INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

RESEARCH PROGRAMME 2021 - 2023 - 2027

Riga

2021

PREAMBLE

Motto: Development of advanced materials for a better World

The global society faces environmental, social and economic challenges such as tackling climate change, efficient health systems, the well-being and security problems, strengthening economic competitiveness, and creating jobs.

New materials are the key to many global challenges. To tackle them, researchers must be able to develop advanced and sustainable materials with the required properties, to improve the recyclability of materials, reduce their carbon and environmental footprint and make sure that a wide community of users will be able to capitalize on them. The materials development cycle ending with components used in real applications is long and entails steps such as theory and modelling, the appropriate technology for obtaining them, characterization, up-scaling and engineering, including industrial environments, and drive cross-sectorial industrial innovation by supporting new applications in all industry sectors. To succeed, there is a need for **research-innovation ecosystem** with advanced research infrastructure and modern technological facilities (Fig.1).

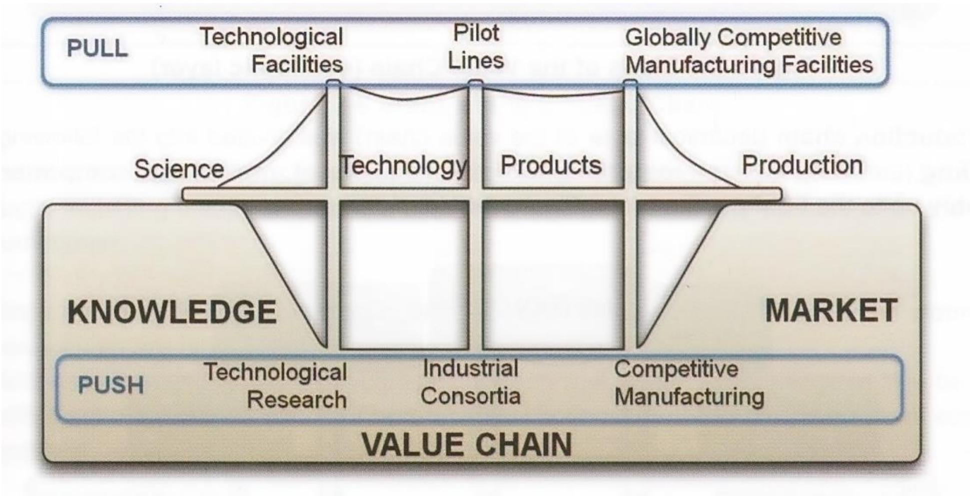

Fig.1. The scheme of the value chain.

To tackle these challenges, new European Commission`s (EC) Programme “Horizon Europe” (2021-2027) is being developed (Fig. 2). People are put in the centre of the program, focussing on their needs and concerns, managing the transitions.

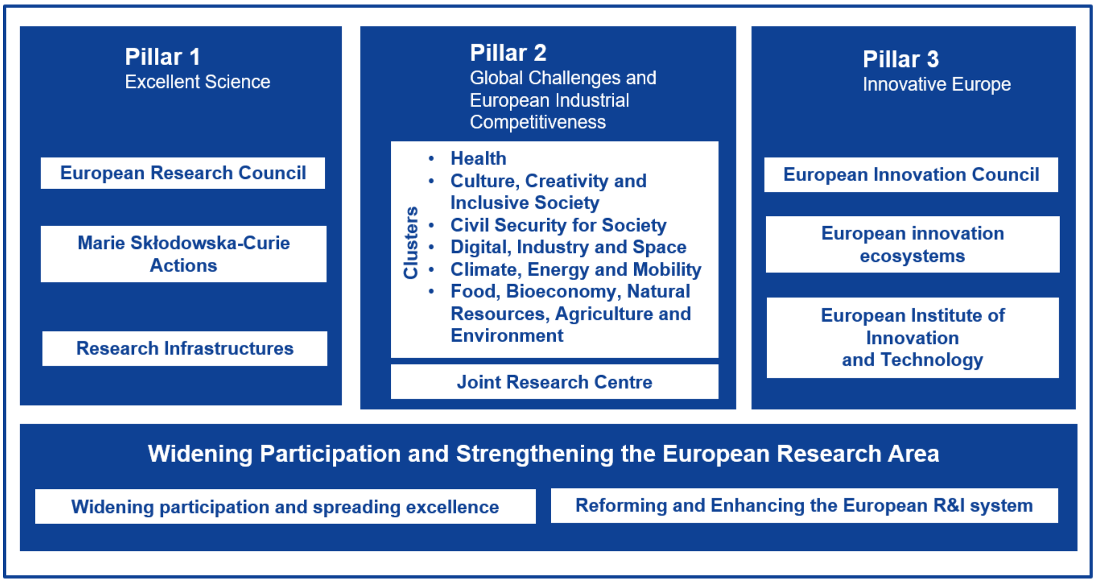

Fig.2. Structural outline of Horizon Europe programme.

European Partnerships introduced by Commission are proposed as an integral part of Horizon Europe's strategic planning process. Its Cross-Cluster Strategy aims to promote EU industrial leadership and will advance Key Enabling Technologies as "general purpose" technologies, producing solutions to global challenges:

- Health: medical, technologies, medical devices up-scaling infrastructures, metrology;
- Inclusive Societies: technology assessments, future of workplaces, inclusion and technology diffusion, materials for preserving cultural heritage, metrology;
- Secure Societies: cybersecurity, security application of new technologies, security by design, metrology;
- Climate, Energy and Mobility: advanced materials for energy harvesting, transmission and storage (notably batteries and photovoltaics); low-carbon footprint, industrial symbiosis, manageable waste, the lifecycle approach, clean, connected and automated mobility, electrification, hydrogen, materials for construction, metrology;
- Food and Natural Resources: circular systems, materials for circular economy, bioeconomy, bio materials and life cycle assessment, plastics, packaging materials, ocean ecology preservation, metrology.

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INTRODUCTION

"Great things are done by series of small things brought together"

Vincent Van Gogh

The Institute of Solid State Physics, University of Latvia (ISSP UL) is an internationally recognised leader in the materials sciences and cross-disciplinary topics in Baltic Sea Region. Its scientific capacity and the research and innovation ecosystem are currently being further developed through the Centre of Advanced Material Research and Technology Transfer project "CAMART^2". ISSP UL aims to transfer excellence in materials science and solid-state physics into highly educated people and into innovative products, processes and services.

Important challenge for the Institute is to translate the new knowledge coming from fundamental research into real innovation potential, thereby making it disruptive. It required a new approach: change of mind-set that fundamental research should also be directed towards the technological needs and challenges of industries. Research will be directed towards the **application-driven cross-laboratory R&I domains** where discoveries can make the change, thus initiating and establishing the value chain. ISSP UL has created a suitable research-innovation **ecosystem** that allows new ideas to be feasible.

Much attention in the Institute is devoted to the education and to renewal of professional and highly qualified scientific personnel. Adequate and specific curricula – updated master's programme has been developed as the basis for future creation of knowledge and industrial competitiveness of young researchers. A lot of effort is dedicated to ensuring cooperation with international partners, institutions of higher education, training of students and specialists as well as to attracting entrepreneurs and investors.

Research infrastructures such as the advanced technology facilities, almost complete set of equipment and methods for materials research and characterization, are by nature **interdisciplinary**, since the outcomes of the research conducted in their premises can be **deployed in many R&I domains**, fulfil specific industrial needs or find an industrial application in fields different from those where they have been produced. In addition to the existing highly developed ISSP UL experimental and technology infrastructure, which includes spectroscopy and microstructure research tools and more than 600 m^2 of clean-room space for thin film deposition, nanofabrication and characterization, it is important to synergy with a world-leading large-scale X-ray absorption spectroscopy (XAS) research facilities (as PETRA-III/DORIS (Hamburg), SOLEIL (Paris), ELETTRA (Trieste), and ESRF (Grenoble) synchrotrons). Also, an access to a number of new ESFRI facilities, such as European Spallation Source (ESS) and X-Ray Free Electron Laser Facility (XFEL) can drive innovative solutions thanks to their unique analytical techniques and expertise. Institute's computational resources (LASC - Latvian SuperCluster) are remarkably scaled-up and complemented by an access to International High-Performance Computing centres, like HELIOS (Japan), Piz Daint (Switzerland), CINECA MARCONI (Italy).

European Partnerships aim to mobilise Horizon Europe, national and other funding for research and innovation actions on a number of topics, which are of importance to most of the EU countries, including Latvia, and which are prioritised in **Smart Specialisation Strategies**.

The Smart Specialization Strategy of Latvia is defined by 5 topics:

1. Knowledge intensive bio-economy
2. ***Biomedicine, medical technologies and biotechnology***
3. **Smart materials, technology and engineering**
4. ***Advanced Information and communication technologies (ICT)***
5. ***Smart Energy***

The main research activities of Institute of Solid State Physics are directed at topic 3, **"Smart materials, technology and engineering"**, with significant work done also on topics 2, 4 and 5.

The Research Programme will be synchronized at appropriate time period with:

- Horizon Europe Programme (2021 – 2027), linking basic material research in Pillar I, with applied material research in Pillar II;
- Europe Green Deal 2050;
- EURATOM (EUROfusion) 9th Framework Program (2021 – 2025) and its Addendum (2026 - 2027);
- CAMART^2 Project (2021 – 2023).

An important challenge for the Institute is to translate the new knowledge coming from the fundamental research into real innovation potential, included in Research Programme **as new initiatives**:

- *Organ-on-a-chip and Lab-on-a-chip devices for biomarkers.* Project will address application in personalized and precision medicine and will be based on expertise in easy-to-use microfluidic device design and fabrication capabilities of ISSP UL for creating a novel and impactful biological study test-bed.
- *Polymer photonics technology platform*. This platform offers standardized polymer photonic device preparation methods to academic and industry. This system is based on three main parts – computational simulations of optical devices, materials and element fabrication workflow, and producible photonic elements.

The new initiatives are pursued within the traditional strength of the ISSP UL based on the **three research priorities of the Institute**:

- Science: theory and experimental studies;
- Technology and experimental methods;
- Application: applied research of materials for radiation conversion (sensors, scintillators, detectors), materials for photonics and electronics, and materials for energy harvesting and storage.

The Research Programme will serve an "entry-point" for advanced materials-related R&D&I challenges, inquiries, and proposals. It will help launching projects with a scope wider than that of a specific single research domain.

The long-term mission of the ISSP UL Research Programme 2021-2023-2027 and strategic development plan is to raise Institute's scientific capacity and to better integrate in the European

Research Area by heightening the involvement in joint research programs and projects with EU Member States, especially within the Baltic Sea region.

The mid-term milestone in Research Programme for ISSP UL is year 2023, the year to complete the Teaming project CAMART[2], when it comes to evaluating the planned achievements in quantified Key Performance indicators format, as well as when a full sustainability of the Institute must be achieved and demonstrated.

The short term activities will be prepared for each year within this period. The First Annual Action Plan is prepared for year 2021.

SCIENCE: THEORY AND EXPERIMENTAL STUDIES

This sub-section includes the following topics:

- Development of existing and novel theoretical and experimental tools combined with computer simulations to predict particular crystallographic structures and materials with tailored optical, electronic and magnetic properties;
- Quantum chemistry and molecular dynamics study of fine structural effects followed by mesoscopic modelling;
- Computational modelling of materials and devices;
- X-ray absorption spectroscopy;
- Identification of native and radiation-induced point defects and studies of their structure in solids;
- Experimental research of mechanisms of luminescence and electronic processes in solids.
- Studies of non-linear optical effects in organic- and nanomaterials

THEORETICAL MATERIAL SCIENCE AND MODELLING

STATE OF THE ART

Simulations based on density–functional theory and many –body perturbation theory have become an efficient tool for understanding and for designing new advanced high- performance functionalized nanomaterials. Hybrid approaches, coupling data- driven and physics-based models, can be of great interest in improving the predictive power of materials modelling.

Special attention is paid to nanomaterials and low-dimensional systems, as well as to modelling of processes under realistic working conditions, *i.e.* high and low temperatures and gas pressures, harsh radiation environment, *etc*. For this purpose thermodynamic approach based on the first principles total energy calculations of advanced materials and their vibrational properties are used. The tools available allow to address a wide spectrum of systems including bulk, surfaces, interfaces, heterostructures, molecules, or clusters- albeit with increasing computational costs depending on the system sizes considered [1,2]. Most of theoretical researches are performed in close collaboration with experimental In particular, combining traditional calculations of the optical absorption and luminescence with modelling magnetic resonance and vibrational spectroscopic methods in order to monitor the development of the radiation damage in several functional materials for nuclear applications. Of great importance is understanding a specific role of impurities in materials performance, e.g. their radiation resistance [3,4].

OUR POSITION

Activities of two Theoretical laboratories at ISSP UL (Laboratory of Computer Modelling of Electronic Structure of Solids, Laboratory of Kinetics in Self-Organizing Systems) are related to the multiscale computer modelling of advanced materials combining *ab initio*, kinetic Monte Carlo and Molecular dynamics, focusing on the role of defects and impurities in materials, predominantly interesting for energy applications: fuel cells, batteries, micro-energy harvesting, photocatalytic H_2 production and photovoltaics, nuclear fuels and functional materials for fusion reactors.

Both labs have a strong background in the large-scale first-principles computer simulations on advanced materials, their surfaces, interfaces and nanostructures. Massive parallel computer modelling combines the use of the commercially available first principles quantum mechanical computer codes with the home maid advanced thermodynamic analysis, pair potential approach, molecular dynamics, kinetic Monte Carlo and simpler formalisms. Such an approach allows to obtain reliable atomic and electronic structure of complex advanced materials and nanomaterials, as well as to get the multi-scale picture of physical-chemical processes in a large variety of materials with numerous technological applications. For instance, we study the influence of shape and size of perovskite nanoparticles on the piezoelectricity based on *ab initio* calculations. Different ferroelectric particles with defined sizes and shapes of plates, cubes and/or wires are synthesized by our partners and systematically self-assembled on a substrate, e.g. for the energy-harvesting devices. We developed theory of such self-assembling process and suggest how to control this process.

Our main focus is on the following topics:

- **Defects in solid state.**

Computer modelling of the atomic, electronic and magnetic structure of pristine and defective nanostructured interfaces. Materials for nuclear fusion applications [5,6].

- **Surfaces and interfaces of materials.**

Calculations of surface property of nanostructured ABO_3-type perovskites for efficient water splitting [7,8].

- **Vibrational properties of materials.**

First principles calculations of the vibrational properties of nanostructured materials. Calculations of the IR and RAMAN spectra for hybrid nanostructures [9,10].

- **Electronic structure and processes at nanoscale.**

First principles calculations of electronic properties of nanomaterials and heterostructures at nanoscale. Excited state calculations of hybrid nanostructures for photocatalysis. Calculations of the properties of hybrid metallic-carbon nanotubes. First principles calculations of charge transfer processes in nanostructured photoelectrodes. Computer simulations of adsorption properties of Cu-decorated graphene in the presence of external electric field. Study of perspective materials to be used in UV photon sensors [11, 12].

In 2019 two theoretical laboratories published 32% of the total number of publications of the ISSP UL; accordingly, citation rate was 43% of that for a whole ISSP UL.

FUTURE ACTIVITIES

Labs future activities will be focused on understanding of chemical and physical material properties in the photocatalytic processes and design of the effective photocatalysts for water splitting hydrogen production based on perovskites crystallites and nanoparticles. This needs a combination of the band gap engineering and selection of proper catalysts, in a close collaboration with leading experimental teams in Europe. In all these areas our activities are already well known internationally. In most projects we have industrial partners which are supposed to realize our theoretical predictions into real applications. Most of our future activities will deal with energy issues, including batteries, fuel cells, photovoltaic, nuclear fuels, functional materials for fusion reactors, water splitting. For efficient water splitting with nanocrystals our goal is to predict ways to increase efficiency of renewable energy converting devices, first of all, water splitting with electrochemical cells based on nano-scaled oxides. Main effort will be devoted to integrating and combining different theoretical methods toward a multi-scale approach. The ultimate central challenge will be to generate a multiscale modelling platform that will be used world-wide for conducting state-of-the-art multi-scale property prediction of materials. This action intends to focus on bridging the knowledge gaps between different theoretical methods and computer codes in order to facilitate the discovery of novel materials for energy conversion. We will perform large scale computer simulations of different nano-materials based on ABO_3 perovskites and complex oxides, modelling of water splitting and intermediate products, estimate of process efficiency dependent on the polarity and composition.

Our another goal is theoretical prediction of new cathode materials operating at intermediate temperature in fuel cells effectively transforming chemical energy into electricity. This requires understanding of: (i) the decisive structural properties for sufficient proton conductivity; (ii) conditions for the majority of proton uptake by acid-base water incorporation or by redox reaction; (iii) link between mechanical properties and water incorporation. The primary target materials of the proposed research are perovskite-type ferrites and cobaltites.

In line with EU’s Green Deal, recently announced by the EC’s President, wind/solar combined shares target up to 70 % of electricity generation, for 2050 EU full de-carbonization scenario. The intermittent nature of these sources is the major obstacle for such targets, due to demand mismatches, grid instabilities, negative pricings and wasteful curtailments. Thus, maximized wind/solar capacities impose grid-scale storage challenges, for peak loads to be absorbed with upgraded capacity factors and intermittent generators to be turned into grid-dispatchable sources.

NETWORKING

Theoretical Laboratories have close collaboration with the following experimental and theoretical groups:

Prof. M. Kuklja, University of Maryland, USA (Dept of Materials Science and Engineering; Institute for Research in Electronics and Applied Physics);

Prof. J. Maier, Max Planck Institut für Festkörperforschung, Stuttgart, Germany (Abt. Physikalische Festkörperchemie);

Prof. R. Dovesi, University of Turin, Italia (Theoretical Chemistry group);

Prof. D. Fuks, Ben-Gurion University of the Negev, Beer-Sheva, Israel (Department of Materials Engineering;

Prof. I. Lubomisrsky, Weizmann Institute of Science (Dept of Materials and Interfaces), Rehovot, Israel

Prof. A. Lushchik, Institute of Physics, University of Tartu, Estonia

Prof. R. Evarestov, St Petersburg University, Russia (Dept of Quantum Chemistry)

Dr. T. Bjorheim, University of Oslo, Department of Chemistry, Norway

Prof. T. Scherer, Karlsruhe Institute of Technology (KIT), Germany

Dr. R. Vila, CIEMAT, Madrid, Spain

Prof. E. Spohr, Faculty of Chemistry, University Duisburg-Essen, Essen, Germany

Dr. M. Krack, Paul Scherrer Insitute, Switzherland

Prof. P. D'yachkov, Institute of General and Inorganic Chemistry of Russian Academy of Science, Russia

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EXPERIMENTAL STUDIES

While most experimental material studies nowadays are targeted with highly specific applications in mind, part of these studies are also of a more general interest, covering general research techniques or some wider class of materials or specific, still not understood phenomena. These are listed in this subsection, while the rest are presented in the Technology and Applications sections.

X-RAY ABSORPTION SPECTROSCOPY

STATE OF THE ART

The structure of materials determines their properties and performance, therefore knowledge, deep understanding and control of structure are crucial for material practical applications. X-ray absorption spectroscopy (XAS) using synchrotron radiation is an excellent analytical tool to probe the local atomic and electronic structure, it can be used to study crystalline, nanocrystalline and disordered solids as well as liquids and gases. XAS using synchrotron radiation is rapidly evolving but also already a mature field of research that is tightly connected with the tremendous progress in large-scale synchrotron facilities. The structure in the bulk, at the surface and around impurities can be probed equally well using specifically designed experimental techniques. Nowadays, there are about 50 active synchrotron facilities around the world, 17 of them are located in the EU Member States. A coherent and strategic vision on the future development of the best large scale facilities in the European Union is summarized in the European Strategy Forum on Research Infrastructures (ESFRI) Roadmap 2018, which will be updated in 2021.

During the last ten years, there were on average about 3000 papers published in peer-reviewed journals per year (according to the WoS database) on the development and application of XAS as a result of research activities involving more than 3500 active researchers. XAS is a multidisciplinary field of research that comprises studies of materials and their transformations in material science, physics, chemistry, life sciences, environmental sciences, cultural heritage and medicine. The technique provides a wide range of opportunities for *in-situ* and *operando* studies, which were recently reviewed in [1-2]. The theoretical description of X-ray absorption spectra is based on Fermi's Golden Rule, and the spectra are usually computed numerically using the multiple-scattering theory [3-4]. The structural information is encoded in the extended X-ray absorption fine structure (EXAFS), and retrieving it from experimentally measured spectra requires significant effort and can be challenging [5-6]. Therefore, the development of the methodology for the analysis of X-ray absorption spectra based on advanced numerical methods [6], including artificial neural networks [7], is a hot topic of current research activities.

The recent advances in Machine Learning and Big Data analysis open new opportunities for autonomous experimentation with automatic control of *operando* parameters and real-time data processing [8, 9]. These will improve the throughput and reliability of experiments and provide paths for the advancement of novel methodologies.

New X-ray and extreme ultraviolet (XUV) light sources generated by free-electron lasers (FELs) in large accelerator facilities offer new insights into time-evolving molecular structures, primary photophysical, photochemical, and biological events, and strongly coupled electronic and nuclear dynamics. A novel time-domain picture of electron correlations is emerging, which will have far-reaching implications for the design of new molecules and materials with tailored functionalities. This is achieved by implementing the so-called "pump-probe" experiments using properly synchronized optical excitation by pulsed laser with the X-ray pulses arriving from a synchrotron or FEL [10].

OUR POSITION

The EXAFS Spectroscopy Laboratory is one of the world's leading groups in the development and use of the advanced methodology for the analysis of X-ray absorption spectra, including advanced approaches based on the regularization technique and atomistic simulations such as molecular dynamics and reverse Monte Carlo (RMC) modelling. The Laboratory has world-level competence in an analytical tool such as X-ray absorption spectroscopy (XAS) using synchrotron radiation. The XAS technique already finds a wide range of applications in different areas of research, helping researchers all around the world to solve challenging fundamental and applied problems.

