS signal in AWO_4 compounds is small, being around 10%.

The local atomic structure and dynamics in multiferroic MnWO_4 and $\text{Mn}_{0.7}\text{Co}_{0.3}\text{WO}_4$ have been studied by X-ray absorption spectroscopy at the Co(Mn) K-edge and W L_3 -edge. The analysis of the first coordination shell of metal ions using single-shell Gaussian approximation and regularization-like method allowed us to determine a distortion of $\text{Mn}(\text{Co})\text{O}_6$ and WO_6 octahedra. It was found that the local environment of Co^{2+} ions in $\text{Mn}_{0.7}\text{Co}_{0.3}\text{WO}_4$ is close to that in CoWO_4 , whereas the presence of cobalt ions reduces the distortion of MnO_6 octahedra in comparison with pure MnWO_4 .

LOCAL STRUCTURE AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE NiO POWDERS AND THIN FILMS

A. Anspoks, A. Kalinko, R. Kalendarev, N.Mironova-Ulmane, A. Kuzmin

Non-stoichiometric nickel oxide (Ni_{1-x}O) thin films were prepared by DC magnetron sputtering technique in mixed Ar/O_2 atmosphere and studied by synchrotron radiation Ni K-edge x-ray absorption spectroscopy, x-ray diffraction and scanning electron microscopy. The use of advanced modelling technique, combining classical molecular dynamics with ab initio multiple-scattering extended x-ray absorption fine structure calculations, allowed us to describe the structure relaxation and dynamics in nanocrystallites and to estimate their size and the concentration of nickel vacancies.

Nickel oxide powders with the grain size of 13-1500 nm have been studied by neutron scattering, scanning electron microscopy and vibrating sample magnetometry. We have found that the atomic structure and the antiferromagnetic ordering are nearly

independent of the average size of grains. The existence of the uncompensated spins in nanoparticles with the grain size below 100 nm has been detected.

LOCAL STRUCTURE STUDIES OF $\text{SrTi}^{16}\text{O}_3$ AND $\text{SrTi}^{18}\text{O}_3$

A Anspoks, J Purans,

In this work we report on the local structure of Ti in $\text{SrTi}^{16}\text{O}_3$ (STO16) and $\text{SrTi}^{18}\text{O}_3$ (STO18) investigated in the low temperature range (6 – 300 K) by extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) spectroscopy at Ti K-edge and by optical second harmonic generation (SHG). By comparing XANES of STO16 and STO18 we have identified the isotopic effect which produces at $T < 100$ K a noticeable difference in the measured mean square relative displacements (MSRD) of Ti–O1 bonds: while STO16 follow the expected Einstein-like behaviour, for STO18 we have measured an increase of MSRD values with decreasing temperature. This is an indication of an increasing off-center position of the Ti atoms in the TiO_6 octahedra.

GALLSTONES STUDIES BY EPR AND EDX SPECTROSCOPY

Maksims Polakovs, Nina Mironova-Ulmane, Andrejs Pavlenko, Vera Skvortsova

In the present work we report results of investigations of gallstones. Different types of gallstones were studied. Accordingly the paramagnetic composition gallstones could be divided on three main types: cholesterol, brown pigment and black pigment stones [1]. The objective of this work was to analyze the phase and micro elemental compositions of gallstones removed operatively from patients in an attempt to solve this task; we have investigated the phase and microelement compositions of a collection of human gallstones using X-ray fluorescence analysis (EDX)

LABORATORY OF HYDROGEN ENERGY MATERIALS

RESEARCH AND DEVELOPMENT OF MATERIALS AND DEVICES FOR HYDROGEN ENERGY TECHNOLOGIES

G.Bajars, J.Chikvaidze, J.Hodakovska, L.Grinberga, A.Knoks, J.Kleperis, J.Klavins,
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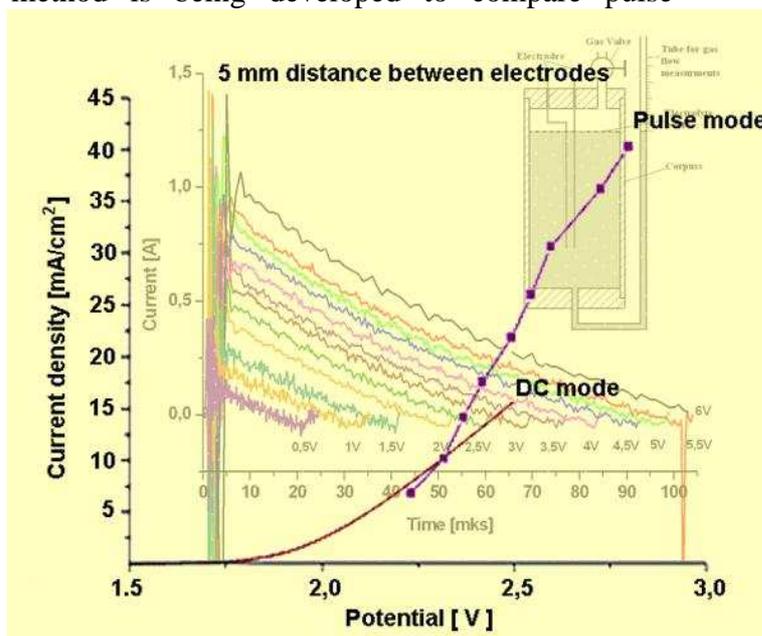
Latvian Association of Hydrogen

P.Lesnichenoks, A.Sutka, J.Zemitis

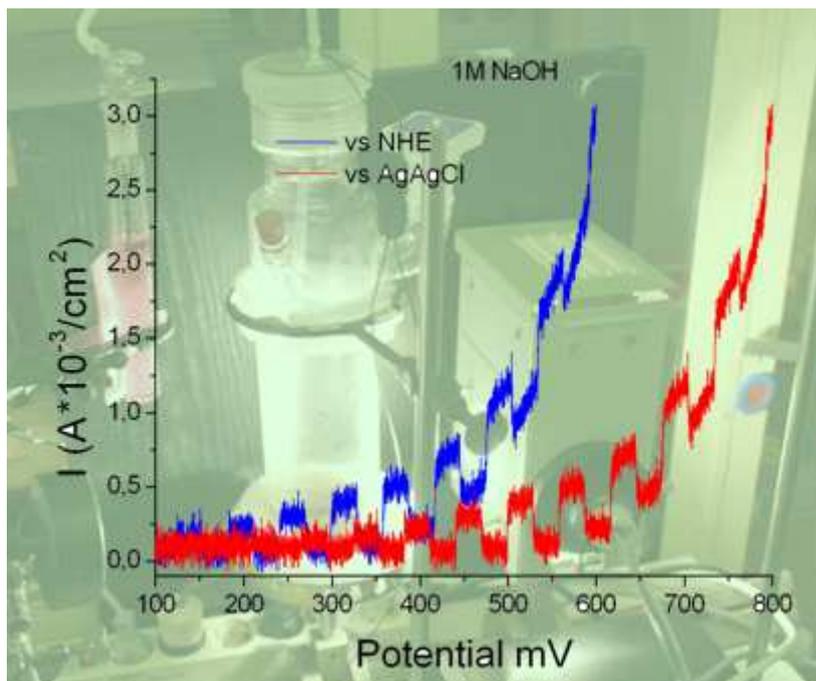
Faculty of Material Science and Applied Chemistry, Riga Technical University