A set of leading ab initio (full-) multiple-scattering XANES/EXAFS software codes from the partners provides a solid background for the experimental data analysis at ISSP UL. The use of theoretical simulations is supported by a high-performance computing (HPC) infrastructure (Linux Cluster) with a theoretical peak performance of about 150 teraflops. This allows ISSP UL researchers to reveal the full potential of XAS, providing a natural way to incorporate the static and thermal disorder into the structural models, thus opening new possibilities for the investigation of the structure-property relationships for emerging materials.

The research area at ISSP UL includes but is not limited to different functional nano-materials and materials for energy applications, as well as disordered materials (thin films, glasses, etc.). More than 40 projects have been implemented in the last 10 years at PETRA-III/DORIS (Hamburg), SOLEIL (Paris), ELETTRA (Trieste), ALBA (Barselona) and ESRF (Grenoble) synchrotrons, resulting in more than 90 peer-reviewed publications. The results of these experimental projects have been used in the implementation of 15 international and national research projects (9 projects have been directly related to the use of the XAS method). The laboratory is in the process of starting to use a new Max-IV synchrotron in Lund. The laboratory represents Latvia in the European Synchrotron and Free Electron Laser User Organisation (ESUO) as well as in the International X-ray Absorption Society (IXAS).

Besides the implementation of own projects, the Lab provides consulting services for other research groups all around the world on EXAFS data analysis and interpretation. This activity is currently growing due to the increasing popularity of the group and the EXAFS method and is likely to significantly expand the geography of cooperation and open up new opportunities in the future.

There are several groups around the world that have been active in the field of advanced XAS data analysis for a long time, and they can be viewed as "competitors". The group from Wigner Research Centre for Physics (Hungary) is the ancestor of the RMC method and is developing it for application to disordered materials such as solutions and glasses. Another group from Camerino University (Italy) is the main developer of the GNXAS code for ab initio XAS simulations but provides also RMC part dedicated to disordered materials. The international group including the teams from ISIS, University of Cambridge, University of Oxford, Queen Mary University of London (UK) and NIST (USA) is involved in the development of the reverse Monte Carlo method for the simultaneous analysis of many data types (neutron & X-ray total scattering & the Bragg profile, EXAFS, single-crystal diffuse scattering). Currently, there are only a few major players in the field of machine learning applications for XAS - Brookhaven National Laboratory (USA) and Smart Materials Research Institute at the Southern Federal University (Russia), but shortly their number will grow due to the potential of the method. At the same time, numerous groups (e.g. from Sapienza University of Rome (Italy)) working in the fields of liquids and disordered compounds use the molecular dynamics method to simulate the configuration-averaged XAS spectra.

FUTURE ACTIVITIES

The future directions of the research of the EXAFS Spectroscopy Laboratory will be closely connected with the recent trends in the European research area, summarized in the Strategy Report and Roadmap developed by the European Strategy Forum on Research Infrastructures (ESFRI). The research activities will exploit available large-scale European synchrotron facilities, having the size of the user community in 2017 at least 24000 users. EXAFS Laboratory is open for collaboration within the EC 9FP Programme "Horizon Europe" and any other programs.

The main directions of research will involve energy materials, extreme-conditions science, information technologies and environmental science.

An increase in energy consumption and limited natural energy resources are the main challenges to address by our society. The EXAFS Spectroscopy Laboratory plans to be involved in the investigation of irradiated materials (e.g. W) produced by the International Fusion Materials Irradiation Facility DEMO Oriented Neutron Source (IFMIF-DONES), which will play a strategic role in the Energy (ENE) domain for the implementation of nuclear fusion solutions to the massive production of energy, as well as for the role of Europe as an active actor in the development of nuclear fusion technologies. This activity will be realized within the EUROfusion project, in which the laboratory is already participating. Besides, we plan to continue researching multifunctional materials (e.g., tungstate/molybdate solid solutions, oxide thin films) for thermochromic, electrochromic, photocatalytic, thermoelectric and other energy applications [11, 12, 13].

The materials science at extreme-conditions such as ultra-high pressures and temperatures provides a promising route towards new materials that would not form under conditions of conventional material synthesis and processing techniques. These conditions can be created, for example, in diamond anvil cells (DACs) which can operate at very high pressures and extremely high or low temperatures. Together with the emergence of theoretical structure prediction tools based on ab initio quantum chemistry calculations, these activities will accelerate the field of materials discovery and provide a better understanding and control of their properties. The EXAFS Spectroscopy Laboratory is involved in such studies within the collaboration with two synchrotron centers at SOLEIL (Paris) and ESRF (Grenoble) [14, 15].

Key challenges in the field of information technologies include the growing demand for storage capacity, computing speed, smart sensors and energy-efficient IT solutions. New technology solutions are needed that require the development of novel nanomaterials with properties that are based on intriguing atomic and electronic interactions. The EXAFS method in conjunction with advanced analysis methods and ab initio simulations will provide an invaluable analytical tool for future in-situ and operando studies of emerging materials (e.g. 2D van der Waals and core/shell nanostructures), which we plan to realize at PETRA-III and future PETRA-IV facilities [16, 17, 18]. Mastering new experimental methods (e.g., Resonant X-ray Emission Spectroscopy (RXES) and X-ray Excited Optical Luminescence (XEOL) detection mode) will make a significant contribution to understanding these materials. These will be implemented in close collaboration with the groups at DESY within the upgrade program of the PETRA storage ring, in which EXAFS Spectroscopy Laboratory actively participates. Two Scientific Instrumentation Proposals (SIPs), "High-k EXAFS end-station for revealing the secrets of 2D layered materials" and "RXES studies of functional materials based on 5d transition metals", have been submitted in November 2020 for the development of the PETRA IV beamline portfolio. High-k EXAFS end-station is a general-purpose X-ray absorption spectroscopy beamline allowing the acquisition of EXAFS spectra in a large operational energy range (from 4 keV to 50 keV) up to high-k values (at least up to 18-20 $Å^{-1}$) with high signal-to-noise ratio, exceptional reproducibility of the energy scale, and beam stability at the sample with the aim to probe the structure and dynamics of 2D layered materials with a particular emphasis on the study of weak interlayer interactions. RXES instrument, based on von Hamos and Johann-type spectrometers, is proposed for *in-situ* and *operando* resonant X-ray emission experiments, including XES, RIXS, HERFD-XAS, with the aim to study the influence of spin-orbit coupling and the effect of crystal-field splitting on electronic structure of functional materials based on 5d transition metals.

One of the key challenges that society is facing nowadays is environmental protection. Studies in this field will greatly benefit from the local structure and low concentration sensitivities of X-ray absorption spectroscopy together with the high brightness of novel storage rings. Recovery and separation of heavy elements (e.g. rare-earths), understanding of chemical reactions at the atomic scale and behaviour of nanoparticles in various environments are among hot topics of future research [19, 20].

The sustainability strategy of the Laboratory is based on three main activities: 1) the continuous search and involvement of young students and PostDoc researchers; 2) the continuous improvement and development of team potential and available resources using the in-lab seminars and discussions, international schools/workshops/conferences; 3) the participation of young researchers in synchrotron experiments, a collaboration with main players in the field to maintain and improve the team competitiveness.

The EXAFS Spectroscopy Laboratory team has developed several demonstrators realized as software packages for EXAFS data analysis and available to the community from the web site of the lab. They are used also for teaching purposes during international schools. Locally, the EXAFS Spectroscopy Laboratory is involved in the teaching process at the University of Latvia providing an MSc course (64 hours) "Microscopy and spectroscopy characterization methods".

NETWORKING

EXAFS Spectroscopy Laboratory at ISSP UL already provides consulting services to other research groups all around the world on EXAFS data analysis and interpretation. This activity is currently growing due to the rising popularity of the EXAFS method and the number of synchrotron centers around the world. The geography of cooperation will likely expand and open up new opportunities in the future. EXAFS Laboratory is open for collaboration within the EC 9FP Programme “Horizon Europe” and other programs.

ISSP UL already has a strong collaboration with European synchrotron radiation centers such as PETRA-III (HASYLAB/DESY, Hamburg), SOLEIL (Paris), ELETTRA (Trieste), ALBA (Barcelona), ESRF (Grenoble), and MaxIV (Lund). The application of XAS in the field of materials science and nanotechnology is carried out in close cooperation with numerous international partners such as, for example, Karlsruhe Institute of Technology (Karlsruhe, Germany), Ceit & Universidad de Navarra (San Sebastian, Spain), Centre of Physics, University of Minho (Braga, Portugal), Department of Chemistry, St. Petersburg State University (St. Petersburg, Russia), Stony Brook University (Stony Brook, USA), Department of Chemistry, Paderborn University (Paderborn, Germany), Paul Scherrer Institute (Villigen, Switzerland), NaMLab GmbH/TU Dresden (Dresden, Germany), Wigner Research Centre for Physics (Budapest, Hungary), the International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University (Kumamoto, Japan) and Joint Institute for Nuclear Research (Dubna, Russia).

Collaboration with the high-tech industry is possible mainly within long-term projects due to the specificity of the XAS method. However, the short-term consulting service can be provided in particular cases.

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OPTICALY ACTIVE DEFECTS IN SILICON DIOXIDE

STATE OF THE ART .

There is a large number of optical and photonics applications, requiring low-loss optical fiber waveguides, deep-ultraviolet transmitting optics, optical elements suitable for work in ionizing or particle radiation environments, or for transmitting high-power laser light. In most cases the best material for these applications is pure or doped glassy SiO_2. Its large band gap, ≈9eV, the largest among all glassy materials, makes it the material of choice for three application groups: (i) optical elements and devices operating in the ultraviolet (UV) spectral range: windows, lenses, filter and grating substrates, thin film coatings, UV fiber waveguides [1]; (ii) high optical power applications, ranging from fibers for laser surgery or for metal welding [2] to fs-laser writing [3] and lenses for laser-ignited nuclear fusion [2]; (iii) photonics devices made from glassy SiO_2 are among the most resistant to radiation damage and are used and studied for nuclear energy and space applications [3,4]. Presently emerging hollow-core fibers [5] show promise for even higher power optical power transmittance and for higher radiation resistance.

A key phenomenon, crucial for all these applications, is the presence or generation of optically active point defects in the material. This problem has been treated in many works and a considerable level of understanding is achieved (see, e.g., reviews [3,4,6]). However, a number of problems are still not solved. Among them are: the specific origins of defect-related absorption in the deep UV region, the influence of technological impurities (chlorine, carbon) , the incorporation of fluorine and the related defects in highly fluorine-doped SiO_2 glasses, the effect of internal surfaces in amorphous structure of SiO_2 on optical and photochemical properties.

OUR POSITION

Researchers of the Laboratory of Optical Materials have detailed knowledge and long experience with SiO_2-based optical materials. Their past work has been crucial for identification and establishing of optical properties and radiochemical transformations of a number of basic defects in glassy SiO_2, like oxygen dangling bond ("non-bridging oxygen hole center", NBOHC), divalent Si ("silicon oxygen deficiency center", SiODC), interstitial hydrogen H_2, oxygen O_2 and O_3 (ozone) molecules in SiO_2. They have authored several well-cited reviews on this field (see, e.g., ref. [6] and references therein). Most recently, this group has tackled the problems of chlorine, a "technological impurity" in synthetic SiO_2 made from $SiCl_4$ [7], the dynamic properties of O_2 interstitials in SiO_2 [8] and the similarities and differences of defects in crystalline and glassy SiO_2 [9]. The group is well-qualified in optical, vibrational and magnetic spectroscopies. It can make use both of the in–house built equipment, such as vacuum-UV spectrometry, thermostimulated luminescence, radio-luminescence, and of the recently upgraded general-use equipment of ISSP UL. Most recently, the capability for in-laboratory sol-gel synthesis of silica glasses was added.

FUTURE ACTIVITIES

- Studies of factors limiting transparency of SiO_2 glass in ultraviolet, deep-ultraviolet and vacuum-ultraviolet spectral regions. This problem is most important in the context of developing wide spectral range and radiation/solarization-resistant optical fibers, which are required for analytical, medical, nuclear energy-fusion diagnostics and space applications. The importance of deep ultraviolet transmission materials is recently additionally boosted by prospective UV-disinfection applications in the wake of COVID-19 pandemics.
- Studies of chlorine- and carbon- related defects in SiO_2 – based glasses. Presently, a transformation from chlorine-related to carbon-related technology in the synthesis of SiO_2 glasses is gradually taking place. This is caused in part by ecological considerations and in part by the detrimental effect of Cl trace impurities on optical properties and solarization resistance of SiO_2 glass and optical fibers. While the properties of Cl impurities are known to some extent [7], the nature and optical properties of carbon dopants are much less understood.
- Studies of fluorine-related defects in glass. Fluorine is widely used in optical fiber technology to decrease the refraction coefficient and/or to reduce the fictive temperature of glassy SiO_2. Fluorine doping is presently studied as a way to further reduce the Rayleigh scattering in ultra-low loss optical fiber waveguides [10]. It generally increases the radiation resistance of the glass [2]; however, this effect decreases at large F concentrations. In contrast to other dopants, the properties of point defects related to fluorine still have not been identified. This knowledge is needed in order to optimize the optical fiber technology.
- Studies of the effects of SiO_2 glass morphology on the optical and photochemical properties of the material. Amorphous SiO_2 can be obtained in a large number of different forms with different morphologies (nanoparticles, nanofibers, nanoporous, micro- and mesoporous materials, porous crystalline (zeolite-like) structures. These materials possess large internal surfaces facilitating their use in chemical and biomedical applications.
- Developing of experimental capabilities supportive to the R&D needs of Latvian fiber optics industry

NETWORKING

- The group has long-standing active international collaborations with research groups in:
- France: Prof. Sylvain Girard, Youcef Ouerdane (Univ. Saint-Etienne), Dr. Nadege Ollier (Ecole Polytechnique, University of Paris-Saclay);
- Japan: Prof. Koichi Kajihara (Tokyo Metropolitan University), prof. Hideo Hosono (Tokyo Institute of Technology);
- Italy: Prof. Marco Cannas, Simonpietro Agnello (Palermo University)
- Lithuania: Dr. Audrius Alkauskas (Center for Physical Sciences and Technology, Vilnius)
- The group collaborates with Latvia-based fiber-optics industrial companies, Ceram Optecs and Light-Guide Optics.

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ANALYSIS OF PARAMAGNETIC DEFECT STRUCTURE IN FUNCTIONAL MATERIALS

STATE OF THE ART

Functionality of solid-state materials is inextricably linked to structural imperfections on atomic scale. Point defects are responsible for mechanical, thermal, chemical, electrical, magnetic and optical properties of the material. Peculiarities of intrinsic defect formation and activator ion incorporation have been well-documented in high symmetry hosts e.g. simple oxides and halides [1,2] – point defects can be categorized into electron centers, hole centers, interstitials and substitutional defects. The defects can occur in different charge states, often require charge compensation, may be localized at impurity ions and even form pairs and composite defect structures, therefore their properties and stability vastly differ. As it stands characterization of point defects in lower symmetry systems with several cationic and/or anionic positions in the crystal lattice is still an on-going quest in fundamental science. Some examples of recent results published in top tier journals include identification of intrinsic defects and rare earth impurities in optical materials [3,4], determination of defect structure and thermal stability of neutron-irradiated oxides [5,6], incorporation and properties of transition metal ions in biomaterials [7–9] and others.

A key aspect in the characterization of point defect structure in complex matrices is application of advanced spectroscopic techniques. Electron paramagnetic resonance (EPR) spectroscopy has been established as the central method for the investigations of paramagnetic centers in solids allowing unambiguous identification of the defect model and its local structure. A modern approach is to include variable temperature multifrequency EPR measurements, double resonance experiments, pulse techniques, spectra simulations in correlation with complementary investigatory techniques and theoretical calculations.

OUR POSITION

ISSP UL is in possession of a modern Bruker continuous wave (CW) EPR system with multifrequency (X and Q band) capabilities in variable (4-300 K) temperature range with possibilities to conduct electron nuclear double resonance (ENDOR) experiments at the X band. There is also a custom-built optically detected magnetic resonance (ODMR) setup for the studies of luminescence mechanisms and origin of optical absorption bands in materials. Advanced complementary spectroscopic techniques are also accessible at ISSP UL.

The EPR group of Laboratory of Spectroscopy has expertise in defect analysis in systems ranging from single crystals [10–12] to nanomaterials and composites [13–15]. The main research activities are performed on inorganic solid-state materials to identify and analyse the presence of paramagnetic species – intrinsic defects and activator ions – and their role in the performance of the material.

FUTURE ACTIVITIES

- Radiation defect creation and evolution in functional materials, including materials for fusion applications. Determination of defect local structure models and their stability characterization via correlated EPR and thermal annealing experiments.
- Intrinsic defect and activator ion characterization in optical materials – luminescent and persistent phosphors, photochromic materials, optical temperature sensors. Establishing the role of defects in optical processes via combined optical and magnetic resonance techniques – EPR measurements during luminescence and ODMR.
- Studies of paramagnetic defects and impurities in biomaterials. Development of variable temperature multifrequency EPR methodology including ENDOR and pulse (in collaboration with other groups) techniques.
- Nanomaterials and nanocomposite materials ranging from nanoparticles, thin films to multiphase functional materials.

NETWORKING

There are several on-going academic collaborations:

- Sol-Gel Chemistry Group, Vilnius University, Lithuania; prof. habil. Dr. Aivaras Kareiva, assist. prof. Dr. Aleksej Zarkov; applications of advanced EPR in biomaterials.
- Kazan Federal University, Russia; prof. Dr. M. Gafurov; multifrequency and pulse EPR methods.

There is a colaboration with the local fiber optics company Light Guide Optics International.

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ELECTRONIC PROCESSES AND CHARGE TRANSFER MECHANISMS IN LUMINESCENT MATERIALS

STATE OF THE ART

The research of luminescent materials having band gaps over 3 eV is of interest due to wide applications of these materials [1]. It is focused on luminescent centers, both doping-induced and intrinsic ones, electronic processes, generation and relaxation of excited states as well as on the charge transfer. This is an active research field with numerous studies dedicated to understanding the luminescence mechanisms (e.g., [2,3]). Among these studies, the research groups at ISSP LU stand out in the fields of luminescent dosimetry and persistent luminescence, i.e., photoinduced long-lasting luminescence (Optical Materials laboratory and Laboratory of Spectroscopy).

Materials emitting visible or ultraviolet luminescence must possess sufficiently wide band gap and are counted to insulators or wide-gap semiconductors. Apart from the "local" properties of the luminescence centres, the luminescent properties of these materials are to a large extent determined by charge carrier generation/ionization, transport, trapping and de-trapping or tunnelling. The exact fundamental mechanisms of these processes and their peculiarities in different luminescent materials are still not entirely understood [3,4].

OUR POSITION

Significant work is invested world-wide in studies of long-lasting (persistent) luminescence of solids. While this phenomenon is the basis of numerous applications (visualization in darkness, various indicators, traffic signs etc.), the underlying fundamental mechanisms providing the ultra-long luminescence decay time are not clearly understood.

The team within the Optical Materials Laboratory has performed a series of in-depth studies of electronic processes in long-lasting luminescence materials [5, 6]; a new mechanism of long-lasting luminescence involving electron tunnelling has been proposed [7]. The work of this and other international groups on mechanisms of long-lasting luminescence mechanisms is summarized in our recently published topical review paper [8].

In scintillator/dosimetry field, the radio- and photoluminescence studies of prospective scintillator ZnO:In and ZnO:Ga were conducted. The results of experiments show an extremely fast subnanosecond decay of near-band-edge luminescence [9]. The time constant determined for the decay of this luminescence was ≈17 ps [10] and it is very close to the present best result 15 ps found by M. Kano et al. [11].

Thermostimulated luminescence investigation of Al_2O_3:C layer on metallic aluminum was conducted [13] and it was shown that the charge traps in Al_2O_3:C layer are similar to those known in the widely used thermoluminescent dosimeter TLD – 500. An understanding of the electronic processes in these layers is necessary to develop radiation-detecting 2D screens.

FUTURE ACTIVITIES

For persistent luminescence materials:

The studies of the impact of spatial distribution of donor-acceptor pairs on persistent luminescence are planned. These studies should be fruitful for finding the material with temperature independent persistent luminescence significantly expanding the list of possible applications of such materials. .

The two main directions are foreseen for ZnO based scintillator materials:

- to elucidate the main mechanism(s) contributing to room temperature luminescence;
- to find a more efficient donor and its optimal concentration in ZnO for an efficient suppression of charge carrier trapping at intrinsic defects.

For Al_2O_3:C and Al_2O_3:Cr based dosimeters, the research of underlying mechanisms will be performed as a part of optimisation of synthesis methods. The main aim is focused on two aspects: firstly, the scalability of synthesis for production of 2D dosimeters will be studied, and secondly, studies of electronic processes involved in optically stimulated luminescence (OSL) are planned.

NETWORKING

- Prof. P.Rodnyi (Peters the Great Saint Petersburg Polytechnic University, Russia)
- Dr. P. Boutachkov (GSI Helmholtzzentrum für Schwerionnenforschung, Germany)
- Dr. E. Gorokhova (Federal State Unitary Organization “Research and Technological Institute of Optical Materials All Russia Scientific Center”, Russia)
- Dr. V. Lahty (Tampere University), Dr. M. Lastusaari (University of Turku), Finland
- Dr. P. Bohacek and Dr. M. Nikl (Institute of Physics AS), Czech Republic
- Dr. S. Zazubovich and Dr. A. Krasnikov (Institute of Physics, University of Tartu), Estonia

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THIRD ORDER NON-LINEAR OPTICAL EFFECTS, MATERIALS AND DEVICES

STATE OF THE ART

In the last years third-order nonlinear optical materials have seen a new rise in interest due to the development of soliton microresonators [1] for microwave applications, telecommunications, and optical sensors as well as for quantum photonics [2] with the main focus on entangled photon sources and non-destructive photon interaction. In all of these technologies materials with a strong Kerr effect play a key role [3]. One of the main limitations for this technology transition from laboratory tests to commercial applications is the lack of efficient materials with strong Kerr effect and low optical losses. On the other hand, materials with high optical loses due to strong Two-photon absorption (TPA) can be used in optical limiting applications. In case of developing slow thermo-optical switches materials with a strong thermo-optical effect is desirable. At same time for ultra-fast all-optical switches pure electronic part of the Kerr effect is essential and the interference from other effects must be limited. Although there are plenty of published papers about Kerr effect estimation [4–6], distinguishing between thermo-optical and Kerr effects, separating Kerr effect into fast electronic response and slower molecular effects and evaluation of relaxation time for each effect are among important methodological problems in investigations of third-order nonlinear optical materials [7]. Most of scientific groups use different methodologies, making it difficult to correctly compare the studied materials.