Hydrogen production studies

Electrolysis: Experimental method is being developed to compare pulse electrolysis with DC electrolysis. Essence of the method is based on the acquisition of polarization curves in the process of pulse electrolysis from root mean square (rms) voltage and current values. By changing the pulse amplitude also changes the values of rms voltage and current, thereby producing a number of points VA plane, resulting in a polarization curve for pulse electrolysis process. It further can be compared with the DC polarization curve, measured directly with potentiostat. The results show that in 0.1 M KOH solution electrolysis in pulse regime on stainless steel (SUS 316L brand) is more intense in comparison with DC electrolysis. If the polarization curve approximates to a straight line, it is seen that the slope of pulse electrolysis is nearly twice as large as that for DC electrolysis. On the other hand, at a higher concentrations of KOH electrolyte (0.3 and 0.5 M) both processes, pulse and DC electrolysis, are similar.



Photocatalytic water splitting: Electrochemical and gas analysis methods are developed for studying the light sensitivity properties of photocatalytic semiconducting materials. Basic research unit is three electrode photoelectrochemical cell with working electrode – semiconducting material coated onto conducting substrate, counter electrode - platinum sheet, the reference electrode - platinum wire with the potential close to the normal hydrogen electrode, 1 M NaOH electrolyte. Cell has a quartz window and a light modulator – for periodic illumination of the sample. All electrochemical measurements are performed with potentiostat Voltalab PGZ 301. The photocurrent is determined by measuring the volt-ampere

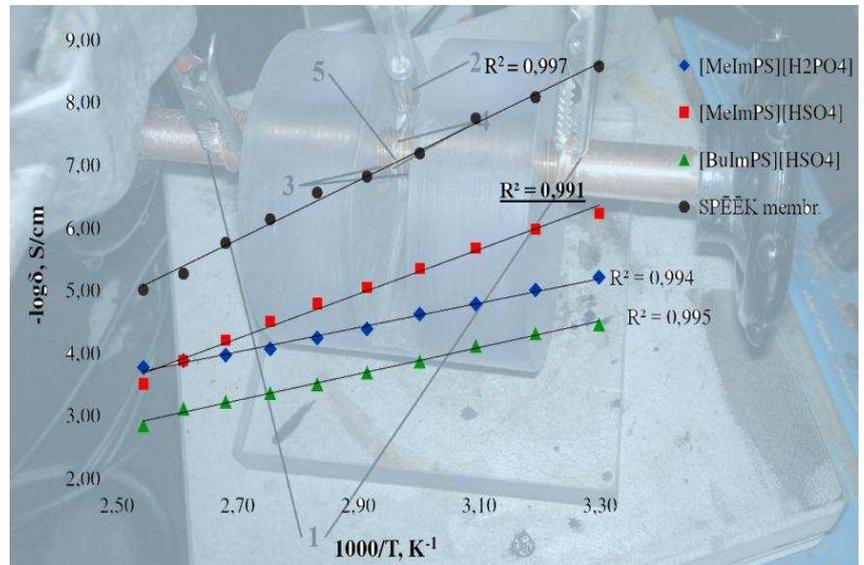


characteristic from -100mV to 600mV with a voltage scan rate of 2 mV/s and periodic light pulses of 5-10 s. Flat band potential and charge carrier concentration are determined from Mott - Shottky curves obtained from impedance spectra allowing calculating the capacity of barrier layer on interface. Photo-electrochemical properties of thin film investigated in this report. Thin films of α - Fe_2O_3 are sputtered on glass substrate coated with ITO film by using a spray pyrolysis method. Photo-electrochemical activity is evaluated from the resulting photocurrent values measured in photo-electrochemical cell. From Mott – Shottky curve the flat band potential around 0.7V and charge carrier concentrations about $2 \cdot 10^{19} \text{ cm}^{-3}$ are calculated. The width of optical forbidden gap of thin layers is measured from light absorption spectra and for indirect transitions the value 2.0 eV obtained. Self-assembling TiO_2 nanostructured coatings are grown on titanium foil by electro chemical anodizing. After anodization the samples are crystallized in 500 $^{\circ}\text{C}$ temperature for 4 hours to obtain anatase structure confirmed by XRD analysis. Obtained nanotube array coatings are tested with UV lamp for their efficiency split water based electrolyte in oxygen and hydrogen.

Biohydrogen: Biological production of hydrogen by bacterial anaerobic fermentation of widely available renewable resources is a promising and advantageous area, given that substrates are industrial by-products, for example, crude glycerol. Glycerol can be metabolized using different bacteria, but optimal results can be achieved using anaerobic fermentation process. Hydrogen concentration analysis in liquid phase were made using Clark electrode microsensor (Unisense, Denmark). For hydrogen analysis in the gas phase the RGAPro-100 mass-spectrometer connected to the experimental test-system was used. In order to measure different bacteria hydrogen production yields, inverted test-tube system was used and gas samples with syringe for gas content analysis were taken and measured in the mass-spectrometer. Test-systems were optimized to allow on-line estimation of hydrogen production in liquid and gaseous phase and the factors, influencing the bacterial capability to produce hydrogen at fermentation of crude glycerol, as well as the possibilities to optimize the measuring process were investigated.

Hydrogen transport in membranes and storage studies

The demand for electric power in the world is growing constantly. To meet these demands, various alternative energy sources are of growing importance, due to their low environmental footprint and longevity. One of such examples are fuel cells of various types, of which proton exchange membrane fuel cells (PEMFC) could be suitable as energy source in vehicles and portable electronic devices. In fuel cells like these, a polymer membrane serves as 1) a non-conducting layer, which separates anode and cathode,



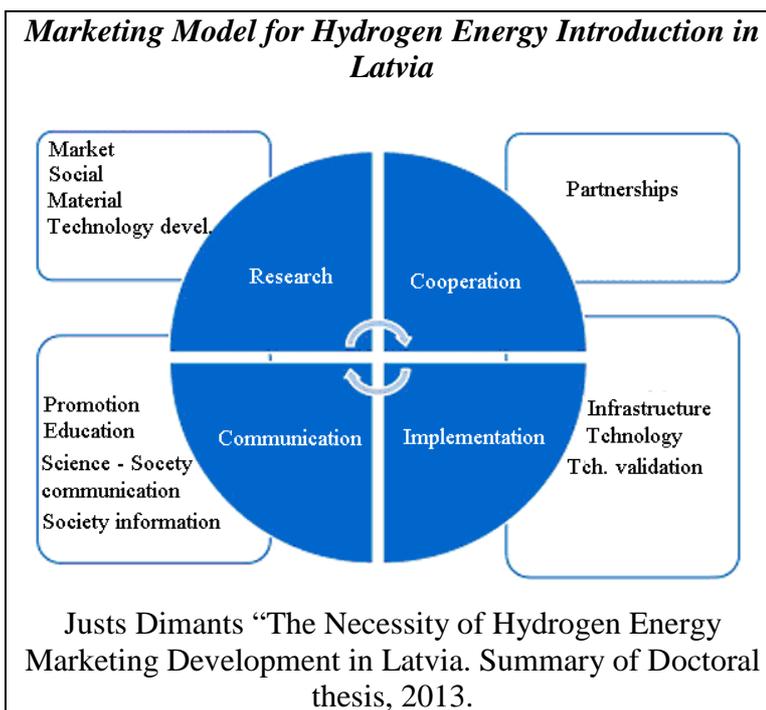
as well as 2) a proton conductor; unfortunately the conductivity is provided by water inside the membrane, which means that the temperature range of these membranes is below 100 degrees Celsius. One approach of solving this problem could be making a composite of membrane and acidic ionic liquid, and using it in PEMFC. In our work several acidic ionic liquids were synthesized and used to make IL-SPEEK (sulfonated poly(ether ether ketone) composite membrane. Thermal stability was determined by using TGA/DTA. Conductivity of membrane was obtained from impedance measurements using Autolab setup in temperature range 20-120 °C. Electrochemical exfoliation of graphene, graphene oxide accomplished by electrochemical exfoliation method, where graphite industrial waste of compressed rods or less dense graphite blocks can be pulled apart by electric current till few atomic layer graphene thickness. Observations of materials characteristics show the extreme expansion of raw material while heating in hydrogen atmosphere. This demands consideration of adsorption study with a device that consists of smaller dead volumes or moving parts within the experiment chamber. Also the lightness of material suggests avoiding usage of small samples during the adsorption testing with thermogravimetric method. Because of the sample production the method specifics is based on contact of graphite with different ions in exfoliation solution, as well as previous preparation method for usage in metallurgy or elsewhere, the basis of this study are the reports suggesting the usage of it as cheap and effective raw material to obtain graphene or graphene oxide for hydrogen storage purposes.

Hydrogen application and public acceptance studies

Hydrogen and electricity together is considered to be an interesting option for developing more sustainable energy systems because both are energy carriers. Since 1970s the hydrogen has been claimed to be a good alternative to replace fossil fuels which create pollution and has large carbon footprint. Many research institutes and companies worldwide are working hard to develop technologies that can efficiently exploit the potential of hydrogen energy. Especially interest is to use hydrogen in zero-emission transport and as energy carrier in large scale energy storage – the combination of hydrogen with renewable energy (wind, solar). To offer consumers a competitive alternative, many technical

and otherwise challenges must be overcome, public acceptance and other societal issues including, related with the introduction of a new energy carrier into everyday use. Hydrogen introduces different safety and regulatory issues which need to be understood and tackled by appropriate authorities; public expectations towards hydrogen systems must be met. For fuel cells and hydrogen, the EU started a unique public - private partnership supporting research, development and

demonstration - the Fuel Cells and Hydrogen Joint Undertaking. Within the European program HORIZON 2020 the FCH JU will run from 2014–2020 with a total budget of 1,4 billion euro for two basic headlines: clean transport and large energy storage with hydrogen. In this research the local drivers and local resources for hydrogen in Latvia are analyzed. Exhaust emissions were calculated in one of the Riga street canyon - Brīvības Street at Dzirnavu Street intersection. It was concluded that the main polluting vehicle categories are cars and motor buses. Light vehicle replacement mostly depends on individuals, therefore public transportation bus category was analyzed - the existing Euro 3, next generation - Euro 5 and hydrogen bus accordingly their NO₂ emissions. When converting to electric/hydrogen buses, the NO₂ emissions would be equal to 0. Such a shift would substantially reduce the PM10, noise and vibration levels in the Riga city center. Decreasing the amount of CO and NO_x reduce smog and hence the heat-island effect. Reducing emissions in the city a significant improvement in microclimate will occur. Research is made toward the implementation the research results on power electronics and material science areas in the development of autonomous, the wind and hydrogen energy-based power system, which could replace the existing fossil fuel-based systems, such as domestic diesel generators, gas microturbines.



Education is an important first step in making the transition from traditional energy technologies based on fossil resources to alternative energy technologies based on renewable resources and hydrogen as energy carrier (storage agent like electricity). Solar Cup is organized in Latvia from 2008 for students from middle and high school classrooms.. Renewable energy resources and technologies can be used to teach basic scientific principles: the Sun, Wind, Water and Biomass as renewable sources of Earth's energy, conversion of energy from one form to another, electricity generation, electricity storage and finally – a reasonable spending power in stationary and mobile applications. Building up solar powered small cars and boats is giving understanding as in renewable energy technologies as well as in energy saving and storing topics. Every year about 40-60 teams from more than 35 schools of different regions are participating in Solar Cup competitions. In Latvia already for several years are organized events of presentation of achievements in use of alternative fuel in cars, including hydrogen. During the event in 2010 was performed marketing research by help of survey to get information on readiness of the public to use alternative fuel in their personal cars. The data for the study was collected via a questionnaire. All respondents were residents of Latvia. In the questionnaire were questions on respondent's environmental knowledge, attitudes, behavior as well as information on socio-economic characteristics of respondents. As the survey results show, most of the respondents are very positive (with surprisingly high evaluations) to alternative energy technologies. The main conclusions was that there appears to be a lack of knowledge about hydrogen energy and technologies and people are willing to know more about renewable energy opportunities and offers per se. During last years in largest Latvian higher education establishments number of students for bachelor, master science and doctoral level studies are chosen topics about hydrogen technologies. ISSP UL participated to organize in Riga the International Conference "Hydrogen technology opportunities for sustainable development of cities" On 20 March 2013, in cooperation with Latvian Hydrogen Association and Riga Energy Agency, as well as the HyER, and Riga was accepted as a member in HyER (Hydrogen Fuel Cells and Electromobility in European Regions). International meeting on same topic together with demonstration of hydrogen bus (Van Hool) and hydrogen car (Hyundai) for Riga City Municipality and public was performed with frame of International Technology Exhibition "Environment and Energy" October 2013. Also in 2013 the Energy Agency of Riga is inviting representatives from ISSP UL and LHA to become Experts in Advisory Council of Riga City Major in the field of hydrogen technologies, and the Riga City join HyER cities introducing hydrogen transport.