For practical application mainly two third-order NLO effects have been considered – Kerr effect and Two-photon absorption. These effects characterize refractive index and optical absorption variations with changes of optical field intensity. The main issue with third-order NLO studies is the correct interpretation of nonlinear refractive index changes – are they induced by thermo-optical or Kerr effect and how large are each of the Kerr effect components – electronic, vibrational and reorientational. To study these effects, the term Optical Kerr spectroscopy has been present in the scientific literature for a while [3]. Most of these works are mainly based on Beam-Deflection or specific Pump-probe measurement methods to study temporal and some spectral aspects of Kerr effect. At the same time, many publications have already indicated that pulse repetition rate [5], polarization resolved Z-scan [8] and other measurement methods can give significant information a-bout nonlinear refractive index of material absent from the previously mentioned Optical Kerr spectroscopy works. To step forward in this field, a more detailed study of TPR Kerr spectroscopy incorporating Z-scan and Beam deflection methods with pulse width, pulse repetition rate and polarization-resolved measurements is necessary.

To employ for practical applications third-order effects like Optical Kerr effect (OKE) and two-photon absorption (TPA) effect [9] -, various material groups as NLO media are being studied with different pros and cons. These include:

- ***Metamaterials*** that allows for creation of materials with unique electromagnetic properties;
- ***Inorganic/organic hybrid materials*** for whom d-orbital electrons can increase polarizability and coulombic interaction lead to strong local field;

- ***2D NLO materials*** with strong non-linear absorption properties. Also 2D delocalization of π-electrons provides enhancement of third-order nonlinearities;
- ***Organic materials*** with possibility to tune NLO properties with structural alterations and low production costs are very promising for possibility to find efficient and cheap NLO materials for practical applications. Especially for applications in visible range of light where most alternatives possess strong absorption.

Compared to other material groups organic materials are promising for all-optical applications due to immense number of molecular structures, compatibility with other commonly used inorganic and organic materials, low price, and possibility to tune material properties by varying material structure and ability to form flexible photonic devices. Recent studies have demonstrated significant growth in organic material OKE coefficient values [9], making them a promising substitute for silicon in photonic devices. OKE values of organic materials have been demonstrated to be four orders larger than of pure silicon – reaching 0.17 cm^2/GW in the visible range of light [10]. Depending on application type, different material selection rules can be used. Material requirements for optical limiting are large TPA coefficient, while for all-optical switching two terms are used as figures of merit (FOM): (i)OKE coefficient, (ii)$T=2\cdot\alpha_2\cdot\lambda/(n_2)$, where α_2 is TPA and n_2 is OKE coefficient [11]. Material to be used in all-optical switch device should have large OKE values while satisfying $T<1$ condition.

For practical all-optical device implementation it is necessary to achieve a high confinement of light. To realize such confinement, typically waveguide and photonic crystal devices are considered. Such devices should employ NLO material with optical intensity-dependent refractive index or absorption. Despite that the subject of all-optical devices is growing in popularity, only some experimentally validated examples have been demonstrated as summarized in the review article [9]. Current state-of-the-art includes few examples of devices using graphene for optical switching [12] or polariton opto-optical devices using organic materials [13]; even so, these devices are still in early development phase. Due to the low efficiency of available third-order materials, just a limited amount of waveguide devices have been experimentally validated and reported. Fortunately, there is no shortage of reported waveguide and photonic crystal theoretical device designs that may be used to create novel all-optical switching devices. The most common include whispering gallery mode (WGM) resonators [14], waveguide MZIs [15] and photonic crystal cavities [16] which have been used in sensing, communications, spectrometry and other applications.

OUR POSITION

The competence of Laboratory of organic materials at Institute of Solid State Physics allows dealing with the main issues related to studying properties and assessing applications of NLO materials. We have broad experience in structure-property relation studies of second- [17–19] and third-order [6,20] NLO organic materials. Along with these studies, we have gained experience in performing Quantum Chemical Calculations (QCC) to obtain first and second-order hyperpolarizabilities of organic materials.

Great attention has been given to development of experimental methodology for investigation second-order [21,22] and third-order NLO [6] properties. Development of polarization-resolved Z-scan measurements [23] allows us to study in more detail the origin of Kerr effect in specific media. This is especially essential as only the electronic part of Kerr effect is applicable for high-bandwidth all optical processing.

Laboratory of Organic materials has conducted research to create photonic devices based on SU-8, PMMA and active NLO organic materials. By combining SU-8 as passive material for optical waveguides with guest-host system of active NLO chromophores and PMMA as active materials, we have been able to demonstrate functioning electro-optical switch [15] as well as all-optical gas sensor [24].

Laboratory of Organic materials has long established a workflow for characterization of second-order NLO properties. The workflow includes: a) sample preparation; b) characterization of linear optical properties (Spectrophotometer Cary 7000; Spectral ellipsometer Woollam RC2, Metricon 2010); b) second-order NLO properties (Maker-fringe method for SHG measurements; Hyper-Rayleigh scattering measurements; Mach-Zehnder interferometer and Teng–Man method for electro-optical measurements). For third-order NLO studies custom built Z-scan and Mach-Zehnder interferometer setups are developed at ISSP UL.

All NLO effects studies at ISSP could be supported by exceptional set of lasers covering excitation from UV to the Mid-IR and pulse durations from the ns to fs:

- Nanosecond laser (1064 nm 8 ns) with pulse repetition rate from 200 – 40 000 s-1;
- Tuneable picosecond laser (400-1600 nm, 15 ps) with a pulse repetition rate of 1000 s-1;
- Femtosecond laser (1030 nm, continuously tuneable 200 fs – 10ps pulse duration with pulse repetition rate from 1 kHz – 1 MHz);
- Tuneable femtosecond laser (OPA, 190 nm – 2500 nm, < 190 fs pulse duration with pulse repetition rate up to 1 MHz).

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FUTURE ACTIVITIES

The important goal of future activities will be acquiring new knowledge that will contribute: a) to basic understanding of third-order NLO effects in organic materials; b) to develop correct measurement methodology to characterize their NLO properties. This could lead to new structure–property studies and third-order NLO organic materials designs. Moreover, the planned development and verification of Quantum Chemical Calculations (QCC) methods for third-order NLO material property calculations could lead to faster molecule screening. For the scientific community such results may serve as a crucial stepping-point towards the development of novel NLO organic materials that may be used in building the ultra-broadband communication networks or in the next-generation quantum computing systems.

Development of measurement methodology

Measurement methodology developments will be supported by project "Development of Time and Polarization Resolved Kerr (effect) Spectroscopy":

- ***Polarization-resolved Z-scan measurements*** will be extended to fs range with tuneable fs laser (should be available at beginning 2021). In combination with already available (tuneable 15 ps and 1064 nm 8 ns Nd:YAG laser). Such laser systems with different pulse repetition rates, spanning wavelengths ranges from the UV to the Mid-IR and pulse durations from the fs to ns allows us to perform fundamental studies of Kerr effect origins and develop third-order NLO materials for practical applications;
- ***Beam-deflection method*** as alternative to z-scan for Kerr effect characterization;
- ***Fluorescence anisotropy measurements*** to study in more detail two-photon absorption properties of materials will be implemented.

Development of Kerr effect evaluation through Quantum Chemical Calculations (QCC)

Use of reliable QCC for predicting and/or describing non-linear optical properties of materials allows to improve significantly the efficiency of the structure screening through rationalizing the structure–property relationships. With the goal to validate selected QCC methods, great attention will be paid for the comparison of QCC results with the experimentally measured data for all contributions to Kerr effect. By means of QCC we plan to obtain:

- ***Linear polarizability values,*** which allows us to estimate reorientation contribution [25];
- ***Raman scattering intensities and frequency,*** which allows us to calculate the vibration contribution [26];
- ***Second-order hyperpolarizabilty*** values, which allows us to calculate the electronic contribution [27].

For reorientation and vibration effects additional attention will be given to time constant calculations [7].

Development of third-order NLO materials

Compared to other material groups organic materials are promising for all-optical applications due to immense number of molecular structures, compatibility with other commonly used inorganic and organic materials, low price, and possibility to tune material properties by varying material structure and ability to form flexible photonic devices. Therefore, we are planning to work in two directions:

1. ***Development of Organic materials*** for third-order NLO applications. This includes the goal of finding NLO organic materials with large third-order NLO values (exceeding 0.1 cm^2/GW that is four orders larger than silicon and corresponds to the state-of-the-art materials for NLO applications) from which an amorphous thin-films can be produced;
2. ***Enhance NLO response of organic materials through plasmonic structures***. This will include studies of NLO response of nanoparticles, designing of plasmonic structures/metamaterials and how nanoparticles and plasmonic structures enhance third-order NLO response of organic materials.

Development of photonic devices based on third-order NLO materials

Development of all-optical photonic devices will proceed for the following applications:

- ***All-optical sensors*** -two types of all-optical sensor devices – Asymmetric Mach-Zehnder interferometers and Whispering Gallery Mode resonators;
- ***All-optical switch*** - *d*evelopment of organic all-optical transistor will be based on third-order NLO organic materials studied by Laboratory of Organic Materials. Device design will be based on Mach-Zehnder interferometer with active third-order NLO cladding that will allow for interaction between two beams in adjacent waveguides. Here the main focus will be on materials with large electronic part of Kerr effect to ensure ultra-fast processing;
- ***Soliton microresonators*** - research will be conducted towards development of soliton microresonators implementing third-order NLO organic materials. We plan to use organic materials that possess large Kerr effect values and low TPA in near infrared and visible spectral range. The goal is to create a microresonator that could convert CW laser pulse into multiple peaks covering wide spectral range. While this theme is very

prominent in the latest *Nature* publications, such devices based on organic materials still have not been demonstrated;

- ***Entangled Photon sources*** - third-order NLO materials can be used for entangled photon pair generation using Spontaneous Four-wave mixing. The main goal would be to develop such light source for visible spectrum based on organic materials. Mainly two design types will be considered – Whispering Gallery Mode resonator and Delay line with active cladding.

NETWORKING

Latvia:

- Riga Technical University – Institute of Applied Chemistry
- Ceram Optec optical fiber company

Europe:

- Kaunas University of Technology - Faculty of Chemical Technology
- Swiss Federal Institute of Technology Lausanne – Photonic Systems Laboratory

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RADIATION DAMAGE STUDIES IN FUNCTIONAL MATERIALS FOR FUSION AND PARTICLE PHYSICS

STATE OF THE ART

Optical and dielectric materials will play a substantial role in various diagnostic systems of future deuterium-tritium fusion reactors, which have to withstand 14 MeV neutron irradiation of unprecedented intensity. The development of novel neutron resistant optical and dielectric functional materials becomes an unavoidable part of EUROfusion Roadmap, because radiation induced lattice defects strongly affect functionality of different functional components (windows, lenses, fibres, etc.) and therefore deep understanding of the defect creation in solids is of fundamental importance.

Research and development of scintillating materials and novel ionizing radiation detecting devices for particle physics, neutron research and medical imaging - such as positron emission tomography, single photon emission computed tomography that are in the priority list of European grand research centres: CERN, ESS, Helmholtzzentrum für Schwerionenforschung (GSI), Grand Accélérateur National d'Ions Lourds (GANIL), Institute Laue-Langevin (ILL) and many others outside Europe: Japanese National Research and Development Agencies (RIKEN) , Australian Nuclear Science and Technology Organisation (ANSTO), etc. Novel crystal detectors are continuously being discovered and developed in academia and industry.

All these materials are working in a harsh radiation environment, where various particles, such as γ rays, neutrons, and even charged hadrons, are expected. Thus it is of fundamental importance, to understand, control and predict their radiation damage under intensive neutron/gamma radiation environment.

The key point for all these applications is the formation of point and extended defects in the materials, understanding their defect structure, the processes of defect interconversion and annihilation. Many works have been devoted to this problem, and a significant level of understanding has been achieved (see, for example, reviews [1-4]). Among numerous insulating materials, in general, wide-band gap refractory oxides, nitrides and diamond show the highest radiation resistance. Specific attention within the fusion research program was given to MgO, Al_2O_3, $MgAl_2O_4$, BeO, AlN, Si_3N_4, diamond and few others. The available from literature threshold displacement energies [1-4] as well as some optical characteristics of point defects therein are documented in our recent reports [1,3].

However, a large number of problems remain unresolved. In particular, at present, more or less enough information is available on structure and mutual/thermal behaviour of radiation defects only for binary oxides – ionic MgO and partly covalent Al_2O_3, common model objects because of simplicity and being structural units of $MgAl_2O_4$ spinel. The corresponding detailed systematized data on radiation damage (especially, induced by fast neutrons) in other materials, including $MgAl_2O_4$, is practically absent. One very important aspect of radiation damage that should be mentioned is impurity effects. Although impurities themselves are quite well characterized in all important materials, the appropriate data on their contribution to neutron/gamma damage is very rare and scarce. We further notice that the nature, the structure of radiation induced oxygen interstitials and the possible role of impurities in their stabilization is more or less established only for the most simple MgO crystals, where the formation of the $(O_2)^-$ superoxide ions, stabilized near unknown impurities and/or other structural defects was perfectly established by EPR and theory. Note that the vast majority of the experiments on point defects were performed using an optical absorption and luminescence, while such rapidly developing techniques as Raman spectroscopy and neutron scattering methods were used only in very rare cases. Note that optical absorption methods do not work in the region of large defect concentrations due to the optical density saturation, which apparently explains the poorness of existing experimental results, while laser-based methods of Raman spectroscopy were not yet widely available.

OUR POSITION

Over the past ten years, Laboratory of Kinetics in Self-Organizing Systems, ISSP LU has been actively involved in the solving of the above problems via the following projects:

- EUROfusion: Multiscale modelling of radiation effects in $MgAl_2O_4$ spinel and general oxides.
- EUROfusion: Advanced experimental and theoretical analysis of defect evolution and structural disordering in optical and dielectric materials for fusion applications
- Radiation damage studies in scintillator materials for high-energy physics and medical applications.

In November 17, 2017, after the successful presentation of the research report at Crystal Clear Collaboration Board at CERN, the appropriate collaboration agreement between ISSP UL and CERN was approved and signed on February 5, 2018 by both sides.

Since November 2020, our group is participating in a National Research Programme "High Energy Physics and Accelerator Technologies" has been launched to strengthen the development of the Latvian scientific community in cooperation with CERN.

Our group had performed comprehensive studies of defect structure*, in-situ* defect evolution and their post-irradiated thermal annealing in many materials, including MgO, Al_2O_3, MgF_2, $MgAl_2O_4$, $Y_3Al_5O_{12}$, $Gd_3Ga_5O_{12}$, BeO. More than 30 papers were published in the last 3 years, some of them are referenced in refs [5-12].

FUTURE ACTIVITIES

Future research, to be carried out in subsequent EUROfusion projects and CERN-related National Research Programme, will be focused on detailed theoretical calculations of the atomic, electronic and magnetic (EPR) structure; optical absorption, Raman and IR spectra; and annealing kinetics of the basic defects in functional materials, including:

- Development of efficient method for accurate calculations of the vibrational spectra of defects in functional non-metallic materials based on the first principles computer codes;
- First principles calculations of the atomic, electronic, vibrational properties for diamond doped with N, B and diamond containing vacancies and internal cavities;
- Experimental Identification of the Raman and IR modes due to above-mentioned defects/impurities;
- Calculation of dielectric properties and tg δ for defective/irradiated diamond, Al_2O_3, AlN and SiOx;
- Modelling of the interfacial effects in diamond covered by thin AlN and SiOx films;
- Theoretical analysis of peculiarities of diffusion controlled processes in heavily irradiated insulating materials;
- Analysis of the radiation-induced disordering though defect annealing kinetics measured under different neutron, proton, fast electron or heavy ion fluencies in AlN, SiC, SiO_2 and diamond.

NETWORKING

The group has long-standing active international collaborations with research groups in:

- France: Prof. Dr. Helmut Schober (Institut Laue-Langevin);
- Germany: Prof. Dr. J. Maier (Max-Planck Institute, Stuttgart), Prof. Dr. T. Scherer (KIT, Karlsruhe), Dr, G. Pintsuk (Forschunzentrum Julich GmbH);
- Spain: Dr. Rafael Vila, (CIEMAT, Madrid);
- CERN: Dr. Etiennette Auffray, K. Dreimanis;
- Estonia: Prof. A.Ch. Lushchik (University of Tartu).

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TECHNOLOGY & EXPERIMENTAL METHODS

THIN FILM AND COATING TECHNOLOGIES

STATE OF THE ART.

The EU aims to be climate-neutral by 2050 – an economy with net-zero greenhouse gas emissions. This objective is at the heart of the European Green Deal and in line with the EU's commitment to global climate action under the Paris Agreement [1]. Thin film coatings are widely used in variety of applications in optical, electronic, optoelectronic and photonic devices, including mirrors, smart windows, solar cells, coatings preventing corrosion and to ensure antistatic and adhesion properties and chemical attributes and for food wrap to provide a specific performance characteristic due to their physical and chemical attributes. The global thin films and nanocoatings market includes coatings, which exhibit e.g. superior abrasion resistance, ductility, hardness, lubricity and transparency, as compared to other conventional coatings. A shifting demand towards inorganic nanocoatings instead of polymer coatings, mostly due to superior properties and low Volatile Inorganic Compounds' Impact Air Quality (VOC) emissions, are expected to be major driving forces for the nanocoatings market. In addition, an increasing awareness of the benefits of antibacterial and antiviral (anti-COVID-19), self-cleaning and chromogenic coatings in energy, building, mechanical and aerospace applications is expected to increase the market demand [2].

Thin films technologies today are considered as Green Nanotechnologies (PVD, MOCVD, PLD, ALD etc.)[3] and are key technologies for many large area (solar cell, smart windows, etc.) and multifunctional coatings (antimicrobial, self-cleaning, etc.). Nanocoatings could demonstrate up to 99.9998% effectiveness against bacteria, formaldehyde, mould and viruses, and are up to 1000 times more efficient than previous. Nanocoatings companies already have partnering with global manufacturers and cities to develop anti-viral facemasks, hazard suits and easily applied surface coatings. Thin films activities will contribute as well to reducing the greenhouse gas emissions and enable European industry to stay globally competitive and to fulfil the goals of the Lisbon Treaty [4].

New plasma technologies of High-power impulse magnetron sputtering (HIPIMS) bear an enormous potential for manufacturing coatings with properties exceeding those of state of the art by far: better thin film morphology, denser and smoother films can be achieved when compared with standard DC coating technology [5,6]. The major benefit of this new technology is a very high degree of ionised target material, leading to superior coating properties, such as high density, good adhesion, very smooth droplet-free surfaces. The capability of multi targets, hot target, and liquid target HIPIMS to produce new advanced multicomponent high-performance functionalized nanomaterials and multilayers. Improvement will be available in the fields of antibacterial and antiviral coatings, photovoltaics, smart windows, mechanical engineering, medical applications, photo catalytic [5-7].

State-of-the-art of energy-efficient windows is based on low-*energy* and/or solar-control coatings. However, these static windows are not efficient enough throughout the season and cannot get rid of the excess of visible radiation in a dynamic way. The energy savings can be much higher if a switchable (dynamic or smart) window is used rather than a static one. Unfortunately, these windows are still rare in buildings because today's commercially available smart windows are based on electrochromic devices, which consist of five layers, two electrodes and an electrolyte together with the electrochromic and ion storage films. The complexity of the fabrication process makes smart windows costly [2,3], about 800 EUR/m^2 for a complete insulating glass unit. The implementation of smart windows based on materials with a photochromic effect i.e., exhibiting reversible colour change as a result of the absorption of electromagnetic radiation, allow the development of passive devices, without the need for any extra layers or sensors. Such windows will be activated by solar light, and will need neither electricity nor control unit to function and switch automatically on-demand without need for human intervention [8].

Gallium oxide has become one of the most investigated materials of today. The reason for this large interest is the extremely promising properties for electronic and optical applications of this wide bandgap material, together with the relatively un-expensive substrate wafers. Advanced technologies for growing epitaxial multilayers at high temperatures: MOCVD, PLD and off-centre magnetron sputtering (PVD) demonstrate an enormous potential for manufacturing epitaxial layers with properties exceeding those of state of the art by far [9].

OUR POSITION

Based on more than 35 years of experience in vacuum deposition thin film technologies, a well on equipped instrument park of technological facilities, including HIPIMS, MOCVD, PLD and on related characterization methods and equipment, nowadays ISSP UL becomes a recognised centre of excellence for thin film nanotechnologies in Baltic countries.

The Thin Films Laboratory mainly focused on thin film deposition and nanocoating of a wide variety of inorganic materials, using different deposition techniques, including the PVD vacuum multifunctional cluster (thermal, e-beam and magnetron sputtering), high power impulse magnetron sputtering (HiPIMS), as well as PLD (Pulsed Laser Deposition), MOCVD (Metal Organic Chemical Vapour Deposition), and ALD (Atomic Layer Deposition). Current scientific projects are targeted on the development of novel advanced materials and coatings. A list of selected publications and patents related to this activity is given below [10-15]. We have patented and published technologies of deposition: (i) an antiviral, yeasticidal and antibacterial nanocoatings; (ii) novel R-HiPIMS technology of deposition of functional TMO (transition metal oxides) thin films and multilayers on flexible substrate and upscale the process (patent (EU) - EP20020352.9 and (LV) LVP2020000040 + roll-to-roll process technology description); (iii) cryogenic process - p-type ZnO-ZnO_2; HIPIMS dual magnetron yttrium monoxide; novel thin films ReO_3-WO_3 and ReS_2 with advanced electric and optical properties [11,12].

Thin Films Laboratory is well positioned to explore new materials for different applications and aimed to increase the research and innovation capacity of the Institute in the area of thin film and technology which is further supported by an extensive publication track-record in both basic and applied physics journals, as well as patents. Thin Films Laboratory is granted by many high rating scientific proposals for 2021-2024 years. In recent years we have developed nanocoating technologies approved by patents and papers for selected themes.

Deposition technologies developed in the last years at the ISSP UL are widely and extensively used for thin films and coatings productions. Cutting-edge plasma HIPIMS and dual magnetron co-sputtering technologies developed at ISSP UL are approved by many EU patents [10] and become the process of choice in many EU and LV applied projects and applications: (i) antiviral and antibacterial, (ii) transparent conducting oxides (TCO), multifunctional electrochromic and photochromic thin films etc. Especially HIPIMS processes developed at ISSP UL using dual magnetron sputtering play an important role for deposition new materials: ZnO-IrO_2, ZnO-Al, ReO_3-WO_3, NiO-IrO_2, WO_3/Cu/WO_3) [10]. As evaluated by EU referees, the proposals are of excellent quality with the goal to develop novel and advanced procedures for metal oxide sputter coating of extended surfaces. Such coatings are extremely versatile and used in a variety of electrooptical and semiconductor based applications.

The SAF25/50 multifunctional R&D cluster plant installed at ISSP UL cleanrooms in 2015 and upgraded in 2019 is intended for research and development in the field of thin film technologies. The plant is a multifunctional, expandable, modular and flexible system. The plant comprises an input/output chamber with ion gun, a central substrate transfer chamber with radial telescopic transport arm and up to 7 deposition chambers. The substrate is positioned horizontally on a holder. Deposition zones are configured for substrate rotation or displacement during upward deposition.

Pulsed laser deposition (PLD) is a valuable tool for production of thin films and epitaxial heterostructures from various materials with complicated stoichiometry. PLD allows a one-to-one transfer of elements from target to substrate, what is a strong advantage for the deposition of multiple element systems. Different atmospheres (Ar, O_2, N_2, H_2, H_2S) of deposition allow varying of properties of films in a wide range: ZnO, Ga_2O_3, MoS_2, etc. ISSP UL has experience in making high-quality thin films of perovskite structures by PLD as lead-free ferroelectric thin films for non-volatile memories and NEMS, in studying structure and surface topology (by AFM), in characterization of dielectric and electromechanical properties [www.cfi.lu.lv].

MOCVD reactor Aixtron (AIX-200RF) is available for the synthesis of epitaxial thin films using liquid metal-organic compounds and gaseous non–metal chemical hydride and oxide gases. The equipment is suitable for the synthesis of classic LED structures, Si, ZnO, and group III nitride 1D nanostructures, as well as for deposition of functional ultra-wide bandgap gallium oxide and metal oxide (GaMeO) thin films and multilayers for optoelectronic and electronic applications. Novel reflecting optical coatings (on mirrored sapphire substrate - MSS) for LED device structure fabrication based on MOCVD grown epitaxial Ga_2O_3/Al_2O_3 multilayers (prototype, patents, technology description) for adaptive optics. There is a possibility to dope the materials, in order to obtain n- or p-conductivity. MOCVD equipment provides wide possibilities to manipulate chemical reactants creating different 1D, 2D, and hybrid structures.

FUTURE ACTIVITIES

The future directions of the research of the Thin Films Laboratory will be closely connected with the recent trends in the European research area summarized in the Strategy Report and Roadmap developed by the European Strategy Forum (Vision and roadmap for European raw materials). The activities will be in compliance with several goals and RIS3 priorities. The research activities will exploit available ISSP UL clean room and thin films facilities in strong collaboration with industrial partners in Latvia and EU. Laboratory is open for collaboration within the EC Programme “Horizon Europe” and any others.

A roadmap for ISSP UL for the forthcoming 7 years activity will be built in line with current Laboratory approved projects and forecasted industrial and societal challenges laid out in the “Horizon Europe” Programme, including “Buildings and industrial facilities in energy transition”, “Advanced Materials”, and “Key digital Technologies.

The main goals will be to develop cutting-edge technologies for deposition and epitaxial grows thin films and multilayers:

- High rate dual-magnetron R-HIPIMS technology for deposition of functional TMO thin films and multilayers on flexible substrate and upscale to the roll-to-roll process;

- Hot target (Ga) and off-centre HIPIMS grows of epitaxial ultra-wide bandgap gallium oxide and metal oxide (GaMeO) thin films and multilayers for deep UV optoelectronics and electronic applications;

- MOCVD technology for epitaxial grows Ga_2O_3 and $ZnGa_2O_4$ layers and to establish n- and p-type Ga_2O_3 and $ZnGa_2O_4$ epitaxial film growth processes for deep UV optoelectronics and electronics applications;

- PLD deposition of lead-free ferroelectric thin films for non-volatile memories and NEMS;

- PLD deposition of 2D materials MoS_2, WS_2, ReS_2;

The aim of UVWB research activities will be to develop advanced high rate PVD magnetron sputtering and MOCVD technologies for deposition of functional ultra-wide bandgap gallium oxide and metal oxide (GaMeO) thin films and multilayers for optoelectronic and electronic applications. Novel reflecting optical coatings (on mirrored sapphire substrate - MSS) for LED device structure fabrication based on MOCVD grown epitaxial Ga_2O_3/Al_2O_3 multilayers (prototype, patents, technology description) for adaptive optics. The research methodology is focussed on making gallium oxide viable for a broader range of semiconductor material applications by forming it as p-type through the controlled insertion of dopants or its formation as a ternary material with addition of Zn. The extension of this to the formation of amorphous films is also included though less well developed as an idea. PVD magnetron sputtering technique will be adapted by the researchers to control the properties of the films using high rate magnetron sputtering and having targets at elevated temperatures. In parallel, the researchers will develop an MOCVD approach for epitaxial growth of the films.

The aim of 2D research activities will be to develop advanced 2D layered materials. A rich choice and high tunability of 2D materials promote the development of next generation electronic, opto-electronic and energy devices with specific functions. We are planning to investigate hybrid systems of layered CDW materials grown on substrates with hexagonal crystal structure stable in the corrosive sulfur atmosphere such as GaN, InN and ZnS, and materials which can be converted into sulfides such as ZnO (into ZnS) and CdO (into CdS). Layered CDW materials to be studied are mainly TMDs materials (TaS_2, VS_2, $TiSe_2$, etc). Multiple synthesis techniques will be used and compared to grow CDW material shell (such as pulsed laser deposition, magnetron sputtering, atomic layer deposition, etc).

In the framework of approved projects for Laboratory, we will develop following technologies and advanced materials:

- high rate PVD magnetron sputtering technology for deposition of pure and doped (p-type dopants and RE) amorphous and crystalline gallium oxide Ga_2O_3 thin films and $ZnGa_2O_4$ thin films. The applications in focus are: (I) high power electronics; (ii) deep UV TCOs/TSOs optoelectronics; (iii) efficient inorganic luminescence devices (a-Ga_2O_x:RE);

- MOCVD technology of Ga_2O_3 and $ZnGa_2O_4$ thin films deposition and to establish epitaxial n- and p-type Ga_2O_3 and $ZnGa_2O_4$ thin film growth processes for deep UV optoelectronics and high power electronics applications;

- advanced multifunctional smart metal oxide large area nanocoatings and multilayers: electrochromic (WO_3, ReO_3, MoO_3, NiO, IrO_2), photochromic (RE-O-H) and thermochromic systems;

- PLD deposition of 2D materials MoS_2, WS2, ReS_2; hybrid systems of layered CDW materials grown on substrates with hexagonal crystal structure stable in the corrosive sulfur atmosphere such as GaN, InN and ZnS, and materials which can be converted into sulfides such as ZnO (into ZnS) and CdO (into CdS);

- antibacterial, antiviral catalytic and photocatalytic coatings for Green Large-Area Surfaces (Cu-WO_3, $BiVO_3$, WO_3-TiO_2;

- cryogenic technology of PVD magnetron sputtering for UV-VIS-IR transparent conducting oxides (TCO) thin films: n- and p-type ZnO-ZnO_2, a-In_2O_3-SnO_2 (ITO) for flexible optoelectronics.

NETWORKING

The activities at Thin Film Laboratory will be further based on the development of existing collaboration with strong European partners: (i) Royal Institute of Technology (KTH) Stockholm; (i) RISE - Research Institutes of Sweden, Stockholm; (iii) Department of Engineering Sciences, Uppsala University; (iv) Fondazione Bruno Kessler, Centre for Materials; (v) Fraunhofer Institute or Surface Engineering and Thin Films IST Braunschweig, Germany. The collaboration is built to achieve synergetic effects among the participating international partners, capitalizing on a strong background of fundamental and applied research, and exploiting recent advanced infrastructure at ISSP UL.

Thin films and nanocoating technologies represent an enabling core technology platform at the ISSP UL, where the Institute already has well-established collaboration with local nanocoating and thin film industry (e.g. SIDRABE, GroGlass, EuroLCDS, RD ALFA Microelectronics and others). There is, however, a much larger potential for thin film technologies, nanocoatings and devices that can contribute to strengthen of European industries.

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(b) **J.Purans**, EU Patent EP2881973A1 Device and method for PVD process diagnostic using X-ray fluorescence local probe (2015-06-10);

(c) **J. Purans** et al. Patent Nr.LVP2020000079, An antiviral, yeasticidal and antibacterial nanocoating (23.11.2020);
(d) **M.Zubkins**, EU Patent EP20020352.9, A method for magnetron sputtering deposition of Zinc peroxide films at cryogenic temperature (04.09.2020);
(e) **A.Azens** , LV Patent LVP2020000040, Device for magnetron sputtering deposition (15.05.2020);
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0D, 1D, 2D AND MIXED-DIMENSIONAL NANOMATERIALS

STATE OF THE ART

Nanomaterials are defined as materials with at least one spatial dimension in the scale of 10^{-9} m, or usually below 100 nm [1]. They exhibit physical and chemical properties different from their bulk counterparts due to the large surface/volume ratio and, thus, the important contribution of surface atoms, as well as quantum confinement and other quantum phenomena [1]. Nanomaterials are classified by the number of dimensions in the nanoscale. 2D materials have one dimension below 100 nm, 1D and 0D materials have 2 and 3 dimensions in nanoscale, respectively. Examples are nanoparticles and quantum dots (0D), nanowires and nanotubes (1D), layered van der Waals materials (2D).

Zero-dimensional (0D) nanomaterials are the cornerstone of nanotechnology. Due to the inherent structural properties of 0D nanomaterials, such as ultra-small sizes and high surface-to-volume ratios, they have more surface area per unit mass. The high surface-to-volume ratio and quantum confinement effects of 0D nanomaterials provide improved or novel properties such as, for example, high photoluminescence (PL) quantum efficiency and enhanced catalytic activity. Various 0D nanomaterials have been extensively explored: carbon-based quantum inorganic quantum dots (QDs), magnetic nanoparticles, noble metal nanoparticles, upconversion nanoparticles. 0D nanomaterials have numerous potential applications in materials science, photovoltaic science, catalysis, energy, sensing, biomedicine and ink-jet printed devices [2].

1D nanostructures - nanowires (NWs) and nanotubes (NTs) — are being explored as promising materials for applications in electronics, optoelectronics, photonics and microelectromechanical systems (MEMS) [3]. Two different approaches of NW integration in devices are used – single-NW devices consist of individual separate NWs, whereas “bulk” devices contain periodic NW arrays or randomly dispersed NWs. The challenge is to develop a scalable device fabrication process that could compete with current technologies, such as silicon microfabrication. This is an active research field. Several concepts have been proposed, for instance, controlled printing of NWs with roll-to-roll technology that uses microfluidics to align the NWs [4]. Besides upscaling problems, the current 1D materials research focuses on finding new NW-based materials and studying their fundamental properties for novel applications [5]. NW characteristics can be engineered by creating core-shell heterostructures – modifying NW by a thin (compared to the diameter of the NW) coating of a different material [6]. Surface of NWs has a significantly reduced lattice mismatch restriction compared to conventional semiconductor thin film growth thus enabling greater flexibility in choosing the materials to produce heterostructures and in engineering their properties [7,8].

2D layered van der Waals (vdW) materials have attracted great interest since the isolation of monolayer graphene in 2004, due to their unique structure and the promising physical properties that appear when the thickness of the material is reduced to one atomic layer. These materials have an atomic structure similar to well-known graphite – strong in-plane bonds and weak interlayer bonding [9]. Bulk materials of this group have been widely studied in the last century, as most of these materials are quite abundant and have been used in different technological fields, however until 2004 it was believed that it is not possible to obtain an only one separate stable layer [10]. There was some research done in 1960s that showed that electrical conductivity in a few-layer graphite is higher when measured laterally in-plane rather than between the planes, but it was still assumed and assumptions justified by experimental and theoretical research that stable two-dimensional (2D) atomic crystals cannot exist separately in nature, as all attempts to obtain such were unsuccessful – with the used methods the layers tended to curl, roll or deform in other ways [11–13]. The ground-breaking discovery by K. Novoselov and A. Geim in 2004 proved otherwise – by mechanically exfoliating highly crystalline graphite with a Scotch tape they were able to obtain one atomic layer of graphite (graphene) on an oxidized silicon substrate and measure its electrical properties [10]. Graphene exhibits extraordinary electrical and mechanical properties [14]. For their contribution, Geim and Novoselov were awarded The Nobel Prize in Physics in 2010.

Afterwards, 2D materials became one of the “hottest” topics in modern physics – in 2011 an intensive research started on layered transition metal dichalcogenide (TMD) semiconductors, mainly MoS_2 and WS_2 [15–17], and around 2015 more exotic compounds were started to be studied, such as NbS_2 and ReS_2 [18,19].

TMDs are described by a general chemical formula MX_2, where M is a periodic table Group 4 – 7 transition metal and X is a chalcogen, and have a potentially useful property of thickness-dependent bandgap [20]. TMDs layers have terminated surfaces without dangling bonds, bound together by weak vdW forces, therefore, they can be sequentially stacked unstrained without any covalent interlayer bonding and even if materials are slightly lattice-mismatched [21]. Large-scale synthesis methods of TMDs on different substrates need to be developed, before any practical applications could be realized.

The family of 2D materials includes several subgroups, classified by materials chemical formula and atomic structure: (1) transition metal dichalcogenides (i.e. MoS_2, WSe_2) and their related compounds (2) group IIIA chalcogenides (i.e. GaS, InSe) and (3) Group IVA dichalcogenides (i.e. SnS_2), most of these compounds are semiconductors, semi-metals or metals; (4) insulator hexagonal boron nitride (h-BN); (5) black phosphorus; (6) X-enes (i.e. graphene, germanene); (7) MX-enes (transition metal carbides and nitrides); and other compounds, such as few oxides, halides etc. [22–24] Some of these materials are naturally occurring, however some are only synthesized chemically, h-BN for example.

Combining NWs and TMDs in core-shell heterostructures could lead to new knowledge about the interface formation between different materials and solid-state reactions in such systems, to novel nanostructures with enhanced properties, and development of new TMDs synthesis methods as NWs are a convenient template to study materials growth.

OUR POSITION

In the recent past we have focused on synthesis and investigation of mechanical and tribological properties of 0D and 1D nanomaterials (nanoparticles, nanodumbbells, nanowires, nanotubes) [25-41].

For example, pentagonal Ag and Au nanowires (NWs) were bent in cantilever beam configuration inside a scanning electron microscope [27]. We demonstrated an unusual, abrupt elastic-to-plastic transition, observed as a sudden change of the NW profile from smooth arc-shaped to angled knee-like during the bending in the narrow range of bending angles. Moreover, we found that if the NWs are coated with alumina or silica, the abrupt plastic event is not observed and the NWs can withstand severe deformation in the elastic regime without fracture. The coating may possibly prevent formation of dislocations. Mechanical durability under high and inhomogeneous strain fields is an important aspect of exploiting Ag and Au NWs in applications like waveguiding or conductive networks in flexible polymer composite materials.

More recently, we studied mixed-dimensional core-shell NWs, the shells made of layered 2D materials (WS_2, MoS_2, ReS_2, PbI_2, etc.) [42-46]. We found that the combination of properly chosen materials can bring improved and advanced properties of these NWs.

We found enhanced and fast photoresponse of ZnO-WS_2 nanowires applied as visible light photodetectors [42]. In this work we demonstrated, that even a very thin coating can greatly improve the optoelectronic properties of nanostructures by modifying the light absorption and spatial distribution of charge carriers. To use these advantages, ZnO/WS_2 core/shell NWs with a-few-layers-thick WS_2 shell were fabricated. Then, a single-nanowire photoresistive device was assembled by mechanically positioning ZnO/WS_2 core/shell nanowires onto gold electrodes inside a scanning electron microscope. The results show that a few layers of WS_2 significantly enhance the photosensitivity in the short wavelength range and drastically (almost 100×) improve the photoresponse time compared to uncoated ZnO NWs. The fast response time of ZnO/WS_2 core/shell NW was explained by electrons and holes sinking from ZnO nanowire into WS_2 shell, which serves as a charge carrier channel in the ZnO/WS_2 heterostructure. First-principles calculations suggest that the interface layer i-WS_2, bridging ZnO nanowire surface and WS_2 shell, might play a role of energy barrier, preventing the backward diffusion of charge carriers into ZnO nanowire.

FUTURE ACTIVITIES

There are three main activities of ISSP in field of nanomaterials are planned in near future:

(1) Synthesis and application of 0D nanomaterials for ink-jet functional printing, (2) Development of 1D core-shell nanowire heterostructures based on charge density wave materials for optoelectronic applications, (3) Development of biosensors based on 2D materials for biomolecule detection.

1. Functional ink-jet printing is a promising new technology, cheap and environmentally friendly, and creates a new paradigm in digital manufacturing where electronic devices and circuits can be printed on demand. Our main goal is a development and demonstration of the ink-jet technology, able to print wearable and flexible functional electronic devices, including the inductive antenna, capable of capturing electrical energy in the kilohertz range and feeding printed electroluminescent light-emitting devices implemented as drawings or 2D figures. A complex "kit" of functional inks based on 0D, 1D and 2D nanomaterials (conductive, electro-luminescent, semiconducting and insulating) will be developed to implement this technology. Printing of electronic test components and simple electronic

devices (resistors, capacitors, light-emitting diodes, transistors) will be used to develop printing and post-processing protocols for each ink type.

2. We plan to develop and investigate new charge density wave (CDW) material hybrid nanowire heterostructures suitable for photodetection in a particularly wide wavelength range. The idea is based on the combination of 2D CDW material cladding and semiconductor 1D nanowire core, resulting in hybrid core-shell nanowires. The electronic and optoelectronic properties of the core-shell nanowires will be studied by integrating them into a single nanowire device, such as a field effect transistor and a phototransistor. The research includes theoretical calculations aimed at studying the structure and properties of the core-shell interface.

3. Development of a novel biosensor matrix, based on array of sensor elements, where response signals from each individual sensing element are processed together using a neural network algorithm to characterize a bioanalyte by observing a unique signature response. The envisaged diagnostic and monitoring system is based on new semiconductor two-dimensional 2D materials. The most promising candidates are layered 2D sulfide materials and oxide materials. Due to the unique physical and chemical properties, sensors based on such materials show increased sensitivity and a higher response speed, compared to conventional systems. Similar sensors combined into a matrix allow analyzing various chemical processes in real time. The use of machine learning algorithms for processing signals of such a matrix will significantly increase the sensitivity and selectivity, and will also make possible the deep integration of such systems into the existing digital infrastructure.

NETWORKING

Five Laboratories of ISSP are working in field of nanomaterials: Thin Films Laboratory, Laboratory of Spectroscopy, Laboratory of Materials for Energy Harvesting and Storage, Laboratory of Optical Materials, Laboratory of Computer Modelling of Electronic Structure of Solids.

Of essential importance is ongoing development of ISSPUL research infrastructure and modern equipment, which allows to synthesize and comprehensively study novel nanomaterials, as well as to fabricate prototype devices. Moreover, full spectrum of theoretical modelling and calculations are available to simulate and interpret the obtained experimental results.

Thin Films Laboratory has ongoing collaboration with research groups from Latvia and abroad: Daugavpils University (Latvia), Riga Technical University (Latvia), Institute of Physics and Institute of Technology, University of Tartu (Estonia), ITMO University (Russia), Royal Institute of Technology KTH Stockholm and RISE Research Institutes of Sweden (Sweden).

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PROTOTYPING OF MICROFLUIDIC DEVICES (NEW INITIATIVE)

The Laboratory of Prototyping of Electronic & Photonic Devices is interested in using functional microfluidics for future applications in the healthcare and health-tech. We see personalized and precision medicine as one of the key areas for our work, with a particular focus on:

- Organ-on-a-chip (OOC) for microbiome research and biomarkers;
- Lab-on-a-chip devices for biomarkers in oncology.

There is large interest in both topics right now, and both are reliant on the use of microfluidics, which from ISSP UL perspective in-turn is based on the core function of our lab – physical device prototyping in the cleanroom environment.

STATE OF ART

OOCs are microfluidic systems with controlled, dynamic microenvironments in which cultured cells exhibit functions that recapitulate organ-level physiology. Microfluidic devices allow human organ function replication by culturing relevant epithelial and endothelial cells in separate microfluidic channels that are separated by a porous membrane. Application of shear and mechanical forces onto the confluent monolayers of cells grown in the microfluidic channels result in cell activity levels and biomarker expression in the same level as it would be in living conditions [1]. This implies that in OOC devices it is possible to replicate physiologically relevant microenvironment for cell growth. OOC devices have the chance to ultimately replace animal testing due more relevant organ-function models, where actual human cells are used [2,3]. This is still pending regulatory approval, although FDA (in USA) is already involved in OOC testing, and has recently allowed vaccine and drug testing for Covid-19-related projects to be done on lung-on-chip devices. OOC devices could be the ultimate test bed for various pharmaceutical developers and research institutions that need accurate human model systems that are more repeatable, cheaper, and more ethical. The focus of our group in the OOC area is on use of novel materials (and subsequently fabrication methods), as the currently available OOC devices are not performing to the standards expected by the pharmaceutical industry. OOC devices are based on the concept that it is possible to replicate certain functions of a human organ by culturing the relevant human organ cells (e.g., gut epithelial cells and endothelium cells for simulating intestine function) in horizontal microfluidic channels separated by a porous membrane [4]. The culture media is flowed over both sides of the membrane ensuring that cells are supplied with culture medium and metabolic waste is removed. As the cells proliferate and form a confluent monolayer on both sides of the membrane, an OOC system is formed that can mimic an organ tissue response to external stimuli. In the current state of the art, OOC technology has already been shown as a promising model system for pharmacokinetic (PK) drug responses, toxicity studies, viral disease studies, and cancer studies [1,4-6]. OOC can be 'personalised' to reflect individual physiology, for example by including blood samples, primary human tissue, and cells derived from iPSC [7]. Alongside the use of biological material from the patient, it is possible to tune personal physico-chemical parameters to mimic the in vivo cell culture conditions. As such, this shows the opportunities for person-specific drug efficacy and safety testing presented using OOC technology, thus paving the way for truly personalised medicine [7]. In conclusion, current state of the art is:

- accurate single-organ model system with focus on accurate cellular composition representation;
- PK/PD studies on a single organ level;
- Personalisation of chips – actual patient cell utilisation in OOC model building.