SCIENTIFIC PUBLICATIONS

1. **E Pentjuss, A Lusis, G Bajars, J Gabrusenoks** (2013) Investigation of carbonized layer on surface of NaAlSi glass fibers. *IOP Conf. Ser.: Mater. Sci. Eng.* 49 012044 doi:10.1088/1757-899X/49/1/012044
2. **I.Liepinā, G Bajars, A Lusis, G Mezinskis, M Vanags** (2013) Preparation and characterization of nanostructured Fe-TiO₂ thin films produced by electrophoretic deposition. *IOP Conf. Ser.: Mater. Sci. Eng.* 49 012060 doi:10.1088/1757-899X/49/1/012060
3. **Kucinskis, Gints; Bajars, Gunars; Kleperis, Janis.** Graphene in lithium ion battery cathode materials: A review. *Journal Of Power Sources*; Volume: 240 Pages: 66-79 Published: OCT 15 2013
4. **Sutka, A.; Paerna, R.; Zamovskis, M.; V. Kisand, Mezinskis G., Kleperis J., Maiorov M., and Jakovlev D.** Effect of antisite defects on the magnetic properties of ZnFe₂O₄. *Phys. Status Solidi A* 210, No. 9, 1892–1897 (2013) / DOI 10.1002/pssa.201329039
5. **Vanags M, Kleperis J, Bajars G, Nemcevs V.** "Electrodeposition of Nanoporous Nickel Layers Using Inductive Voltage Pulses" , 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* 49 012008 doi:10.1088/1757-899X/49/1/012008
6. **I.Dirnena, I.Dimanta, A.Gruduls, J.Kleperis, D.Elferts, V.Nikolajeva.** Influence of the initial acidification step on the biogas production and composition. *Biotechnology and Applied Biochemistry* 2013. <http://onlinelibrary.wiley.com/doi/10.1002/bab.1163/abstract>
7. **Aizpurietis P., Vanags M., Kleperis J., Bajars G.** Ni-Al Protective Coating of Steel Electrodes in DC Electrolysis for Hydrogen Production. *Latvian Journal of Physics and Technical Sciences*, No.2, 2013, p.53-59
8. **Kleperis, J., Lesnicenoks, P., Grinberga, L., Chikvaidze, G., Klavins, J.** (2013) Zeolite as material for hydrogen storage in transport applications. *Latvian Journal of Physics and Technical Sciences*, 50 (3) 59-64.
9. **I.Dimanta., A.Gruduls, V. Nikolajeva, J. Kleperis, I. Muiznieks** (2013), Assessment of bio-hydrogen production from glycerol and glucose by fermentative bacteria. *Power Engineering*. <http://www.lmaleidykla.lt/ojs/index.php/energetika/article/view/2704/1536>
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11. **E. Blokhin, E. Kotomin, A. Kuzmin, J. Purans, R. Evarestov, J. Maier,** Theoretical modeling of the complexes of iron impurities and oxygen vacancies in SrTiO₃, *Appl. Phys. Lett.* 102 (2013) 112913:1-4.
12. **N. Mironova-Ulmane, M.G. Brik, I. Sildos,** Crystal field calculations of energy levels of the Ni²⁺ ions in MgO, *J. Lumines.* 135 (2013) 74-78.
13. **J. Timoshenko, A. Kuzmin, J. Purans,** An efficient implementation of the reverse Monte Carlo method for EXAFS analysis in crystalline materials, *J. Phys.: Conf. Ser.* 430 (2013) 012012:1-4.
14. **Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin,** Probing vacancies in NiO nanoparticles by EXAFS and molecular dynamics simulations, *J. Phys.: Conf. Ser.* 430 (2013) 012027:1-4.
15. **Kalinko A., A. Kuzmin,** Interpretation of EXAFS in scheelite-type AWO₄ (A= Ca, Sr, Ba) compounds using molecular dynamics simulations, *J. Phys.: Conf. Ser.* 430 (2013) 012075:1-4.

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17. A.M. Balagurov, I.A. Bobrikov, J. Grabis, D. Jakovlevs, **A. Kuzmin**, M. Maiorov, **N. Mironova-Ulmane**, Neutron scattering study of structural and magnetic size effects in NiO, *IOP Conf. Ser.: Mater. Sci. Eng.* 49 (2013) 012021 (4pp).
18. J. Jankovskis, N. Ponomarenko, **N. Mironova-Ulmane**, D. Jakovlevs, The study of correlation between microstructure of ferrites and their complex permeability spectra, *IOP Conf. Ser.: Mater. Sci. Eng.* 49 (2013) 012045 (4pp).
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22. **A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin**, Local structure relaxation in nanocrystalline Ni_{1-x}O thin films, *Thin Solid Films* (2013), DOI:10.1016/j.tsf.2013.08.132.
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25. Naidoo, Q. Naidoo, E. Musil, V. Linkov and **G. Vaivars**. Precipitation and calcination synthesis methods forming nano-sized platinum catalytic particles for methanol and hydrogen oxidation. *Advances In Natural Sciences: Nanoscience And Nanotechnology (IOP Conference series)* 4 (2013) 015014 (4 pp); doi:10.1088/2043-6262/4/1/015014: <http://iopscience.iop.org/2043-6262/4/1/015014/>
26. V.Garaev, S.Pavlovica, I.Reinholds and **G.Vaivars**. Mechanical properties and XRD of Nafion modified by 2-hydroxyethylammonium ionic liquids. 2013 IOP Conf. Ser.: Mater. Sci. Eng. 49 012058 doi:10.1088/1757-899X/49/1/012058
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30. Natalija Borodajenko, , Kristaps Rubenis, Agnese Pura, Inga Narkevica, Edmunds Tamaniš, **Nina Mironova-Ulmane**, Jurijs Ozolins, Liga Berzina-Cimdina .*Studies*