Previous examples have been focused on a single organ replication, yet human physiology must be studied at a systemic level to ensure accurate modelling of the system response [8]. Subsequently, state of the art in systemic human representation includes multi organ chips and their linking together. Multi-OOC devices have been used to develop models for quantitative prediction of PK response to drugs; this has been done in by interconnecting intestine, liver and kidney chips using a sophisticated pipetting robot which ensures the interconnection [1,9] or fluidic interconnects [10]. Another example is cancer modelling (and subsequent PK-PD) via multi OOC devices, as it has been in the case of four organs [11].

There have been numerous seminal studies done by various groups utilising OOC technology, yet at the core of the device design not much has changed in the last decade or so since OOC chips have been around [4,6,12]. The vast majority of the chips are fabricated from PDMS, which has significant small molecule absorption and is notoriously hard to upscale in terms of manufacturing [13,14]. This leads to problems of utilisation of OOC devices in pharmaceutical research and significant prices of the devices, respectively. Furthermore, gas permeation in the PDMS devices is somewhat limiting truly anaerobic condition generation, not exactly representative of human intestine conditions. Consequently, the uptake of OOC devices in the research industry has been limited [15]. Use of alternative materials would allow to fabricate these OOC systems using mass-manufacturing compatible methods, thus providing room for significant price reduction and ability to supply the experiments at volumes required by the industry. By selecting alternative materials, it would also be possible to tackle the issue with gas permeability in the OOC systems, e.g. to create truly anaerobic conditions in the intestine cell chambers allowing better representation of microbiota. OOC technology offers to build multiple organs and even organ systems, for example, to observe PK/PD responses to drugs and evaluate their toxicity.

OUR POSITION

The focus of our group in the OOC area is on use of novel materials (and subsequently fabrication methods), as the currently available OOC devices are not performing to the standards expected by the pharmaceutical industry. We have shown lung-on-chip device fabricated from SEBS material with currently on-going biology tests at a partner organisation.

Our group is focused on the design and development of novel OOC devices that would be suitable for large scale manufacturing. Furthermore, there have been shown proof of principle (POP) devices that integrate TEER [16] and various gas and pH sensors [17]. Yet most of these are POPs; therefore, we are investigating robust and scalable techniques in fabricating these crucial sensing elements for OOC technology. In terms of TRL levels, in the past year we have developed PDMS-alternative OOC devices from styrene-ethylene-butylene-styrene (SEBS) with polycarbonate membranes, which now are undergoing biological testing in Latvian Biomedical Research and Study Centre (BMC). Should the biological testing succeed, it would result in a state-of-the-art OOC device from an engineering perspective. Furthermore, we have developed an OOC device, where both channel blocks and membrane consist of off-stoichiometry (OSTE). More testing and development work in necessary, but this is a completely new approach to OOC device fabrication, one that is using scalable materials and processes and a likely source of IP. With biological testing pending, SEBS and OSTE devices have a TRL of 4. We have a parallel work on-going in this area, where we will integrate oxygen and trans-epithelial electrical resistance (TEER) sensors in the form of luer-like plugs, intended for easy integration in chip and assembly. This work is on-going and the current TRL is between 2 and 3 depending on the sensor type.

Regarding oncology-related biomarker work, our core interest is connected to Line group in BMC, where group interests lie in EVs. EVs are a heterogeneous group of membrane-enclosed vesicles that are released by various types of cells, including MSCs. Their ability to transfer different types of molecules from cell-to-cell that influence the behaviour of recipient cells has led to an increased number of studies about their role in cancer progression and potential applications in cancer treatment [18]. EVs have been shown to transfer genetic material, proteins, bioactive lipids, and other signalling molecules, among cells in a paracrine and systematic manner in all human biological fluids, thereby mediating intercellular communication and regulating normal physiological conditions and pathological processes. In the last few years, EVs have emerged as novel putative therapeutic tools and biomarkers for the treatment and diagnosis of various diseases, including cancer [19]. Theoretically, EVs can be studied and applied in clinics by their concentrations in biofluids, their cargo, density, electrical potential, refraction index and their functional effects, however, methodologies remain as one of the major challenges within the field. Therefore, new methods for EV isolation from high volume samples are necessary to enable urine EV and cell culture media EV implementation in different disease diagnostics and therapeutic EV production in cell culture bioreactors [20,21]. Current state of the art includes:

- EV capturing from highly concentrated liquids (such as blood plasma);
- EV analysis using separate, lab-grade equipment.

Our collaboration with BMC aims to develop a device that allows for recovering EVs from cell culture media and urine. Since the yield of the existing methods is highly variable and leads to variable research results, this project aims to develop a device suitable for EV isolation from large volume samples with high reproducibility. The device is based on particle separation through field-flow fractionation (FFF). This project sets out to utilise the working in principles of FFF, but a device that does not require concentration steps from the user, thus significantly easing the sample preparation and further reducing the time consumed. Currently, ISSP has developed its design while the BMC group has tested selected materials for device manufacturing. PDMS, the current golden standard in microfluidics, was compared with OSTE and SEBS materials that are more suitable for largescale manufacturing based on EV and fluorescent dye *CellVue* absorption. OSTE was selected for device fabrication and testing in the future based on preliminary results. We have not yet demonstrated the working concept of EV separation device, but we have done an appropriate material selection; therefore, within the next year we expect the first results of EV separation efficiency using these devices. Subsequently, this project has TRL 2 on the way to 3.

FUTURE ACTIVITIES

Further work in this area will be devoted to multiple models supporting the necessary design changes for various models. Further research at ISSP UL side will be in the area of sensor integration (TEER, O_2, CO_2 and pH), and membrane engineering, which would allow to naturally support the biological models requiring 3D cell arrangement, such as, *villi* structures in intestine.

Our core contribution will be in the domain of Health. The OOC technology is relevant in the context of the Health, especially in the realm of drug discovery, diagnostics, and personalised medicine; subsequently, we could part take with all the OOC related capacity and knowledge. Our current EU partners are from KTH and VITO; eventually, we would expect to take part in the project submission proposals with these partners (and obviously other institutions).

Fundamentally, the future direction of the work in the biotechnology realm from the Prototyping lab perspective is in the field of applied microfluidics and microfabrication, which corresponds to the group's competencies. The core principle of the research work done here is that the impact of the work should be well beyond just the POP demonstration; it should have an industrial or applied science application, and an increased commercialisation opportunity. Our work will continue in the area of OOC technology, biomarkers for oncology, especially in the personalised medicine area and point of care diagnostics.

Currently, our core direction in OOC technology is design and development of OOC devices from scalable materials and suitable for large volume manufacturing. Alongside, we will be investigating integration of sensing technology to these chips keeping the ethos of scalability and compatibility with volume manufacturing. This research goes together with research into advanced biological model development at BMC, where these chips are deployed. Subsequently, design and devices changes are driven by our collaboration partner. Future directions will include 3D engineering of membranes used in OOC devices with the goal of enhancing cell adhesion and accurate biological model representation at a cellular distribution level. Subsequent steps will be multiple organ devices that combine inputs and outputs of multi-organs systems, again requiring collaboration with biological partners. Our work in this will be engineering of multi-organ device integration and potentially multi-organ fabrication in a single chip. OOC technology is an active IP generation and publishing area due to its' potential impact on pharmaceutical developments, but also serving as a general model system that is highly representative of human physiology. As mentioned previously, in the last 5 years, 16% of publications were published in *Nature, Science* or *Cell* (all with IF close to 40). In terms of commercialisation, OOC technology is has an estimated total addressable market (TAM) of EUR 4.5 billion annually, in the pharmaceutical discovery market alone. TAM estimate is obtained via estimating the saving of R&D costs per drug and imposing that over the average number of approved drugs per year. Previously mentioned tool acquisition would significantly enhance group's competitiveness in international scale.

Our biomarker research efforts will be associated with EV-related research due to the great promise that EV technology holds in the area of cancer diagnostics and treatments. EVs are scarce, and purification and concentration of these nanoparticles is still far from efficient; therefore, our short-term effort will be focused on the EV separation. Future directions of EV-research will be the use of lab-on-chip technologies to develop not only EV capturing, but also on-chip analysis capabilities. An example of such activity are two ERD project proposals about on-chip EV capturing and optical sensing submitted together with Line group from BMC and Laboratory of Organic materials from ISSP. On-chip sensor integration for EV probing on-chip could also be implemented in the form of impedance sensing and electrochemical sensing, all of which are reliant on groups core capability – microfabrication design and technology development. Our efforts in the sensor area currently are in the form of collaboration with Dr Qin Wang from RISE on graphene sensor development and associated PostDoc project proposal for Dr Tom Yager, who, if accepted, will focus on graphene sensing technology development that could also be used for EV detection and analysis. Intricate sensor development will require hiring postdoc/experienced personnel in this area as this competence in group is limited. Tooling-wise, cleanroom is currently well equipped for tackling this area, but injection moulding or hot-embossing technology would allow to work with materials better suited for industrial applications of EV separation.

The main potential industrial partners are pharmaceutical companies in Europe. None of the pharmaceutical companies make their own OOC devices – R&D is done using collaborations with academia and companies. This is a new field for pharmaceutical companies, and technologies available on the market are early stage with a particular focus on proof of concept, thereby the currently available systems are not user friendly or have a high experimental throughput necessary for industrial applications. ISSP UL proposal to this problem would offer a well-engineered system consisting of engineered microfluidic devices and an instrument to run these, and well-developed cell culture protocols that would be prepared in cooperation with BMC. Pharma industry has started to work with OOC systems only in the last couple of years; therefore, it is a fantastic opportunity to start cooperation early, which would result in a symbiotic cooperation. Some of the companies, who have started to work with organs on chips:

- AstraZeneca (we have engagement);
- GlaxoSmithKline (we have engagement);
- Roche (we have engagement);
- Pfizer;
- Bayer.

However, the big pharma companies are unlikely to develop their own OOC systems, they are more likely to buy an existing solution or collaborate with a highly skilled group, which presents an opportunity for ISSP UL within this area. In terms of value chains affected, OOC devices will contribute to the drug efficacy and toxicity studies in the first few years of their development. Although replacing animal studies and animal models is the most obvious application of such technology, it is unlikely that the OOC devices will be replacing animal trials in the near future (< 5 years). This is due to the current legislation, which carries large momentum and would require more than 5 years and large number of evidences for any meaningful change in the drug testing area. It is estimated that 10 – 24% of drug R&D costs could be saved through a strategic use of organ on chip technology [22].

NETWORKING

Cooperation partners:

- Biomedical research and study centre, J.Klovins group, (Latvia);
- Flemish institute for technological research VITO, I.Nelissen group (Belgium);
- KTH Royal Institute of Technology in Stockholm (Sweden), A.Herland group;
- The Karolinska Institute (Sweden),
- R.Loranzo, Katajitso lab;
- O.Parlak, Richter-Dahlfors Laboratory;
- RISE, Dag Ilver and Anatol Krozer (Sweden);
- The Max Delbrück Centre for Molecular Medicine in the Helmholtz Association, Forslund lab, (Germany);
- BIOS Lab on a chip (University of Twente);
- Riga Stradins University, Cakstina's group ;
- The Wyss Institute for Biologically Inspired Engineering at Harvard University;
- University of Twente BIOS: Lab-on-a-chip group;
- Massachusetts Institute of Technology Griffith Lab.

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POLYMER PHOTONICS TECHNOLOGY PLATFORM (NEW INITIATIVE)

STATE OF THE ART

Integrated circuits are essential parts of almost all modern technologies from personal computers, medical devices to cars and spacecrafts. Much of the functionality of these electrical components can be replaced with photonic components to create photonic integrated circuits, which use light instead of electrons. Higher speed, lower energy consumption and greater bandwidth are just a few advantages as compared to conventional circuits.

In the last couple of decades, huge effort has been put into the development of photonics platforms based on various materials such as Si, Si_3N_4, InP, $LiNbO_3$, GaAs and others. Only few of them (Si, Si_3N_4, InP) have turned into eco-systems resembling semiconductors industry of design house, foundries, fabless companies and multi project wafer (MPW) services of photonics integrated circuits (PICs). Silicon photonics is the dominant mostly due to compatibility with CMOS process and MPW services are offered by multiple parties: IMEC, CEA-LETI, IHP, AIM Photonics and others. Silicon nitride photonics is gaining ground owing to the broad wavelength range starting from visible wavelengths allowing applications also in biophotonics among tele/Datacom and optical signal processing. MPW services of silicon nitride photonics are provided by IMEC, CEA-LETI, LionX, IMB-CNM and others [1]. InP allows possibility to implement both active and passive devices on a single chip. MPW services of InP PICs are provided by Smart Photonics and Fraunhofer HHI [2]. While various photonic platforms have matured to industrial level, they still have numerous challenges including limits set by material properties, expensive fabrication and complicated hybrid integration.

Polymer materials provide numerous advantages over semiconductor and oxide/nitride platforms:

1) Combination of passive and active elements – One of the main advantages of polymer material is the possibility to modify its properties. Guest-host polymer materials exhibit second and third order effects. It allows fabrication of both passive and active elements and combine them together on one chip [3];

2) Simple fabrication techniques - Optical polymer layers can be formed by spin-coating and processed using three techniques:

    - standard semiconductor processing methods with lithography and reactive ion etching;
    - direct UV lithographic patterning followed by wet-chemical rinsing;
    - nano imprint lithography.

These methods allow fabrication at much lower cost than Si, Si_3N_4 and especially III-V photonics. Silicon wafers are usually taken as substrate, though the technology is also applicable on glass, ceramic, InP wafers and flexible substrates;

3) Integration of other elements for hybrid platform – Integration can be achieved on two levels. Firstly, novel organic/polymer materials can be used for fabrication of active elements. Secondly, polymer devices can be integrated with active elements from other platforms such as InP, Si, $LiNbO_3$ or other;

4) Losses – reduction of losses is an important issue, especially for high power and single photon applications. Losses as low as <0.02 dB/cm for Su-8 [4] and <0.05 dB/cm for other polymers [5] have been reported;

5) Wide wavelength range – polymers can be used in wide wavelength range starting from 400 up to 2200 nm and more opening opportunities for wide range of applications [6].

6) Multilayer structure – polymer allows to fabricate multilayer waveguide structures with low coupling losses between layers. Multi-mode interference couplers have been used to fabricate flexible interconnects [7].

7) Applications – the numerous advantages listed above allow wide range of applications: data/telecom [8], flexible integrated photonics [9], polymer is very suitable for bio functionalization and biosensors [10] quantum.

Polymer Photonics Technology Platform offers standardized polymer photonic device preparation methods to academia and industry. This system is based on three main parts: computational simulations of optical devices, materials and element fabrication workflow, and producible photonic elements.

Computational simulations are based on Finite element analyses method (FEM) and Finite-difference time-domain (FDTD) method. For FEM calculations, we will implement COMSOL Multi physics software, while for FDTD, Lumerical software will be used.

Device fabrication is based on polymer materials that are separated into two groups – passive materials and host materials for other materials to create active elements. As the central passive material, we will use SU-8 as it has excellent chemical and mechanical properties, but, more importantly, it has very low optical absorption at visible range. Parallel list of polymers is available with different refractive and thermal properties for passive cladding material to create multi-layer structures. For active elements, a similar list of polymers is available with different optical properties. This includes PMMA, Polysulfone, Polycarbonate and others.

Photonics platform base is a detailed *library of photonic element*s and their fabrication guidelines separated into includes passive (waveguides, power splitters, directional couplers, frequency filters and multi-mode interferometers), active elements (active claddings, resonators, photonic crystals) and light coupling (edge and grating coupling).

Simulation segment: COMSOL applications are mainly used to calculate effective refractive index of modes in waveguide, as well as to evaluate which part of optical mode is contained in the core, and which part has spread into cladding. Another essential aspect of COMSOL is its Multiphysics module that allows to combine multiple effects. This allows to simulate interaction between mode in passive waveguide and active cladding. As FDTD is based on time domain calculations, Lumerical solutions are used to calculate light propagation through ring resonators as well as coupling efficiency of diffraction gratings. This allows to determine resonance wavelengths of created Whispering gallery mode resonators and photonic crystals. Through these steps, the following parameters can be calculated for passive elements:

- Waveguide: width and thickness for one-mode operation; smallest waveguide bend radius of waveguides with minimal losses for small footprint;
- Splitters and couplers: curvature of waveguides;
- MMI coupler: size of coupler.

The following parameters will be calculated for active elements:

- MZI: Interaction between active cladding and optical mode in waveguide;
- Ring resonator: distance to waveguide for efficient coupling and resonance wavelength calculations;
- Photonic crystals: spectral dispersions dependence on hole size and period.

Materials and fabrication methods: For passive element fabrication, SU-8 is used. Despite recent development of polymer photonics in the last decade, there is no systematic review of polymer materials available. To extend photonic platform to multi-layer structures, passive cladding materials that could serve as separation layer between multi-layer photonic structures are used. Front runner as an active material is PMMA as it has been used as a cladding and material for fabrication of active elements by ISSP among other research groups. PMMA is widely used as an EBL resist and can be easily mixed with other active materials to form guest-host systems. To fit specific optical and thermal properties of the devices better, a list of usable materials is composed based on literature review and experimental tests carried out in ISSP: PMMA, Polysulfone [11], Polyethersulfone, OSTE, Polycarbonate [12], Polystyrene [13], ZPU12 [7] and others.

Fabrication methods are separated into three groups: passive element fabrication, active element fabrication, and optical coupling elements. Since all waveguides are in size over one micron, conventional photolithography will be used to define structures. Both direct development and dry etching is used to produce passive elements. Straight sidewalls are offered to minimize losses.

For active elements, both larger and sub-micron structures are required; therefore, both photolithography and EBL are employed. In case of PMMA, deep-UV and EBL lithography methods can be combined directly patterning PMMA. At first, sub-micron structure is defined by EBL, and then the rest of the material is removed by deep-UV lithography. Reactive ion etching (RIE) is traditional method to define photonic elements, and it will be used to compare with direct patterning. For other materials that can't be patterned directly as PMMA mix and match lithography will be combined together with RIE.

Photonic elements (waveguides, power splitters, directional couplers, frequency filters, MMI couplers, passive cladding, active cladding, resonators, photonic crystals, grating couplers, edge couplers) are based on selected materials and fabrication workflows a library of basic photonic elements has been compiled including specific design rules for each element.

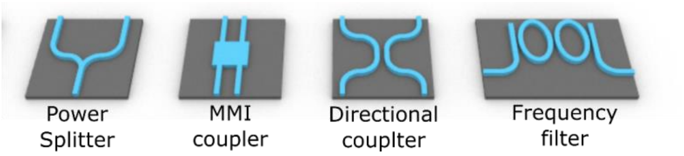

Fig. 3 Passive elements: waveguides, Y branch, crossings, coupler

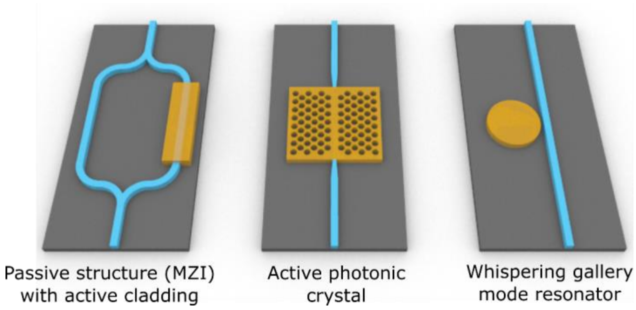

Fig. 4 Active elements: cladding layer that can be used for MZI or other modulators, photonic crystal and ring resonator

OUR POSITION

Laboratory of Organic Materials has vast experience regarding third-order nonlinear optical organic material studies [14,15], as well as the expertise in polymer thin-film fabrication. In last year's research has also shifted towards photonic device designing and fabrication leading to demonstration of organic electro-optical switches [16] and all-optical gas sensor [17].

FUTURE ACTIVITIES

The aim of the photonics platform is to offer a modular set of elements, repeatable technologies and materials needed to create photonic elements for wide range of applications. Ultimate goal is to create a set of standard modules that can be used to design and fabricate sensors, light sources/emitters, modulators, processors with high reproducibility, predictable budget and time. Photonic platform should be integrated with electronics and microfluidics to provide applications needed in most of the societal challenges: health, wellbeing, bioeconomy, security, ICT, environment.

Special attention will be given to structures for edge and grating couplers. In case of edge coupling, light is coupled in and out from the waveguide from its facet using a fibre. This technique usually requires optical quality facets for high coupling efficiencies. This technique not only allows high efficiency, but also broad bandwidth and polarization independence. Disadvantages include larger footprint than grating couplers, fixed coupling positions, and requirement for edge polishing [18]. To increase coupling efficiency facet couplers our team can offer facet polishing, specific taper designing, on-chip groove etching for fibre alignment and optimal coupling angle calculations.

Grating coupling is not as efficient as edge coupling, but provides possibility to couple light from optical fibre anywhere on the chip without a need to cutting and polishing surface. It allows automated wafer-scale testing and provides much wider alignment tolerance. Two major drawbacks of grating couplers are low coupling efficiency and narrow bandwidth (30-40 nm). Due to low refractive index difference between Su-8 (n1.57) and air coupling efficiency is especially challenging and much lower (10-16 % [19]) than for example Si, were sub-dB coupling efficiency has been reported [20]. Su-8 can be patterned directly not only by photolithography, but also EBL, which allows to avoid RIE step for formation of grating [21]. We offer grating formation methods using mix and match lithography. Two-step lithography with RIE will be explored and results compared. FDTD simulations are used to calculate grating design. Focused grating couplers are also available to improve coupling efficiency and use of mirror under the grating evaluated.