of TiO₂ Ceramics Structure after Thermal Treatment at Different Conditions .
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31. **V. Skvortsova, N. Mironova – Ulmane**, L. Trinkler. Optical Absorption and Luminescence of Neutron Irradiated Beryl Crystals. Proceeding of the International Conference Actual Problem of Solid State Physics (SSP-2013), 2013 Minsk, Belarus . T.3, pp. 25-27
32. **N. Mironova-Ulmane, A. Kuzmin**, A.M. Balagurov, I.A. Bobrikov, J. Grabis, I. Sildos, Study of magnetic ordering in nickel oxide by Raman spectroscopy and neutron scattering, in Proc. Int. Conf. on Actual Problems of Solid State Physics (SSP-2013) (October 15-18, Minsk, Belarus) T.1 (2013) 91-93
33. **N. Mironova-Ulmane, M. Polakovs**, A. Pavlenko, T. Zvagule, N. Kurjane, N. Gabrusheva. The retrospective dosimetry and EPR of blood of Chernobyl workers. Proceeding of IV International Conference "Radioactivity and radioactive elements in the human environment" pp. 600-603.
34. **M. Polakovs, N. Mironova-Ulmane**, A. Pavlenko, **V. Skvortsova** , D. Jakovlevs. Gallstones studies by EPR and EDX spectroscopies. Proceeding of the 11 International Conference on Medical Physics in the Baltic States 2013. PP. 24-27.
35. **Vitiņš, A.**, Kizāne, G., Matīss, A., Pajuste, E., Zubkovs, V., Tritium release behavior of beryllium pebbles after neutron irradiation between 523 and 823 K // Journal of Nuclear Materials, November 2013, Volume 442, Issues 1–3, Supplement 1, Pages S490–S493.
36. Lescinskis, A., Kizane, G., **Vitins, A.**, Platacis, E., Lielausis, O., Romanchuks, A., Kravalis, K., Experimental setup for analysis of sorption and desorption of tritium in liquid lithium under different external conditions // IOP Conference Series: Materials Science and Engineering, December 2013, Vol. 49, art. no. 012040, 4 pp.

CONFERENCE PROCEEDINGS

1. **I. Dimanta., A. Gruduls**, V. Nikolajeva, **J. Kleperis**, I. Muiznieks, Assessment of bio-hydrogen production from glycerol and glucose by fermentative bacteria. Power Engineering 2013. ISSN 0235-7208. Publicēta:
<http://www.lmaleidykla.lt/ojs/index.php/energetika/article/view/2704/1536>
2. Pajuste, E., Kizane, G., **Vitins, A.**, Zubkovs, V., Zarins, A., Tritium behavior in neutron irradiated beryllium pebbles regarding their microstructure // Proceedings of the 10th IEA International Workshop on Beryllium Technology, September 19 - 21, 2012, Karlsruhe, Germany / P. Vladimirov, J. Reimann (Eds.), Karlsruhe Institute of Technology, KIT Scientific Reports 7650, KIT Scientific Publishing, Karlsruhe, Germany, 2013, pp. 198-204. Available online at:
<http://bews-10.webarchiv.kit.edu/KIT-SR7650.pdf>

LECTURES ON CONFERENCES

1. **29th Conference of Institute of Solid State Physics, February 20– 22, 2012, Riga**
Program:
http://www.cfi.lu.lv/fileadmin/user_upload/lu_portal/projekti/cfi/CFI_konferences/CFI_konf.programma__20.02.13_22.02.13.pdf
Abstracts:
http://www.cfi.lu.lv/fileadmin/user_upload/lu_portal/projekti/cfi/CFI_konferences/Abstracts_2013.pdf
2. **FMNT-2013, Tartu, Estonia, 21.-24.04.2013:**

- EXAFS spectroscopy and first-principles study of SnWO₄, **A. Kuzmin, A. Anspoks, A Kalinko, J. Timoshenko, R. Kalendarev.** (Oral talk)
 - Analysis of EXAFS data from copper tungstate by reverse Monte Carlo method, **J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin.** (Oral talk)
 - Studies of structural, electrical and optical properties of iridium – zinc oxide thin films deposited by reactive magnetron sputtering, **M. Zubkins, R. Kalendarev, E. Pentjuss, J. Gabrusenoks, K. Vilnis, A. Azens, J. Purans**
 - Joint theoretical-experimental study of iron impurities and oxygen vacancies in SrTiO₃, Blokhin, **A. Kuzmin, J. Purans,** E.A. Kotomin, R.A. Evarestov, J. Maier
- 3. 47th Russian School on Condensed State Physics, (St. Petersburg, Russia, 11-16 March, 2013):**
P. Zhgun, D. Bocharov, S. Piskunov, **A. Kuzmin,** and **J. Purans,** Quantum chemistry calculations on ScF₃ electronic structure and lattice dynamics
- 4. Developments in Optics and Communications 2013, Rīga, Latvia, 10.04.2013-12.04.2013**
M. Zubkins, R. Kalendarev, K. Vilnis, A. Ecis, **A. Azens, J. Purans**
Characteristics of the doped zinc oxide thin films deposited by reactive magnetron sputtering technique
- 5. Conf. on the Structure of Non-Crystalline Materials (NCM12), 07.07.- 12.07.2013 Riva del Garda (Trento), Italy:**
J. Purans, M. Zubkins, A. Azens, J.V. Gabrusenoks, R. Kalendarev - 12th Inter. Local structure and optical and electrical properties of amorphous Zinc-Iridium oxide thin films
- 6. Inter. Conf. "QUANTUM IN COMPLEX MATTER", 27 May- 1 June 2013, Ischia Italy:**
J. Purans (Invited talk) X-RAY ABSORPTION STUDIES OF LOCAL STRUCTURE WITH FEMTOMETER ACCURACY (Oral talk)
- 7. E-MRS 2013 Spring Meeting, Strasbourg, France 27.-31.05.2013:**
- Local structure relaxation in nanocrystalline Ni_{1-x}O thin films, **A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin.** (Oral talk)
- 8. NCM-12, Riva del Garda, Italy, 7.-12.07.2013:**
- X-ray absorption spectroscopy of Cu-doped WO₃ films for use in electrochemical metallization cell memory, **A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko, R. Kalendarev** (Oral talk)
- 9. E-MRS 2013 Fall Meeting, Warsaw, Poland, 16.-20.09.2013:**
- Local structure and dynamics of wurtzite-type ZnO from simulation-based EXAFS analysis, **J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin.** (Oral talk)
- 10. The VI International Scientific Conference "Actual Problems of Solid State Physics" (SSP-2013), Minsk, Belorussia, 15.-18.10.2013:**
- **N. Mironova-Ulmane, A. Kuzmin,** A.M. Balagurov, I.A. Bobrikov, J. Grabis, I. Sildos Study of magnetic ordering in nickel oxide by Raman spectroscopy and neutron scattering (Oral talk)
 - **V. Skvortsova, N. Mironova – Ulmane,** L. Trinkler Optical Absorption and Luminescence of Neutron Irradiated Beryl Crystals (Oral talk).
- 11. The 11 International Conference on Medical Physics in the Baltic States 2013:**
M. Polakovs, N. Mironova-Ulmane, A. Pavlenko, V. Skvortsova. Gallstones studies by EPR and EDX spectroscopies (Oral talk)
- 12. IV International Conference "Radioactivity and radioactive elements in the human environment:**