At the end of the project, a library of photonic elements and standardized recipes will be created that is prerequisite for foundation of established platform and further development of multi-project wafer service.

NETWORKING

Part of sustainable energy research will be development of low-power all-optical devices. This will include all-optical sensors for VOC detection, all-optical telecommunication systems based on third-order nonlinear optical materials and others. Here, Polymer Photonic platform will be used for device fabrication. By combining microfluidics with photonics elements such as microring resonators and waveguides, biosensors will be developed for cancer biomarker detection.

This platform could serve as a base for ISSP UL and specific *industry companies'* long-term partnership for the joint development of new products/solutions. For *academic institutions,* this platform could help for joint exploration and for the identification and early validation for research of their interest. Partners from *academia* would supply application knowledge, while ISSP UL would offer technology knowledge, concept definition, modelling for early validation, and test device development. EUROnanoLAB is a new distributed research infrastructure consisting of over 40 state-of-the-art academic nanofabrication centres across Europe. Its main vision is to accelerate research in the micro- and nanotechnology sector by enabling the transformation of a fragmented landscape of nanofabrication facilities into an integrated knowledge base supporting scientific excellence and providing researchers a fast-track to results. Processes developed by means of this platform will contribute to *EUROnanoLAB* process database.

Existing infrastructure, updated and developed over time period, could serve as a base to create demonstrators and prototypes.

The accession of ISSP UL to EPIC (European Photonics Industry Consortium) should serve as a motivating stimulus for the development of the Platform.

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MORPHOLOGY AND STRUCTURE

STATE OF THE ART

The main focus of material research activities in the last decades is on nano-sized and nanostructured materials and devices; therefore, high-resolution imaging and analytical measurement systems for the relevant length-scales play a crucial role in the development of new materials and devices. Electron and atomic force microscopy techniques are the main methods for characterization of nano-sized materials, structures and devices. Since the advent of the electron microscopy, it has experienced rapid resolution increase (over 10 000 times in the last 9 decades). Presently, sub-Ångstrom features can be resolved with standard laboratory equipment. Now the race for the direct resolution has slowed down and the development of microscopes is more focused on the increase of versatility of the setups, e.g. incorporation of additional spectral instruments, development of new detector technologies and improvements in the application of *in situ* stimuli (heating, cooling, electrical biasing etc.). This has led to improvements in imaging and understanding materials, which have been considered to be difficult by microscopists (high resolution on soft materials, biological samples, 2D materials, *in situ* imaging combined with simultaneous acquisition of chemical information). At the moment, computational microscopy is developing due to the low cost of computational power and increasing amount of data generated by a variety of ultra-fast detectors readily available to researchers. Methods like machine learning-based image acquisition, analysis and sample reconstruction from large data-sets combining imaging with other analytical methods are developed and getting traction in the research community. Our laboratory also participates in the application and development of advanced microscopy methods. For example, the hybrid density functional theory (DFT)/Hartree-Fock (HF) LCAO method was used in combination with the HR-TEM images to provide an insight on atomic lattice formation and growth characteristics of 2D materials [4].

Simultaneously with the enhancements in the field of electron microscopy, other analytical approaches are rapidly developing and taking their place in the routine workflow of material studies. The majority of methods are concerned with the chemical composition, with the notable examples of EDS (Energy Dispersive X-ray Spectroscopy), WDS (Wavelength Dispersive X-ray spectroscopy), EELS (Electron energy loss spectroscopy), XPS (X-ray Photoelectron Spectroscopy) and ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry). These methods are widely used for chemical and electronic state analysis, mapping of the structures, as well as for characterization of surface and/or bulk chemical compositions. These methods are widely used for characterisation in our research institute.

In combination with regular microscopy images, the combined datasets can provide invaluable insight in sample homogeneity, composition and structural specifics of samples.

Nowadays, microscopy setups are used not only for imaging and analysis of samples, but also are often used to alter the structure of the samples by manipulating it at nanoscale. Complex microscopy systems equipped with nano-manipulators and precisely controlled tools/devices can be used for nanofabrication coupled with *in situ* electrical and optical measurement capabilities. Thus, the same setup can be used for the production of novel nanoscale devices as well as for evaluation of them. This allows a rapid prototyping and testing of devices as a part of R&D; that would be otherwise not possible with conventional technology.

OUR POSITION

Laboratory of Materials Morphology and Structure Investigations was established in 2017. It focuses on the study of materials structure, morphology and composition, by using modern experimental and theoretical methods. This is a method-based laboratory, which provides services to other research laboratories.

The laboratory has four main pillars: electron microscopy imaging and spectroscopy (I), X-ray and electron diffraction methods (II), microhardness and nanoindentation methods (III) and atomic force microscopy (IV).

I. Electron microscopy is a relatively new direction at ISSP; however, a significant effort has been involved to obtain the expertise in this field. This has led to multiple research publications already, and the number of publications, where these methods are actively used, increases with every year. In the past 10 years, three SEMs and one TEM have been acquired. The newest addition is a state of the art SEM-FIB system Helios G5 UX. This microscope is equipped with a variety of detectors and add-ons (EBSD and EDS) allowing high-level analysis. Contrary to the conventional SEM systems, this one enables analysis and visualization not only of the specimen's surface, but volume as well. In addition, all measurements can be performed at low acceleration voltage with super-high resolution: 0.7 nm at 1 kV for SEM and 2.5 nm at 30 kV for FIB. The other installed SEM-FIB system, Tescan Lyra is tailored to perform non-conventional studies right in the microscope, such as electrical, optical and force measurements. It is equipped with 5 nano-manipulators for *in situ* measurements and prototyping.

II. X-ray diffraction (XRD) is one of the most used characterization methods at ISSP. As with most characterization methods, the analysis of the results is as important as the acquisition itself; therefore, the laboratory maintains an access to the newest databases and has experience in efficient application of them. Two instruments are in active use: PANalytical X'Pert PRO and Rigaku MiniFlex Benchtop X-Ray diffractometer. X'Pert PRO device (max. 2.2 kW, 60 kV) can be used to provide high resolution powder diffraction data, phase identification and quantitative phase analysis, analysis of thin films and coatings, crystallite size and strain determination, as well as has the ability to perform kinetic and non-ambient experiments. In addition, highly controlled in situ XRD measurements in temperature range from -170 to +450 °C can be performed. Second XRD device (MiniFlex benchtop X-ray diffractometer) is a multipurpose powder diffraction instrument used for rapid phase identification and quantitative phase analysis offering easy and fast sample loading and unloading, which is highly beneficial with large sample series and in industrial research.

Advanced XRD analysis of the results is available: Rietveld refinements of the XRD data are used to analyze X-ray diffraction data by fitting experimentally obtained spectra with theoretical models. Rietveld method is used to determine the phase distribution, sizes and shapes of crystallites and bond lengths of the material, as well as to identify structural defects and to solve crystal structure of the powder sample. The XRD data analysis can be used in combination with electron diffraction measurements done in TEM (SADP) and SEM (EBSD).

II. Surface properties of samples can be studied with microhardness and nanoindentation methods, which are of interest in many fields and applications. Personnel working in the laboratory has decades of experience in microhardness and nanoindentation (Agilent G200) and has a modern setup for such studies.

IV. Atomic force microscopy (AFM) nowadays is used only for very specific studies of samples. Despite that, the researchers from the laboratory successfully apply this technique to various materials and structures, as reflected in published results. With the expansion of the laboratory, purchase of new hardware for AFM is being considered to replace outdated instruments.

Scientific output in form of publications is accompanied by the fulfilment of multiple industry contracts and laboratory provides services for third parties. The recent progress and international cooperation demonstrate the scientific capacity of the laboratory to perform the material morphology and structure characterization.

FUTURE ACTIVITIES

The top priority of the laboratory is to provide high quality support for other laboratories at the Institute, and fulfil the needs of the industry. Keeping in mind that currently the laboratory is method-based (support) laboratory, the strategic development map should be focused on the modern characterization methods.

Therefore, two development threads should be pursued in sync: instrumentation and methods.

Firstly, although the laboratory has a wide range of measurement setups already available, they should be upgraded or expanded. The main concept is the expansion of combined analytical approaches. For example, the setup for AFM currently only supports imaging which is not ideal for extended R&D; therefore, additional features like Conductive Probe AFM, I-V Spectroscopy, Electrostatic Force Microscopy, Kelvin Probe Force Microscopy, Dynamic Contact EFM, Piezoelectric Force and Response Microscopy, Scanning Capacitance and Scanning Spreading Resistance Microscopy, Scanning Tunneling Microscopy, Scanning Tunneling Spectroscopy as well as Photocurrent Mapping methods are necessary.

Despite the presently installed SEM-FIB systems being on a high state-of-the-art level, an addition of analytical equipment dedicated for in-situ SEM measurements is needed. "In-SEM" AFM is a great tool for simultaneous registration of the data from both devices providing better research capabilities and versatility. To expand element analysis capabilities, spatial and spectral resolution and in-volume measurements, the installed SEM FIB system should be equipped with Time-of-Flight (TOF) secondary-ion mass spectrometry (SIMS) as well as with WDS system. With this configuration, a full analysis will be possible inside the same setup, thus providing an extensive data-set.

Similarly, TEM system should be expanded with electron energy loss spectrometry (EELS) detectors. This can be used in combination with X-Ray absorption spectroscopy setup.

Naturally, hardware should be coupled with novel and efficient data analysis methods, and characterisation capabilities should work in tandem with the equipment. Such modern material characterization methods must be the part of industrial R&D workflow, providing the companies with the necessary information to overcome the technological barriers they encounter. Novel and safe material design and reliable manufacturing process development are the basis for the rapid up-scaling and effective quality control, which is much valued by field leaders.

With the development of advanced characterisation techniques, almost any information related to material can be obtained; however, the characterisation processes still require considerable effort to be carried out, and they mostly remain accessible only to trained experts. Therefore, machine learning and AI can be used to automate methods and analysis processes to give new insight from existing data.

A single technique usually cannot provide sufficient information on the material. Consequently, complementary characterization methods are used to map the local chemistry, crystallography, molecular structure as well as the local functional properties. The cross-correlation of complementary methods provides a more in-depth understanding of materials. Incorporation of *in situ* measurements allows to quantify material and device behaviour at working conditions, which is highly relevant for industrial applications.

NETWORKING

Since the laboratory is a support laboratory, we collaborate with many colleagues from other local institutes, as well as from international research institutions and companies.

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SYNCHROTRON RADIATION SPECTROSCOPY OF SCINTILLATORS

STATE OF THE ART

Scintillation is luminescence induced by ionizing radiation in transparent dielectric media. Nowadays, scintillator detectors play an irreplaceable role in high-energy physics, spectrometry of low energy γ-quanta, applications in medical imaging, safety systems, space applications, well and mud logging [1].

The search and development of scintillators in the last decades has been mainly focused towards higher light yield and better proportionality in order to improve the energy resolution at high energy to detect narrow states like the Higgs boson over a large background and at low energy for precise spectroscopy in applications like homeland security. Recent years have seen the emergence of fast timing capability as a new requirement, mainly driven by high-energy physics to cope with higher event rates while minimizing pile-up and time-of-flight positron emission tomography medical applications to improve the image signal-to-noise ratio [2]. Timing resolutions in the 10 ps range are required in both cases, which boosts the research into scintillators with a high light yield, a short rise and decay time, as well as into ultrafast scintillation mechanisms to produce prompt photons [1-3].

However, scintillators as ionizing radiation detectors are naturally subject to radiation influence. Therefore, the stability of their parameters under ionizing radiation and in radiation environment is mandatory. Thus, the search for and development of fast and radiation-resistant scintillation materials is highly relevant and important for many modern applications.

OUR POSITION

The development of scintillating materials is justified by the research infrastructure of the Laboratory of Spectroscopy. The laboratory’s infrastructure has all necessary experimental capabilities for the successful research in the field of scintillating materials involving materials synthesis, structure analysis and spectroscopic characterization including time-resolved technique (tuneable picosecond laser and pulsed X-ray and electron beam setups) with picosecond time resolution. Advanced experiments based on synchrotron methods have been carried out by group members on the European synchrotron centres MAX IV (Sweden) and DESY (Germany). The FinEstBeAMS beamline at

MAX IV has an end station called FINESTLUMI, while SUPERLUMI end station is installed on the P66 beamline of PETRA III storage ring at DESY. Both facilities have been intentionally designed for time-resolved spectroscopic studies of scintillating and luminescent materials. It is worth noting that some of group members played a key role in the design, construction and installation of FinEstBeAMS beamline [4] and FINESTLUMI endstation [5, 6]. They are capable to examine materials of interest under picosecond synchrotron pulses in vacuum ultraviolet and soft x-ray spectral range, which perfectly fits for the successful development of electronic structure of scintillating materials, as well as for understanding the mechanism of ultrafast scintillating processes therein. The members of the Laboratory of Spectroscopy have an extended and long-term experience in synchrotron-based experiments.

Laboratory of Spectroscopy possess a vast experience in the research and development of scintillating materials. Their past work has been crucial for the study of electronic structure and luminescence (scintillating) properties of number topical scintillating materials. Recently, novel significant results have been obtained for: hygroscopic scintillating crystals SrI_2 [7], BaI_2, BaBrI [8], YAG:Ce nanocrystals [9], cryogenic scintillating material CsPbBr [10], complex oxides $SrBO_4$ [8]. Most recently, our group demonstrated pioneering results revealing energy transfer processes in one of the topical $Gd_3(Ga,Al)_5O_{12}$:Ce (or GGAG:Ce) scintillating material [11, 12].

FUTURE ACTIVITIES

- Studies of physical mechanisms of the conversion of high-energy excitation into luminescence (scintillation) signal in topical scintillator materials: GGAG:Ce, LYSO:Ce, $CsPbX_3$ (X = I, Br or Cl), AI_2 (A = Sr, Ba) etc. The strategy to improve (modify) existing compounds to increase time resolution suitable for new generation detectors for high-energy physics and medical applications will be proposed.

- Studies of luminescence and scintillation characteristics topical scintillator materials in form of bulk and nanocrystalline compounds in order to obtain temporal characteristics of luminescence under various excitations. The influence of synthesis parameters, as grown defects as well as reduced dimensionality on the temporal characteristics will be established.

- Investigation of radiation defects and damages as well as of the mechanism of radiation defects formation in topical scintillators to elucidate the role of defects states in energy transfer and scintillation processes.

NETWORKING

The group has long-standing active international collaborations with research groups in:

- Finland: Prof. M. Huttula and Prof. W. Cao (Oulu University), Prof. M. Lastusaari (Turku University)
- Germany: Dr. Aleksei Kotlov (DESY)
- Sweden: Dr. K. Chernenko and Dr. K. Klementiev (MAX IV Laboratory, Lund University)
- Estonia: Prof. A. Lushchik (Tartu University)
- Ukraine: Prof. A. Voloshinovskii (Lviv University)
- Russia: Dr. R. Shendrik (Vinogradov Institute of Geochemistry, SB RAS, Irkutsk)

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SPECTROSCOPIC ELLIPSOMETRY OF ADVANCED MATERIALS

STATE OF THE ART

Unconventional metamaterials and structures [1, 2] have huge potential for new photonic devices. For example, sub-wavelength periodic nanostructures give rise to interesting optical phenomena like effective refractive index, perfect absorption, cloaking, etc. The concept of point of darkness has received much attention for biosensing based on phase-sensitive detection and perfect absorption of light [2].

There are technological hardness and limits for complete suppression of reflection. Kravets et al. proposed a concept known as topological darkness [3]. According to this concept, an optical system that follows the Jordan curve theorem is able to provide a complete suppression of reflection at certain incident angles and frequencies. This concept was first experimentally implemented using plasmonic gold nanoarrays fabricated by electron-beam lithography [3]. Since then, different subwavelength nanostructures have been proposed for the implementation of topological darkness [4]. The suppression of reflection is, in fact, achievable by simple materials by modelling and combination of proper multilayer stack thicknesses.

Since the first roots of ellipsometry, the time progress has been enormous, and given the essential metrological contributions of spectroscopic ellipsometry (SE) to integrated-circuit (IC) technology, its economic impact has been immense.

Advances in many areas of science and technology showed SE as a powerful tool for various non-destructive investigations [5] with broad application fields (academic research, IC, photonics, biomedical, optical metrology):

Anisotropy, optical gradient, nanostructures, periodic structures [6-8]
Biosensing [9]
Plasmonic nanostructures [10]
Multilayer optical coatings [11]
Thermo-optics: phase transitions in the interface, film and on the surface [12, 13]
Impact of the defects, e.g., oxygen vacancies, on optical properties [14, 15]

The fast developments in micro- and nanoelectronics, in materials for photonics and in advances of new hybrid and materials [16-18] have caused a steep rise in interest in the structure, phase state and properties of the surfaces of solids and films. There are only a few existing studies of phase transitions in thin and especially in ultra-thin films (thickness < 10 nm), and the majority of them are destructive methods that demand very specific precise sample preparation. In this situation, it is very attractive to have non-destructive optical methods of research and diagnostics.

The operation of organic, inorganic and hybrid electronic devices is strongly influenced by interphases, optical gradient and anisotropy in the electronic and optical properties of the conjugated material films. Accurate knowledge of the optical constants of these materials is important in optical modelling and design of photonic devices.

OUR POSITION

We have long-term experience with spectroscopic ellipsometry (SE). Our past work has been crucial for establishing of electronic band structure behaviour in dependence of temperature and detecting phase transitions for various materials (e.g. [19-21]).

SE technique has proved to be an effective method for the detection of phase transitions in thin films, as well as an effective technique to establish the quality of thin films while studying the technological aspects, which could cause the optical gradient forming in thin films [19]. Spectra of dielectric function measured by the SE are able to provide information on electronic and phonon band structure.

FUTURE ACTIVITIES

Studies of thermo-optic coefficients of thin films by integrating a temperature controlled hot stage to the ellipsometer and applying the modelling in order to obtain information on the phase transitions in the thin film, as well as in the interface and on the surface of the thin film.

Studies of Mueller matrix-based scatterometry for advanced materials and technology nodes. It is resent that complete Mueller matrix measurements are possible. These measurements open the possibility of studying a wide range of materials that so far have been deemed too complex to measure, and for which data are consequently unavailable.

Developing the method for determining the complex refractive index of ultra-thin films (< 10 nm).

Studying interfaces in organic and inorganic multilayer systems in co-operation with the Laboratory of Organic Materials.

NETWORKING

The group has long-standing active international collaborations with research groups in:

- Czech Republic: Czech Academy of Science, Institute of Physics, Prague (Dr. phys. A. Dejneka)
- Taiwan: National Taiwan University, Taipei (Profs. Li-Chyong Chen, Kuei-Hsien Chen)
- France: Paris Institute of Nanosciences (prof. N. Witkowski)
- Sweden: Uppsala University (Prof. Lars Österlund, Prof. Claes-Göran Granqvist);

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APPLICATIONS

PHOTONICS MATERIALS AND APPLICATIONS

ELECTROLUMINESCENCE AND ORGANIC LIGHT-EMITTING DIODES

STATE OF ART

One of the largest shares of the total energy consumption is consumed by lighting and displays. Highly efficient artificial lighting with good spectral properties is still one of the biggest issues. Organic light-emitting diodes (OLEDs) is one of the possible solutions in these fields. Such diodes systems could be implemented in Smart Cities and highly energy-efficient buildings. Artificial lighting could be implemented in the windows or through the ceiling. Smart TV and displays can be fitted in mirrors or walls. The energy consumption of such systems could be lowered several times [1,2,3]. The number of publications containing the keyword "OLED" has risen from 6 publications in year 1996 to 2029 publications in year 2020 (data from SCOPUS database). At the same time this technology has already taken a large market share in areas like OLED displays. The forecasted market revenue for OLED displays will reach 16 billion US dollars this year with a predicted multiple rise the following decade (data from market research company IDTechEx). Nevertheless, many unresolved problems exist that delay even more rapid growth of this technology. Throughout these years the development of suitable light-emitting organic molecules has always been the main culprit for technological advancement of OLEDs. The first devices featured purely fluorescent compounds, but soon it became clear that these first generation (G1) emitters are fundamentally flawed. Due to the statistics of spin state recombination process, electric charge driven excitation of organic molecules results in excited states that in 25% of the cases are singlets (S), but 75% - triplets (T) [4]. Exclusively singlets are emissive in G1 emitters since the spin-forbidden nature of $T_1 \rightarrow S_0$ transition renders these excited states to being unable to relax through the radiative pathways. Only in 1998 it was demonstrated that internal quantum efficiency of OLEDs can be elevated to 100% with a use of second generation (G2) phosphorescent emitters [5]. Structurally, G2 materials are organo-metallic compounds that feature a heavy transition metal atom. The presence of a large atom induces spin-orbit coupling (SOC) process. This, in turn, drastically changes photo-physical behaviour of the molecules. First, due to the characteristic fast intersystem-crossing (ISC), all the excited states undergo almost immediate transition to the lowest-energy T_1 level [4]. From there, instead of being non-emissive, radiative relaxation takes place for compounds in a form of phosphorescence. This occurs as SOC causes mixing of S and T states, making the $T_1 \rightarrow S_0$ transition probable on a reasonable timescale. Phosphorescence lifetimes (τ) for these compounds are usually 1.5-5 microseconds long, in contrast to second-long lifetimes for typical purely organic fluorophores. In such way OLEDs based on G2 emitters can harvest all the excited states, elevating internal quantum efficiency of the devices from 25 to 100%. Transition metals as osmium, rhenium, rhodium, platinum and iridium are used to synthesize these materials, with the last two being the most commonly applied. Up to this moment, G2 emitters are the go-to materials among OLED industry members due to a combination of relatively low emission lifetimes, chemical stability and wide selection of attainable emission wavelengths. The only exception is blue-light emitters. Operational stability of organic emitters is mandatory, as practically used emitters must retain 95% of the original brightness (T_{95}) after 10000 h of device operation [6]. In contrast, state-of the-art blue G2 emitters show T_{80} of less than 160 h [6]. This is the reason, why G1 emitters are still exclusively used as blue-light source in commercial OLEDs. As a consequence, blue-light generation consumes about 50% of driving power for such devices as modern smartphone displays [7].