M. Polakovs, N. Mironova-Ulmane, A. Pavlenko. The retrospective dosimetry and EPR of blood of Chernobyl workers (Oral talk).

PATENTS

1. **G. Chikvaidze, A.Kelle.** Method for Refining Silicon using an Electron Beam.
Application number: EP13196587.3
2. **Jānis Kleperis, Jānis Straumēns.** Šķidrums līmeņa līdzsvarošanas sistēma. Latvijas Patents Nr. 14698; pieteikums Nr. P-13-36 no 22.03.2013.
3. **Jānis Kleperis, Jurijs Kuzņecovs, Jānis Baumanis** „Kapilāro kanālu izveidošanas paņēmiens” Latvijas patents Nr. 14701 (20.10.2013); Pieteikums Nr. P-13-68 no 22.05.2013..

LABORATORY OF RADIATION PHYSICS

Head of laboratory Dr. habil.phys. J.Berzins

RESEARCH AREA AND MAIN PROBLEMS

The following main investigations are developed in the laboratory:

- experimental and theoretical investigation of nuclear structure at medium and high excitation energies;
- development of the nuclear spectroscopy methods for the identification of radioactivity and nuclear materials in Latvia;
- development of gamma spectrometric methods for investigation of radionuclides, their migration in the environment, soils and ground waters in the most potentially polluted regions of Latvia;
- application of the liquid scintillation methods for the monitoring of tritium content in environment and drinking waters of food industry;

International projects:

Participation in the project „**Investigation of nuclear structure via (n, γ), (d,p) and (d,t) nuclear reactions**” with Institute of Nuclear Physik (Rzez, Czech Republic), Technical University Munich, Institute Laue -Langevin (Grenoble, France).

Scientific Staff:

Dr.hab. J.Berzins
Dr.hab. M.Balodis
Dr.hab. V.Bondarenko
Dr. L.Simonova
Dr. T. Krasta
Dr. D.Riekstina
Dr. O.Veveris
Dr. J. Proskurins

Scientific visits abroad

Dr. hab. J. Berzins, European Commission Euratom, Brussels,Belgium (8 days), 2013.
Dr. hab. J. Berzins, Cyclotron Workshop, Ispra, Italy 11-12 December 2013.

COOPERATION

Latvia

1. University of Latvia, Institute of Chemical Physics (Dr. G. Kizane)
2. Institute of Technical Physics, Riga Technical University (Dr.J.Ruža).
3. Institute of Silicate Materials, Riga Technical University (Dr. hab.ing.V. Svinka)

USA

1. Mississippi University (Prof. A.Afanasjev).

Germany

1. Technical University Munich (Prof. T. von Egidy, Dr. H.-F. Wirth)

France

1. Institute Laue-Langevin, Grenoble, France (Dr. W. Urban, Dr. M. Jentchel).

Canada

1. Memorial University of Newfoundland, Newfoundland (Dr.A.Aleksejevs)

2. Department of Physics, Acadia University, Wolfville, NS (Dr.S.Barkanova)

Czech Republik

1. Nuclear Research Institute, Řež (Dr. J.Honzatko, Dr. I.Tomandl).

Denmark

Riso National Laboratory, Roskilde, (Dr. S. Nielsen)

MAIN RESULTS

STUDIES OF ODD-ODD RHENIUM AND IRIDIUM NUCLEAR STRUCTURE

J.Bērziņš, M.Balodis, T.Krasta, Ļ.Simonova

Characteristic feature of nuclei belonging to the nuclear mass number region $A \sim 190$ is a very high level density due to γ -instability of nuclear shape. High level density is observed even at relatively low excitation energies. The odd-odd nuclei of the $A \sim 190$ region present an extreme challenge for the nuclear structure studies because of the presence of low-energy two-quasiparticle multiplets due to singlet and triplet orientation of valence proton and neutron spins.

For more than two decades our laboratory specializes in the study of transitional odd and odd-odd nuclei with $A \sim 190$. These studies are performed using high precision experimental data obtained in collaboration with physicists of other nuclear research centers.

In 2013, studies have been continued in two directions: a) development of the ^{192}Ir level scheme using earlier published experimental results and comparison of low-lying level structure of $^{190,192,194}\text{Ir}$ nuclei; b) evaluation of ^{186}Re gamma-spectra following the thermal neutron capture reaction with enriched ^{185}Re targets in the high-flux reactor of ILL (Grenoble, France).

Structure of the doubly-odd ^{192}Ir nucleus has been studied using experimental data obtained earlier [1,2] in thermal neutron capture, average resonance capture (ARC) and particle transfer reactions. Consistent analysis of all available data in the frameworks of particle-plus-rotor coupling model with non-axial core deformation allowed to correct and extend the previously known ^{192}Ir level scheme. The proposed level scheme of ^{192}Ir contains 65 levels up to 455 keV excitation energy. For higher energies, five levels from Refs. [1,3] are added. Level scheme includes 51 gamma-transition placements which were unknown in [1].

Structure interpretation has been proposed for 52 levels. Bandheads and/or bands have been found for 21 configurations from 24 formed by 3 lowest proton quasiparticle states ($3/2[402]$, $1/2[400]$, $11/2[505]$) and 4 lowest neutron quasiparticle states ($3/2[512]$, $1/2[510]$, $9/2[505]$, $11/2[615]$).

Several previously unknown rotational structures below 500 keV have been established, including $|K \pm 2|$ side-bands of three lowest two-quasiparticle configurations: the $K^\pi = 4^+$ ground state band, the $K^\pi = 6^+$ bandhead at 12.97 keV, and the $K^\pi = 6^-$ bandhead at 16.02 keV. Characteristic feature of these quasi gamma-bands is a predominant depopulation to the levels of parent two-quasiparticle configuration via E2 transitions.

Proposed decay pattern of the long-lived (241 years) $^{192}\text{Ir}^{m2}$ isomer state gives it spin-parity assignment 11^- , analogously to the isomer state observed in neighboring ^{194}Ir nucleus.

The experimental level scheme of ^{192}Ir has been compared with the results of theoretical calculations in the frameworks of modified oscillator particle-plus-rotor model [4]. It has been found that one can quite successfully use Nilsson single-particle orbits $\Omega^\pi [N n_z \Lambda]$ for classification of low-lying two-quasiparticle states of odd-odd

iridium isotopes. However, in order to describe experimentally observed $|K\pm 2|$ quasi gamma-bands, one should use the non-axiality parameter $\gamma > 20^\circ$.

Level schemes of three neighboring odd-odd iridium isotopes $^{190,192,194}\text{Ir}$ have been compared in order to check the applicability of Nilsson particle-plus-rotor model for the interpretation of nuclear level structure. The data on ^{190}Ir have been taken from Ref. [5], and on ^{194}Ir – from Ref. [6]. The levels scheme of ^{190}Ir is analogous to that of ^{192}Ir . Besides non-axial structures, both nuclei have also quite regular rotational bands with rotational parameters $A < 15$ keV.

In ^{194}Ir , as expected in the case of two additional neutrons, we do not find such regular rotational bands. However, the observed similarities of depopulation patterns of some ^{192}Ir and ^{194}Ir levels, allow to assign Nilsson two-quasiparticle configurations to some of ^{194}Ir bands. Also, the 518.6 keV 2^+ level, connected via E2 transition to the 147.1 keV 4^+ level, can be interpreted as the $|K-2|$ gamma-band, analogous to the 351.7 keV 2^+ band in ^{192}Ir .

The doubly-odd ^{186}Re nucleus has two neutrons less than ^{188}Re which we have studied earlier [7]. It is expected that structure of ^{186}Re levels would be more deformed and regular than that of its neighbor. Comparison of both nuclear structures would give valuable data for the study of nuclear shape phase transition.

Single gamma-ray spectra of ^{186}Re were measured in the energy range from 100 keV to 1.5 MeV employing the high precision crystal-diffraction spectrometer GAMS5 at ILL. Evaluation of single spectra obtained in the first and second reflection orders allowed to obtain energies and intensities of more than 500 γ -lines assigned to ^{186}Re . These data have essentially higher resolution than those of the earlier crystal-diffraction measurements [8]. Most of obtained transitions have been placed in the model-independent level scheme of ^{186}Re . The study of ^{186}Re would be continued in 2014.

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NATURAL RADIOACTIVITY OF BUILDING MATERIALS AND THEIR COMPONENTS IN LATVIA

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Very different building materials are used in modern construction. Latvia is one of a few EU countries in which no one has performed comprehensive measurements of natural radionuclides. The aim of present work was to perform measurements of natural radionuclides in various types of building materials used in Latvia in order to establish their conformity with the Cabinet of Ministers regulations No.149 (adopted on 09.04.2002). These regulations set the maximal allowed limit for K-40 and Th-232, U-238 (Ra-226) decay chain product activity in building materials and construction elements. Employing HPGe gamma-spectrometers, the K-40 and Th-232, U-238 (Ra-

226) activity measurements have been carried out for more than 100 building materials of various types. The greatest attention has been given to materials produced in Latvia.

Measurements have shown that the concentration of natural radionuclides in granite, and some sorts of ceramsite and fireproof bricks exceeds the limits allowed by regulations. An excess of Th-232, U-238 contents has been found also in clay and products made of clay.

Basing on obtained results, we have started a study of natural radionuclide (K-40, Ra-226, Th-232, U-238) contents in clay based building materials produced by different firms.

EVALUATION OF NATURAL RADIOACTIVITY IN BUILDING MATERIALS AND CLAY CERAMICS

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Building materials are a significant source of indoor gamma-ray exposure for the population due to activity of natural radionuclides K-40 and Th-232, U-238 (Ra-226) decay chain products. As yet, Latvia is one of a few EU countries in which no one has performed comprehensive measurements of natural radionuclide contents in these materials [1-2].

The aim of present work was to perform measurements of natural radionuclides in various types of building materials used in Latvia in order to establish their conformity with the Cabinet of Ministers regulations No.149 (adopted on 09.04.2002). These regulations set the maximal allowed limit for K-40 and Th-232, U-238 (Ra-226) decay chain product activity in building materials and construction elements. The most attention in this presentation is given to materials produced in Latvia.

The concentrations of K-40 and Th-232, U-238 gamma radioactivity in different building material samples (bricks, cement, concrete, natural stones, etc.) were determined in the energy range from 50 to 2000 keV using the high resolution HPGe gamma-spectrometers Ortec and Canberra. Uncertainty of measurements was within the range of 3–10 %, the minimal detectable activity – 0.3 Bq/kg for the one litre volume sample.

Results of our measurements have shown that the concentration of natural radionuclides in granite, and some sorts of ceramsite and fireproof bricks exceeds the limits allowed by regulations. High contents of Th-232, U-238 has been found also in clay. With regards to obtained results, we have undertaken a systematic study of natural radionuclide (K-40, Ra-226, Th-232, U-238) contents in clay based building materials produced by different firms in different years.

Natural radionuclide content in building materials is compared between different EU countries. For some of analysed materials the activity concentration index I is determined. Material usage safety requirements provision that this index should be lower or equal to one unit.

The credibility of obtained results is ensured by the quality assurance and control according to the main requirements of ISO/IEC 17025:2008 standard.

1. C.Nucetelli, S.Risica et al., J. Radiol. Prot., **32** (2012) 349-358.
2. R.Trevisi, S.Risica et al., J. Environ. Radioact., **105** (2012) 11-20.