The extensive use of noble metals, such as iridium and platinum, is causing concerns among OLED industry members and academics. The cost and scarcity together with negative environmental impact associated with these metals create limitations for the potential sustainability and expansion of this industrial sector [8]. In order to circumvent the issue and to the develop possible triplet harvesting blue-emitters, the recent years have witnessed extensive development of compounds that exhibit thermally activated delayed fluorescence (TADF). The interest in this research direction sparked in 2012, with the first demonstration of efficient OLEDs with TADF emitters [9]. Often labelled as the third generation (G3) emissive materials, these compounds are purely organic molecules, with no metal atoms present. The ability of G3 emitters to harvest triplet excited states originates from the closely located S_1 and T_1 levels. If this energy gap ($\Delta E_{S1\text{-}T1}$) is not much larger than 0.12 eV, thermal energy at room temperature can elevate T_1 to the higher lying S_1 energetic state. Such process is called reverse intersystem-crossing (rISC). Combination of G2 and G3 emitters could lead to the highest and most stable OLED.

Another disadvantage is the high production costs of the OLED devices. During the device production stage the active light emitting organic components are usually processed using energy intensive and technologically complex vacuum deposition (sublimation) methods. To increase the competitiveness level of OLED devices the new light emitting materials need to be developed, which can be processed with inexpensive solution-based methods (spin-coating, ink-jet printing), while maintaining high efficiencies and chemical stability. At the moment this problem has not been completely solved and a considerable effort is made by research community in this direction.

OUR POSITION

Laboratory of Organic Materials has a long-time experience in the investigation of original organic materials for application in an organic light emitting diode (OLED). One of the first steps is quantum chemical calculations to predict molecule applicability as efficient light emitting material with necessary semiconductor properties. The solution containing organic molecules is further investigated to determine the properties of the compounds themselves. Then, obtained thin films are studied. The laboratory has expertise in the determination of both the optical and electrical properties of organic materials. Optical properties like photoluminescence spectrum, photoluminescence quantum yield, and fluorescence kinetics are essential to define possible organic compound applications in OLED [10]. Nevertheless, semiconductor properties are equally important. Therefore, the laboratory pays great attention to the investigation of energy structure and electrical properties of organic semiconductors [11]. Energy levels of the compounds have been studied by photoelectron emission spectroscopy (PES) and spectral dependence of intrinsic photoconductivity, which provides information about molecule ionization energy (IE). The second method gives a good estimation of the energy bandgap between IE and electron affinity (EA) energy [12]. Local trap states in the bandgap have been investigated by temperature modulated space charge limit current method. Charge carrier mobility has been obtained by Time of Flight (ToF) or Charge Carrier Extraction by Linearly Increasing Voltage (CELIV) techniques [13]. Obtaining complete information about a chemical compound can determine its potential use in the organic light emitting diode. So far, most activities have focused on the investigation of the organic compound. As the main group of compounds, molecular glasses with fluorescence, phosphorescence or thermally activated delayed fluorescence properties have been used. Recently, the laboratory has started the investigation of light emitting organic ionic compounds.

FUTURE ACTIVITIES

In the future, the activities related to the investigation of OLED will be broadened. Investigation of thin film morphology and intermixing of two thin films will be added in the research action. It will be linked to the performance and lifetime of the diode. Use of flexible substrate is one of the advantages of organic light-emitting diode, which should also be developed in the laboratory of organic material.

- Establishment of all necessary experimental methods for investigation of organic light-emitting compounds

Basic knowledge of optical and electrical properties of organic materials is essential for the preparation of high-performance OLED. Up to now, the Institute has established most of the necessary investigation methods that include UPS, XPS, PYS I-V-L curve measurement, TM-SCLC, AFM, SEM, thin film thickness and profile measurement, optical steady-state and time-resolved spectroscopy. Still, some investigations are missing. Two methods to study semiconductors charge carrier mobility will be developed. One is Time of Flight (ToF) method that allows estimating both electron and hole mobility. The second method is Charge extraction with linearly increasing voltage (CELIV). The method is valid for thin films and can be used to investigate charge carrier recombination, but it cannot separately determinate charge carrier mobility for each charge carrier type. Time-resolved electroluminescence measurement is essential for light-emitting electrochemical cells. The completely new system will be established for such measurements. Time-resolved emission measurements in different temperatures are critical for thermally activated delayed fluorescence compound measurements. Edinburgh instruments Photoluminescence Spectrometer FLS1000 could be used for this purpose, but it should be upgraded with the cryogenic system.

- Correlative methods for OLED efficiency and lifetime investigations

Intermixing of the layers and roughness of the layers is one of the reasons for a short lifetime and low performance of organic light-emitting diodes. We will use a correlative characterisation (analyses) method approach to investigate the relation between morphology and the performance of OLED. The deep profile of the OLED will be investigated by XPS, SEM and AFM. The measurements will be done for virgin and aged OLED structures. OLED performance and ageing will be correlated to the changes between original OLED stuck and after the operation. To perform such correlative analyses, we must be sure that all prepared samples are identical as after deep profiling, the sample cannot be used. To overcome this issue, a new approach will be developed. Spectral ellipsometry is a non-destructive method that can provide information about multilayer system and possible layer intermixing. It gives the possibility to measure the same pixel before and after OLED operation. In some cases, in-sity measurements are possible while voltage is applied on OLED.

- Methods for preparation of OLED on flexible substrates

ITO-coated polyethylene terephthalate (PET) films fits for the preparation of a flexible organic light-emitting diode. Cleaning procedure of PET substrate will be developed to increase the wettability of organic compounds. A new type of chucks will be bought in order to perform layer deposition from solution by spin-coating method. Vacuum deposition system and measurement system will be adapted to flexible thin films. Also, new encapsulation methods will be used to maintain flexibility. At the beginning, 25×25 mm^2 will be used, and then they will be gradually increased to 50×50 cm^2.

- Preparation of structured OLED

Structured OLED is the first step for preparation of OLED matrix. Structuration could be done in two ways. One is related to the deposition of the specific shape of electrodes. Then the electrical properties of the electrode should be carefully analysed. The second possibility is the use of the dielectric layer within the OLED stack. In such a case, the electrical properties of thin dielectric films should be considered. In both cases, the lithography method should be applied for structuring the emitting areas of the OLED.

NETWORKING

Laboratory of Organic Materials is the best place in Latvia with all the necessary equipment and competence to produce and investigated organic light emitting devices. Further development of OLED field will be divided into two parts. One is related to the research of new compounds and systems for emitting system, and it will be done in close collaboration with chemists from other academic institutions. The second is related to the commercial offer of OLED investigation to the industry. OLED production and investigation competence will be transferred to new students and young scientists.

Latvia:

Institute of Organic Synthesis (prof. Edgars Suna)
Riga Technical University (prof. Valdis Kokars and prof. Maris Turks)
Daugavpils University (Dr.chem. Jelena Kirilova)
EmiBLUE company
EVOLED company

Europe:

Kaunas University of Technology (prof. Saulius Grigalevicius and prof. Juozas Vidas Grazulevicius)
Vilnius University (prof. Vidmantas Gulbinas)
World:

National Tsing Hua University (Prof. Jwo-Huei Jou)

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LIGHT AMPLIFICATION AND ORGANIC SOLID-STATE LASERS

STATE OF ART

Low-energy consumption light emitters with high energy conversion efficiency are critical for sensor and telecommunication applications. Personalised medicine requires low-cost test probes (like Lab-on-a-chip) that every person can use to get the results of the lab test fast, so that targeted therapy could be applied. One of the principles how the test probes work is the detection of light changes (spectra or intensity). In such a case small, highly efficient, and probably wavelength-tuneable light source is necessary. Organic solid-state lasers could be flexible, wavelength-tuneable, and several micrometres large. They can be integrated in organic or inorganic photonic-integrated chips. Short-range telecommunication could be achieved within the polymer fibres. In such a case, the telecommunication window will be in the near-infrared region. Organic solid-state laser offers highly efficient energy conversion in the infrared spectral region [1,2].

Organic compounds have been widely used in dye lasers. The same or similar compounds can be found in organic solid-state lasers. All type of organic molecules as low molecular weight compounds, dendrimers, and polymers are used. The best systems with the lowest amplified spontaneous excitation (ASE) threshold values (below 1 $\mu J/cm^2$) are dye-doped matrixes [3,4]. Without matrix, the distance between the molecules is small, and significant intermolecular interaction takes place that quenches the excited states. It was partially solved by added bulky groups to the dye molecule, but still, ASE excitation threshold value is one order of magnitude higher [5,6] compared to the guest-host systems. ASE excitation energy is different for various spectral ranges. It is the smallest for blue emitters (below $\mu J/cm^2$) [3]. The same is for green emitters (around below $\mu J/cm^2$) [4]. A yellow emitter has around 10 $\mu J/cm^2$ [7], a red emitter has around 24 $\mu J/cm^2$ [8], and for infra-red emitter it is 20 $\mu J/cm^2$ [9]. Our group has demonstrated that emitting molecular glasses based on pyranyliden derivatives in neat films also show ASE excitation threshold values comparable to the best published in the red spectral region (24 $\mu J/cm^2$). This value is still one order of magnitude higher in infra-red spectral region (165 $\mu J/cm^2$) [8]. Such low threshold values were obtained even despite small photoluminescence quantum yield (PLQY) below 25%. Lower ASE threshold energy values could be achieved if PLQY was higher. One of the possibilities to enhance luminescence in organic material is the introduction of metallic nanoparticles (NPs) into the organic matrix. In the presence of the electromagnetic field, plasmon field emitted by the properly exciting metal nanoparticle can enhance the luminescence of an organic molecule [10]. Still, the are many factors affecting luminescence enhancement, being shape, size, and dimensionality of NPs [11], the orientation of the dye dipole moments relative to the nanoparticle surface normal, dye-metal distances, overlapping of plasmon and organic dye absorption and emission band, radiative decay rate, and quantum yield of luminescent molecules [12]. Luminescence can be increased if appropriate conditions in the metal NPs-organics matrix are created. Among the metallic NPs, silver NPs are the most popular due to their physical, chemical, and biological properties. The advantage of Ag NPs over others metallic NPs is small loss of the optical frequency during the surface-plasmon propagation, nontoxicity, high electrical and thermal conductivity, stability at ambient conditions, low cost in comparison to other metals such as gold or platinum, high-primitive character, wide absorption of visible and far IR region of the light, and chemical stability [13]. Till now, several papers have reported ASE efficiency enhancement by applying nanoparticles [14] and metal nanostructures in gain media [15,16]. It has been shown that the ASE threshold value could be reduced up to 10 times. Surface plasmon interaction with organic semiconductors opened a new type of organic lasers – surface plasmon amplification by stimulated emission of radiation ("spasers") [17,18].

OUR POSITION

Laboratory of Organic materials has started an investigation of light amplification in 2010. During this time, investigation method for a full description of the compounds has been established. Optical properties of solution containing organic molecules have been investigated to determine the further investigated compounds. Investigation of thin film deposition parameters is investigated afterwards. Emission spectra and photoluminescence quantum yield are one of the most important parameters which are studied in thin films. Light amplification properties are obtained via amplified spontaneous emission (ASE) by line method. Specific measurement set-up was made to measure ASE excitation threshold energy, light gain and losses coefficients. More than 100 compounds were investigated during this time in close collaboration with chemists. The investigated compounds emit light in the red and infrared spectral region. All investigated compounds were molecular glasses, and ASE properties were investigated in neat films or polymer matrix. Thin-film preparation from solution and reduced photoluminescence quenching are one of the advantages of molecular glasses.

One of the first works in the field of optical amplification systems was done in 2012, where amplified spontaneous emission of molecular glasses were investigated [18]. 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) red-emitting molecule has served as a base of all derivatives. Glass state of thin films was archived by adding bulky trityloxyethyl groups at the electron donor side of the molecule. The neat film of DCM does not exhibit fluorescence, but the photoluminescence quantum yield (PLQY) of the systems that we have prepared was up to 3% [19]. As a result, amplified spontaneous emission excitation energy as low as 90 $\mu J/cm^2$ was obtained. Further work was done to increase the synthesis yield of investigated compounds with a double increase in PLQY, but without significant changes in ASE excitation energy [20]. It was achieved by substituting metyl group with tert-butyl group (DWK-1TB molecule). Several other modifications were done to electron donor and/or electron acceptor group to improve emission efficiency till DWK-1TB molecule was modified by changing malononitrile group as the electron acceptor to ethyl and one nitrogen group. These changes benefited in the optical properties of the neat thin film. PLQY increased up to 23%, while ASE threshold energy was decreased to 24 $\mu J/cm^2$ [8], which now is close to the best results for red emitters found in the literature. During the investigation of DCM derivatives, bis-DCM derivatives with the light emission in the near-infrared region were developed. The best performance of 170 $\mu J/cm^2$ ASE threshold energy with emission at 743 nm was obtained [21].

FUTURE ACTIVITIES

The results obtained so far are by no means final and conclusive. Further work should be done in the field of hybrid structure. Absorption and emission properties of the organic semiconductor can be improved if metal nanoparticles are mixed in the system due to the organic molecule interaction with metal nanoparticle surface plasmon resonance. Unfortunately, metal nanoparticles should be synthesised in water, but organic compounds cannot be dissolved in water. It means that metal nanoparticles should be transferred in an organic solvent, which is a challenging task. Introduction of Bragg grating in the ASE system is one additional task which should be done in this period.

- Influence of metal nanoparticle surface plasmon resonance on ASE properties of organic materials

Regarding optical light amplification systems, the main goal will be the development of metal layer preparation protocol and selection of plasmonic design for optical amplification of light. To achieve this, we will develop a methodology for nanoscale metal structure fabrication using EBL, optical lithography and vacuum deposition system. This includes selection of adequate photoresist for lithography process and its processing, guidelines for metal deposition and stripping of photoresist. Alongside this, theoretical study of different plasmonic structures will be carried out to select the most appropriate ones for optical modulation and light amplification. For chemical metal nanoparticle synthesis, metal precursor, reducing agent, and stabilizing/capping agents are needed. Reducing agent concentration determines the size and shape of metal nanoparticles. Unprotected metal nanoparticles can easily agglomerate due to their small size; therefore, stabilizing is required. It allows obtaining a stable metal nanoparticle solution. Nanoparticles will be synthesised in aqueous solution, but organic material usually cannot be dissolved in water; therefore, metal nanoparticles will be transferred to an organic solution like chloroform or toluene afterwards. For this reason, reducing agent and stabilizing should be changed to one which can disperse nanoparticles in organic solution. The transfer can be made through a chemical reaction, centrifugation, and ultrasonic treatment. The size of nanoparticles will be tuned to match absorption and/or emission spectra of organic compounds. Synthesised nanoparticles will be mixed with laser dye or laser dyes deposited on the prepared metal nanostructure. Pyranyliden derivatives with one and two-electron donor groups that have been previously investigated in our laboratory will be used as laser dyes. Light absorption and emission of the hybrid systems will be obtained to investigate the impact of nanostructures on the optical properties of organic compounds. Mainly photoluminescence spectra, quantum yield and kinetics will be measured. For the best systems, ultrafast spectroscopy measurements will be done.

Computer modelling and preparation of resonator structure for organic solid-state laser will be fully done in the scope of polymer photonics technology platform.

- OLED preparation methods on flexible substrates

PET or other low-refractive index polymer substrates will be used for the preparation of flexible organic solid-state laser. Cleaning procedure of PET substrate will be developed to increase the wettability of organic compounds. A new type of chucks will be bought to make possible layer deposition from solution by spin-coating method. Possibility of introducing low-index intermediate layer between the substrate and laser active media will be investigated.

The limits of lithography technique for writing diffraction gratings in systems with flexible substrates will be investigated within the scope of the polymer photonics technology platform.

- Preparation of the media for CW organic solid-state laser

To obtain a solid-state laser able to operate in CW conditions, the following scientific solutions for the design of the laser-active media are proposed:

Functionalization and/or re-design of all the components (triplet manager, Alq_3, DCM/DWK-1 molecules as well as the quencher functional groups, structural fragments or molecules if required) necessary for producing the solid-state light-emitting system. All the obtained components can be mixed either in a polymer matrix or into a single glassy film-forming component.

Design and synthesis of solution-processable laser dye based on bulky amorphous phase promoting bulky triphenylmethyl-moiety-containing derivative of DWK-1 with additionally incorporated "triplet manager" fragments, and, if required, one with triplet quencher functional groups. Obtained products also can either be mixed in a polymer matrix with functionalized or non-functionalized Alq_3 or the glassy lasing medium, which can be acquired just from the newly synthesized compounds.

To achieve the goals mentioned above, some technologies and experimental setups should be developed:

- Thin film deposition in vacuum system in GlowBox;
- Time-resolved electroluminescence emission measurement system;
- Time-resolved photoluminescence emission measurement at different temperatures.

NETWORKING

Laboratory of organic materials is the only place in Latvia with all the necessary equipment and competence to investigate organic compounds for light amplification. The further development of organic solid-state laser will be focused on preparation of more efficient gain media and design and preparation of laser resonator. Increase of gain media efficiency will be done in close collaboration with chemists from other academic institutions. ASE investigation and laser production competence will be transferred to new students and scientists.

Latvia:

- Riga Technical University (prof. Valdis Kokars and prof. Maris Turks)
- Daugavpils University (Dr.chem. Jelena Kirilova)

Europe:

- Kaunas University of Technology (prof. Saulius Grigalevicius and prof. Juozas Vidas Grazulevicius)
- Vilnius University (prof. Vidmantas Gulbinas)

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VISUAL PERCEPTION AND IMAGE PROCESSING IN ADAPTIVE OPTICS AND AUGMENTED REALITY

STATE OF ART

Physical optics, photo- and colorimetry are the main study areas to understand and to apply the advances in material science, optics, bioscience, environmental science, and information technology to ensure good, optimum and healthy vision of humanoids [1-4].

Adaptive optics is an area in optics of worldwide interest. It is mainly used in astronomy to correct the effects of atmospheric turbulence on the quality of images and in vision science to correct the ocular aberrations and to improve the visibility of photoreceptors and visual perception as well. In astronomy, near diffraction-limited performance of astronomical telescopes has been achieved. In vision science, single photoreceptors, blood cells and other retinal features can be resolved. The publications mentioned below demonstrate the significance of adaptive optics in astronomy and vision science [5,6].

Coherent diffractive imaging (CDI) is a very fast-growing area in optics. CDI finds applications in astronomy, biology, holography, materials science etc. Many phase retrieval algorithms based on CDI are developed and implemented practically. In the scientific literature, there is a large number of research papers aiming to improve the optical quality of an image based on numeric phase retrieval algorithms. Phase retrieval is also very important in materials science to determine the structure of crystals. For the first time, the phase problem was recognized in X-ray crystallographic analysis, which is a very active field still today. An example of the activities performed in the field of CDI is provided in papers of institutions worldwide [2,7,8].

Microfluidics finds use in many biological applications. It can provide sensing biological molecules by using surface plasmon resonance. Microfluidics can also be applied for wavefront sensing, creating labs-on-chip, for manipulating and synthesizing nanoparticles, etc. [9,10].

The current leading-edge research is focused on the following axes:

1.Development of solutions to improve image perception in sequent stages of technical appliances and of human vision. Use of adaptive optics in studies of absorbance, scattering and diffractive effects affected eye structures that cause a deterioration of visual performance. This applies also to solutions of general optical applications, thus improving their performance and resolution of optical systems. A distinct goal of research is to develop a new kind of wavefront sensors. The new wavefront sensors foreseen for biomedicine and astronomy are based on phase retrieval from intensity measurements. Eye vitreous floaters are simulated in a model eye incorporating a microfluidics system [6,7,9].

2. To develop optical and smart materials and methods to expand opportunities useful in human daily activities and in medical diagnostics. This point concerns studies on how to use materials with a complex set of properties, which allow to implement multiplex control of optical information: controlled focusing and scattering, a possibility to provide binocular viewing in virtual reality appliances and processing of parallel information in augmented reality. That also concerns materials used in advanced vision correction and training appliances based on smart materials and elements, such as custom design contact lenses and electrically controllable liquid lenses [2,4,11].

3. To increase the competitiveness in creating energy-saving and human-centric lighting, free from adverse effects to humans and to non-living environment. The research should combine wide

spectrum of subtasks/problems with the goal to achieve good visibility of light emitting and reflective elements at moderate cost without irreversible damage to observable objects. Even more, light sources should be comfortable to an observer and without adverse impact to physiology and psychology [12-15].

OUR POSITION

The Laboratory of Visual Perception of the ISSP UL has a strong background related to research in the following fields: optimizing phase retrieval algorithms; phase retrieval in a scattering optical media; developing of advanced microoptical elements; wavefront modulators based on microfluidics technologies; tuneable optical elements and their use in virtual reality and vision appliances; smart human-centred means of illumination; hyperspectral colour imaging of surfaces and archiving of data.

Phase retrieval is essential for recovering the structure of an object under study. The phase problem, i.e., the loss of information about phase is faced in various fields of science and especially in optics. An emerging area of phase retrieval in optics is based on mathematical optimization methods using coded diffractive imaging.

At the Laboratory of Visual Perception studies of phase retrieval based on unique modulation of the object under study are carried out within on-going research projects "New generation wavefront sensors based on the method of coded diffraction patterns" and "Reducing/cancelling the effects of vitreous floaters using a phase retrieval method based on coded diffraction patterns". Vitreous floaters are simulated in a model eye incorporating a microfluidics system [16-19].

Hyperspectral colour imaging is currently detected both by convenient methods and by hyperspectral analysis ambient illumination in Latvia.

Smart light (human centric lighting) seeks to minimize the amount of blue light hazard and photothermic destruction both to eye and matter. Electrically controlled focusing and scattering of light are investigated using appliances based on polymer-dispersed liquid crystals and liquid lenses, both causing contrast alteration of an optical image in a real eye and/or model eye and digital photodetector. Thus, the eye lens cataract-induced visual performance loss and/or scattering errors of commercial wavefront analysers can be detected [2,11]. Studies are focused on application oriented research. Tuneable liquid lenses are combined with virtual reality adapter, and now the device is going to be tested in vision training exercises.