APPLICATION OF INAA FOR INVESTIGATION OF MAGNESIUM AND ALUMINIUM OXIDE MATERIALS

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The paper presents investigations of changes in optical absorption and photo luminescence spectra of magnesium oxide, and natural and synthetic magnesium metal ions (Cr, Fe, Mn) and the irradiation with fast neutrons. Six synthetic single magnesium aluminium spinel crystals with different stoichiometry ($\text{MgO}_n\text{Al}_2\text{O}_3$), five natural crystals from Ural and Pamir deposits, and seven MgO crystals were studied. Micro impurities (Cr, Fe, and Mn) and macro component (Mg, Al) quantities have been determined using the instrumental neutron activation analysis technique. Concentrations of impurities in different spinels were found in following ranges: for Cr— $1.9 \cdot 10^{-4}$ to $8.9 \cdot 10^{-2}$ %, for Mn— $2.9 \cdot 10^{-5}$ to 23 %, for Fe— $1.9 \cdot 10^{-4}$ to 1.2 %. Three ranges of luminescence: 380–460, 650–850 and 850–1,050 nm, were established in the most part of the investigated MgO samples. Analysis shows that the intensity of emission in each of these regions is strongly dependent on the concentration of transition metal ions. Great deviation from the stoichiometry of the irradiated $\text{MgO}_{2.8}\text{Al}_2\text{O}_3$ crystal leads to the local structure of $\alpha\text{-Al}_2\text{O}_3$ formation around Cr^{3+} ions. The orange emission is attributed to Mn^{2+} in octahedral coordination, it can be assumed that the band at 570 nm is belonging to the complex centre $\text{Mn}^{2+}\text{-F}$ (or F centre).

PUBLICATION

1. **D.Riekstina, V.Skvortsova, O.Veveris**, Application of INAA for investigation of magnesium and aluminium materials, *J. of Radioanal. and Nuclear Chemistry*, 2013, V. Issua , pp.1907-1911.

CONFERENCE PRESENTATIONS

1. **T.Krasta, M.Balodis, J.Bērziņš, L.Simonova, V.Bondarenko**. Kodola formas maiņas izraisīto efektu pētījumi A~190 apgabalā. Abstract of 29th Scientific Conference Inst. of Solid State Physics, University of Latvia, Riga, February 20-22, 2013, p. 59.
2. **D.Riekstina, J.Berzins, O.Veveris**, Natural radioactivity of building materials and their components in Latvia, Abstract of 29th Scientific Conference Inst. of Solid State Physics, University of Latvia, Riga, February 20-22, 2013, p. 24.
3. J. Alksnis, **J.Berzins**, J.Derums, J.Rudzītis, **D.Riekstina**, A.Popelis, V.Pede, O. Skrypnik, Salaspils nuclear Reactor monitoring in the year 2012, Abstract of 29th Scientific Conference Inst. of Solid State Physics, University of Latvia, Riga, February 20-22, 2013, p. 60.
4. **D. Riekstina, O. Veveris, V.Skvortsova**, Application of INAA for investigation of magnesium and aluminium materials, 24. Seminar Aktivierungsanalyse und Gammaskopie, Garching bei Munchen, Deutschland, 26.-28.02.2013, Abstract Booklet, p. 20.
5. **D.Riekstina, J.Berzins, T. Krasta, O.Skrypnik**, Evaluation of natural radioactivity in building materials and clay ceramics, Abstract: 18th Int. conf. "EcoBalt'2013", Vilnius, 25-27 Oktober 2013, p. 67.

LABORATORY OF ELECTRONIC ENGINEERING

Head of Laboratory *Dr. phys. A. Kristins*

MAIN PROBLEMS

1. Implement developing and manufacturing of unique measuring and monitoring apparatus and systems, which:
 - provide authorised access on the base of Touch Memory™ elements and Proximity Cards to different objects, including
 - ⇒ entrance check-points (entrance gates, access control systems, systems for multilevel parking buildings etc.);
 - ⇒ computers and programmes;
 - ⇒ car and other technical devices (anti-theft systems);
 - execute electronic documentation functions (Touch Memory™ -based electronic invoices, credit cards and so on);
 - test power units (high-voltage switches, automatic disconnecting switches, power-transformers);
 - determine a content of heavy metals (As, Cd, Co, Cu, Fe, Hg, Tl, Ni, Pb, Sn, Zn, Bi, Mn) in liquids, ground, food-stuffs;
 - check various environment parameters (temperature, lighting, humidity, radiation level);
 - control temperature and lighting at the different objects (housings, hothouses, production storehouses);
 - are used in medicine and for determining of agricultural production parameters (digestion systems, fluorimetres, fall number determinators).
 - drive and management of automatic devices.
2. Provide physical measuring and manufacturing process automation.
3. Also solve the other problems, not afore-mentioned.

Scientific Staff

1. Dr. A.Kristins

Technical Staff

1. I.Gvardina
2. J.Melderis
3. J.Veinbergs
4. P.Kalinikovs

COOPERATION

Latvia

1. Joint-stock company
Augstsprieguma tīkls
2. „Fonons” Ltd
3. Latvia Technology Park
4. Riga Technical University
5. *Loks* Ltd,
6. „ADI Kartes” Ltd
7. *GROG* Ltd
8. *Energoremonts Rīga* Ltd

Estonia

1. Tallinn University
of Technology
2. [Competence
Centre ELIKO](#)

More information on the work of the laboratory in the last ten years, see Appendix as well as <http://www1.cfi.lu.lv/radioel/RDO.htm>

OUR CLIENTS

1. Latvijas Krājbanka;
2. Latvijas Pasts;
3. *LatRosTrans*; Ltd;
4. Latvijas Kuģniecība;
5. Latvijas Gāze;
6. Latvian Environment Agency;
7. Latvian Hydrometeorological Agency;
8. Latvijas Dzelzceļš;
9. *Augstceltne* Ltd;
10. CSDD (Road Traffic Safety Directorate);
11. *Avantime Amusement Technology* Ltd;
12. Joint-stock company *Latvenergo*;
13. Latvia's Ministry of Foreign Affairs;
14. *Nienhaus & Lotz Lettland* Ltd;
15. *Godske Latvian Textile* Ltd;
16. *VAIDE* Ltd;
17. *Flexoplastic* Ltd

LECTURES ON CONFERENCES

29th Scientific Meeting of Institute of Solid State physics, University of Latvia, Riga, February, 2013

1. **I.Gvardina, A.Kristiņš, J.Melderis** J.Straumēns. *Swing* Abstracts, p. 98.
2. P.Annus, E. Reilent, A.Kuusik, T.Tammet, **A.Kristiņš**. *New trends in streetlighting control*. Abstracts, p. 99.
3. **I.Gvardina, A.Kristiņš, J.Melderis**. *Doors controllers*. Abstracts, p. 80.