Laboratory closely follows the recent trends in the development of high density displays and their spectral emission to evaluate and control in near future the metabolism of melatonin by enduring eye exposition. Its scientists are in touch with other investigators working in this field. Human centred lighting and comparison between natural and advanced solid state emitters is in focus of many research institutions, e.g., [12-15].

FUTURE ACTIVITIES

The areas pointed out as prioritized in European program documents and belonging to planned Laboratory of Visual Perception research fields are: concerning *health* – retinal imaging, human centric lighting, improvement of human visual performance, developing of visual training methodology applied in absence of medical employees with web-based data transfer, essential during the existing corona virus disease risk; *culture* – hyperspectral imaging, spectroscopy of cultural heritage and data archiving; *climate, energy, industry* – human-friendly economic and ecologic material studies, prototype design of illumination devices.

The main directions of research in Laboratory of Visual Perception will involve:

- Theoretical development of visual information phase retrieval, which plays serious role and helps to adapt methodology to human vision quality;
- Optimizing and standardization of lighting using solid state materials, creating of human centric lighting;
- Optical system metrology, multispectral analysis of surfaces, optimizing of image data archiving;
- Developing and optimization of adaptive optics systems with novel wavefront sensors;
- Retinal imaging, adaptive optics for medical applications, improvement the efficiency of adaptive optics in vision science;
- Optimizing phase retrieval algorithms, multiwavelength phase retrieval; diminishing of impact of eye floaters;
- Optical sensing of biological cells and molecules using microfluidics;
- Investigation and testing of materials used in ophthalmology and advances in novel material processing;
- Development of prototypes using smart materials/devices with controllable optical properties anticipated in vision appliances and visual reality and augmented reality devices;
- Development of methods in optometry and orthooptics, which do not need a direct aid of medical personnel, and with remote data transfer.

In future new areas will be added. Based on the updated infrastructure and the acquired skills in lithography, silicon technologies, micro- and nanostructuring, the research area could be extended to include studies on micro- and nanoelectronics and photonics, MEMS systems, photonics such as light sources, photovoltaics, quantum optics, as well as use of electrically controllable materials in design of optical appliances.

NETWORKING

There are groups around the world that actively work in the fields close to the Laboratory of Visual Perception research areas:

- In the field of adaptive optics, phase retrieval, physiological optics they are: Universidad de Murcia, Laboratorio de Optica (Murcia, Spain); Kungla Technical Högskolan (KTH, Stockholm); Indiana University, Adaptive Optics Laboratory (Bloomington, USA); Durham University, Centre for Advanced Instrumentation (UK); University of California, Computational Imaging Lab (USA); Fraunhofer Institute of Optronics, Adaptive Optics Group (Karlsruhe, Germany);

- In the field of hyperspectral colour analysis, environment and human centric illumination, colour vision testing: Newcastle University, UK; University of Minho, Portugal, Manchester University, UK; City University, UK;

- As partners having common direct interests and publications here can be mentioned Moscow University Adaptive optics, University College Dublin, Centre for Biomedical Engineering; Stockholm KTH Visual Optics research group (together with ACREO as partners within ISSP CAMART[2] project); close creative interaction with neighbouring Vilnius University Lighting Research Group (Lithuania).

Potential academic R&D partners

List of potential academic R&D partners is built on common interests in following research directions in the lab and worldwide: optimizing phase retrieval algorithms; improve the efficiency of adaptive optics; multiwavelength phase retrieval; retinal imaging; optimizing lighting and multispectral analysis; optical sensing of biological cells and molecules using microfluidics:

- The Laboratory of Visual Perception has strong collaboration with the scientific institutions listed below: Universidad de Murcia, Laboratorio de Optica (LOUM) (Murcia, Spain). Contact person: prof. H. M. Bueno. Moscow State University, Laboratory of Optics (LO MSU). Contact persons: N. Iroshnikov, A. Larichev. University College Dublin (UCD), Laboratory of Optics and Advanced Optical Imaging (Dublin, Ireland). Contact person in UCD Prof. B. Vohnsen is adviser of current UL ISSP PostDoc project “Reducing/cancelling the effects of vitreous floaters using a phase retrieval method based on coded diffraction patterns”;

- Optometry and Vision Science Department of UL. They need technical and engineering competence in common field of interest, and the Laboratory of Visual Perception has the vision and colorimetry in depth knowledge for visual application related to physics and physiological optics. And the only lab to have Adaptive Optics experience in LV (also in all Baltic States). The Institute of Astronomy, University of Latvia has shown interest in collaboration with the Laboratory of Visual Perception. The Institute of Astronomy plans focusing of a laser beam through a turbulent atmosphere to remove debris orbiting the Earth;

- City University, Newcastle Universities – with good experience on visual perception, colour research, colour vision test development, modelling of neural processing of visual pathways;

- Minho University and Newcastle University. Experience in human-centred and eco lighting, image multispectral analyse and archiving;

- KTH and RISE. Development of visual and augmented reality designs.

Contacts with these institutions are maintained and the results of research are frequently discussed. Collaboration with the high-tech industry is mainly possible within long-term projects due to the specific interest of physiological optics (optical system and particularly – eye quality optimization) and appliances based on visual reality and augmented reality development.

Industrial interest in the area, potential industrial partners

Following market trends and growth potential exist in the research areas of the Laboratory of Visual Perception: continuous improvement and optimization of human centred and economic lightening; object multispectral diagnostics, analysis and data archiving; materials and designs for vision improvement; applications of adaptive optics for astronomer; military; medical diagnostics.

Potential industrial partners on national and international scales: Sidrabe; Groglass; Barona optika; LED manufacturers (VIZULO); Euro LCD; Optical products manufacturers (like Thorlabs, Edmund Optics).

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TRANSPARENT GLASS-CERAMICS, GLASSES, COMPOSITES.

STATE OF THE ART

Currently, single crystals and glasses are dominant in the global market of transparent optical functional materials. However, ceramics are usually considered to have higher mechanical strength, simpler fabrication process and thus higher cost-effectiveness, when compared with single crystals and glasses. Transparent ceramics can have both superb optical transparency and high mechanical performance. Transparent ceramics have potential applications as solid-state lasers, scintillators, IR windows, solid-state lighting (phosphors of LEDs/LDs), biomaterials and so on [1–9]. A special place in the class of transparent ceramics is reserved for transparent glass ceramics.

Transparent glass ceramics may be viewed as composite materials that combine the advantages of both their components, glasses and crystals. Glass ceramics contain crystalline objects of different sizes inside their bodies. If these micro-crystals are less than the wavelength of visible light, then these materials are called transparent glass ceramics. Since the 1980s, scientists have focused their attention on the synthesis and the properties of transparent glass ceramics with 10–30 nm crystallites, because these inclusions cause minimal light scattering. Incorporation of semiconducting, ferroelectric and non-linear optical phases in glass matrices can produce very promising materials for modern industry [10-12]. This is especially important for transparent glass ceramics for photonics applications, because of the feasibility of its industrial-scale production. Such materials, activated by rare earth elements, play a crucial role in optical amplifiers, up-conversion fibers, solid-state lasers, medical sensors, optical electronic chips, luminescence labels, 3D displays, etc. [13-17].

OUR POSITION

The team has worked intensively on the development of rare earth ion-doped oxyfluoride glass ceramics during the last 10 years and is very experienced in synthesis and photoluminescence investigation of these materials. In order to search for new, efficient up-conversion materials, oxyfluoride glass ceramic containing fluoride crystal phases $Na(Gd,Lu)F_4$, $Ba_4Gd_3F_{17}$, $NaLaF_4$, $Ba_4Lu_3F_{17}$, $NaErF_4$, $NaYF_4$, [18-22] have been obtained. The up-conversion luminescence intensity in the glass ceramics doped with Er^{3+}, Er^{3+}/Yb^{3+} etc. was improved several times compared to the precursor glasses. Up-conversion luminescence measurements and site-selective measurements at room and low temperatures allow to identify the incorporation of Er^{3+} in different cationic sites; in some cases to identify specific modifications in the crystalline phases, which are difficult to identify using other methods. Hexagonal phase of $NaYF_4$ has been introduced in glass ceramics for the first time [22].

Besides the up-conversion luminescence research, the luminescence properties of oxyfluoride glass ceramics containing CaF_2 and SrF_2 nanocrystallites and co-doped by rare earth ions (Eu^{3+}, Eu^{2+}, Tb^{3+}, Dy^{3+}, Sm^{3+}) have been studied in order to identify energy transfer processes between rare earth ions and their efficiency [23].

The other part of the research is devoted to the local structure studies in glasses, glass ceramics and polycrystalline materials containing SrF_2, BaF_2, CaF_2 crystallites, combining EPR and optical spectroscopy techniques [24-26]. The studies are focused on identification of different centres, site symmetries and their properties.

FUTURE ACTIVITIES

- Comprehensive fundamental study on generation of intrinsic and extrinsic defects in oxyfluoride glass ceramics by means of optical and magnetic spectroscopy.
- Spectroscopy research of the rare-earth ions doped oxyfluoride glass ceramics aimed to improve the quantum yield of the luminescence in the materials for applications related to solid-state lighting.

- Elaboration of hot pressing sintering process as well as pre- and post-sintering conditions for the production of transparent ceramics based on simple and complex fluorides and oxides for photonic applications including laser active materials.

NETWORKING

Group has developed a co-operation with academic research organisations from Romania, Lithuania, Kazakhstan, Germany, etc.

- Romania: M.Elisa group from National Institute of Research and Development for Optoelectronics. M.Elisa group investigates phosphate glasses and glass ceramics, doped with rare-earth ions.
- Lithuania: The group of A.Kareiva from Vilnius University synthesizes and investigates tricalcium phosphate polymorphs. Cooperation with Vilnius University included residence of two persons (in 2018-2019) at the ISSP UL performing sample synthesis and EPR measurements and creating joint publications.
- Kazakhstan: In 2019, partners from Kazakhstan, from L.N. Gumilyov Eurasian National University, performed photoluminescence and time resolved spectroscopy measurements of Ce^{3+} doped YAG and YAGG ceramics at ISSP UL.
- Germany: prof. Dr.Stefan Schweizer group from South Westphalia University of Applied Sciences in Soest and Fraunhofer IMWS, working with rare-earth doped glass-ceramic materials.
- In the framework of ERDF project launched in 2020, cooperation with industrial partner "Light Guide Optics International" has been established and development of optical fibre temperature sensors is foreseen.

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NOVEL MATERIALS FOR IONIZING RADIATION AND UV LIGHT DOSIMETRY

STATE OF THE ART .

Thermo- and optically-stimulated luminescence (TL and OSL) have been known and practically used in dosimetry for a long time. At present, standard commercially available dosimeters are used for the needs of most radiation fields (among them the highest-sensitive are LiF:Mg,Cu,P (TL) and Al_2O_3:C (OSL)), but in some areas like 2D-dosis mapping, temperature sensing, UV dosimetry [1,2] there is still a demand for new materials with tailored properties**.** Two-dimensional dose mapping in medical dosimetry at present is done with use of TL, though OSL could be a better choice. Some OSL systems described had demonstrated disadvantages, e.g., Al_2O_3:C has too long luminescence lifetime. TL for temperature sensing needs material with multiple TL peaks that are light-insensitive. The only material with such properties known at present is LiF:Mg,Ti, however, its complex defect structure makes it dependent on the entire temperature history. UV radiation dosimetry is an actual issue: exposure to solar ultraviolet radiation is considered a risk to public health, however, there are still no adequately effective UV dosimeter materials. Usually Al_2O_3:C (TLD-500) is used for UV dose detection, and recently $CaSO_4$:Dy (TLD-900) was tested for this purpose and shows some prospective UV dosimeter features, however, it has high fading rate. Also the traditional areas of TL and OSL dosimetry would benefit from introduction of new materials with enhanced properties. One of the most important and still actual aspects of TL and OSL application is basic research of materials [4], which together with photoluminescence (PL), radioluminescence (RL) and photoluminescence excitation (PLE) studies allows effective revealing of luminescence mechanisms in many fundamental problems.

OUR POSITION

Researchers of the dosimetry group (L.Trinkler, B.Berzina, A. Zolotarjevs) have a long-term experience in studies of dosimetric properties of various dielectric materials, revealed in a number of publications [4-6]. The main task of these investigations was elucidation of the luminescence mechanisms using TL/OSL methods and estimation of dosimetric properties suitable for practical application. The dosimetry group has a specific knowledge of in the field of luminescence processes and modern sophisticated equipment, such as Lexsyg Research TL/OSL reader (Freiberg Instruments) apart from other equipment for spectral measurements. At present the main direction of study is connected with luminescence and dosimetric properties of wide band dielectrics: Al_2O_3, AlN, $LiGaO_2$.

Al_2O_3 (alumina)–based dosimetry materials. The best known and widely used dosimeter material on alumina basis is carbon-doped aluminium oxide Al_2O_3:C (TLD-500) (E_g > 6 eV), used as highly sensitive TL, and OSL material for personal dosimetry [7]. However, as a personal dosimeter, Al_2O_3:C is useful only in the dose range 10 µGy–10 Gy and is not suitable at higher doses. Efforts were undertaken to find other alumina-based dosimeter materials using different dopants. It was found [8] that doping of nanopowdered Al_2O_3 with Cr ions makes it sensitive to higher γ-ray doses (100 Gy–20 kGy without saturation). It was shown by us [9], that only for α phase Al_2O_3 Cr^{3+} ions give the well-pronounced luminescence bands around 690 nm in TL emission spectra. Our previous data, e.g. ref. [5] indicate that dosimetric properties of Al_2O_3 the form of transparent ceramics from nanopowder produced by means of nanotechnology, can possess such advantages as high sensitivity to ionizing radiation, uniform distribution of luminescence centres, appropriateness to high radiation doses and low price compared to corresponding single crystals.

AlN (aluminum nitride) has been previously studied by us for TL and OSL applications (ref. [6] and references therein). It has a number of advantages compared to Al_2O_3, a much higher sensitivity to ionizing radiation and in particular to UV radiation [6], a wider linear dynamic range, lesser dependence of TL response on the readout (heating) rate. However, on the negative side, it has much higher signal fading rate at room temperature. We have assigned the fading to tunnel recombination process between donor –acceptor pairs [10]. Our ideas to diminish the detrimental fading phenomenon include creating deep traps by additional doping or, alternatively, by changing the band gap by adding Ga, thus producing AlGaN, whose band gap width, and by implication, trap depths, depend on Ga concentration.

$LiGaO_2$ (lithium metagallate, LGO) is a wide band gap (Eg=5.6-6 eV) wurtzite-structure crystal, relatively recently proposed for TL/OSL dosimetry with Cu+ as dopant. Our study of nominally pure $LiGaO_2$ crystal [11] has shown that UV light irradiation of this material produces complicated recombination processes, which are followed by TL. Preliminary results show also a presence of a room-temperature OSL signal. This is a new, relatively little-studied material and we plan to investigate luminescence mechanisms in LGO, using the TL and OSL methods in order to estimate its applicability for dosimetry of ionising radiation and UV radiation.

The planned experimental study is relatively well-supported by the existing infrastructure. In year 2020 due to the ISSP UL Infrastructure project, a new, state-of-the-art experimental dosimetric system was obtained, Lexsyg Research TL/OSL reader (Freiberg Instruments, Germany), which enables TL and OSL measurements after X-ray and beta-ray irradiation. Its capabilities are further enhanced by a self-made accesory, allowing an additional sample irradiation UV light. The TL, OSL and radioluminescence signals can be spectrally analyzed using an additional spectrometer and CCD camera. Additionally, the dosimetric studies are complemented by photoluminescence emission and excitation spectra measurements.

FUTURE ACTIVITIES

- Investigation of Al_2O_3 dosimetric material in the form of transparent ceramics, synthesized from nanoparticles
- Study of ways to decrease room temperature signal fading in AlN-based dosimetric materials by doping-induced deep trap creation, and, alternatively, by modifying the band gap via addition of Ga component
- Exploring the luminescence properties and the related charge-carrier recombination processes in $LiGaO_2$ and of the suitability of this material for TL and/or OSL dosimetry.
- TL/OSL Investigation of wide band-gap dielectrics, including oxides single crystals, polycrystals, powders and ceramics, for application in medicine, radiation safety, environment, industry, placing the main emphasis on material study for UV light dosimetry.
- Future development of the TL/OSL measurement equipment is planned in the following directions: - upgrade of the Lexsyg research TL/OSL reader for irradiation with a UV light source (UV lasers, Deuterium lamp), using the optical lightguides; - upgrade of the Lexsyg research TL/OSL reader software; - development of the OSL experimental setup using LED sources of different wavelengths.

NETWORKING

Historically the studies were implemented in cooperation with scientists from

- Riso National Laboratory, Denmark (Dr. P. Christensen and Dr. L.Botter-Jensen)
- Nice University, France (Dr. M. Benabdelsalam).

At present the active scientific cooperation is developed with

- Sun Yat Sen University, Taiwan (Prof. Dr. Mitch Chou and Prof. Dr. Liuwen Chang)
- Center for physical Sciences and Technology, Semiconductor Optics Laboratory, Vilnius, Lithuania Dr. R. Nedzinskas and S. Tumenas).
- Technological group of Riga Technical University (Dr. J. Grabis)
- Company Freiberg Instruments, Freiberg, Germany (Dr. M. Richter).

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UTILISING UP-CONVERSION LUMINESCENCE PROPERTIES IN NANOPARTICLES FOR VARIOUS APPLICATIONS

STATE OF THE ART.

Up-conversion (UC) luminescence is a process where in rare earth doped materials visible and even ultraviolet luminescence is emitted after incoherently absorbing multiple infrared photons [1]. Up-conversion luminescence in macro materials can be utilised in many areas like: light sources, temperature sensors, laser beam indicator cards etc. Transiting from macro materials to nanomaterials allows to expand UC luminescence application possibilities.

It is well-known that plain or core-shell structured nanoparticles exhibit UC luminescence and core shell nanoparticles often show greater efficiency of UC process. Synthesis recipes can be found in many scientific reports [2-4]. Such synthesised nanoparticles can be later used for various applications like: in cancer medicine, cell biology, temperatures sensors, photolithography, "invisible ink" [5, 6] etc.

Preparation of active microstructures from photoresist/chromophore systems would benefit in cost-efficient device fabrication. Unfortunately, most organic chromophores absorb almost all of the blue light used for photolithography at the surface of the thin film and there is no light interaction with photoresist within the whole thin film. This drawback could be overcome by adding photoactive nanoparticles in photoresist exhibiting UC luminescence. Such nanoparticles absorb infrared light and emit blue light within the film. Depending on the needs different structures are possible to prepare.

Other perspective area for utilising UC luminescence in nanoparticles is related to "invisible ink" as additional security element in money, passports, ID cards or other documents. In nowadays it is standard to use "invisible ink" that exhibit visible luminescence under ultraviolet excitation as security element. Adding additional layer of "invisible ink" that exhibit UC luminescence only under excitation with infrared light allows creating an additional security level.

OUR POSITION

Laboratory of Spectroscopy has acquired great experience of studying UC luminescence process in various materials: polycrystalline macro powder, glass ceramics [7, 8]. Our recent research and efforts have been focused on studying UC luminescence process in rare earth doped nanomaterials. Utilising UC luminescence properties in nanomaterials creates new opportunities for various application.

Our experience with various experimental techniques in ISSP UL (UP luminescence, photolithography, etc.) allows to start new research area that combines previous obtained experience. At the moment nanoparticle synthesis setup is being updated to achieve more controlled synthesis process and to improve repeatability. First experiments of UC photolithography in photoresist/nanoparticles composite material show promising results. Further actions are related to build more sophisticated experimental setup for UC photolithography, and further development of nanoparticles synthesis process.

For such a complicated research area a strong team of scientists is needed. Therefore, an appropriate scientific team of young and experienced researchers is gathered together from three laboratories: Laboratory of Spectroscopy, Laboratory of Organic materials and Laboratory of Chemical Technologies.

FUTURE ACTIVITIES

- Synthesis of nanoparticles with appropriate spectroscopic properties.
- Research and analysing on nanoparticle compositions with, for example, photoresists: spectroscopic properties, agglomerations etc.
- Doped photoresist mixing with organic materials and performing photolithography
- Development of experimental setup and methodology for photolithography under 975 nm excitation.
- Investigation of possible use of nanoparticles for "invisible" ink applications.

NETWORKING

This new research direction come from inside of the ISSP UL where three laboratories combine the strength of their scientific expertises to achieve common goal. Search of new partners (scientific and enterprise-level) and demonstrating them the abilities and the competences of ISSP UL is ongoing. Greater milestones could be related to finding new local industrial companies and/or international cooperation for the projects like Horizon Europe, ERA-NET, etc.

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PERSISTENT LUMINESCENCE MECHANISMS AND APPLICATIONS IN WIDE BANDGAP MATERIALS

STATE OF THE ART

Persistent luminescence (PersL) – light emission lasting from seconds to many hours after ceasing of excitation source, is observable in inorganic solid-state wide bandgap materials. Use of the PersL materials is covering different areas such as applications in displays, luminous paints, safety signs, glow-in-the-dark decorations etc. Presently the interest about the PersL materials is much increased due to its application in biomedicine for testing of the biological processes in tissues and organs of living organisms.

At present, the materials emitting PersL from green and yellow spectral regions are the best investigated, whereas there are considerably less information on the blue and especially, the red light emitters, where the latter are essential for biomedical applications. Development of new prospective PersL materials is actual and there are numerous studies in this field (see papers [1-3] and references therein). Among the main problems are elaboration of new materials and undestanding the PersL mechanisms, which would help to increasae the Persl intensity and to obtain the desired emission wavelength range.

OUR POSITION

Researchers of the Laboratory of Spectroscopy in ISSP UL have detailed knowledge, long experience and appropriate equipment for spectral characterization of various luminescent materials (e.g., refs. [4-9]). The group is well-qualified in optical and magnetic spectroscopies as well as material synthesis.

FUTURE ACTIVITIES

The proposed research includes synthesis and studies of luminescence properties and mechanisms in two groups of materials. (I) Transition metal ion- and rare earth ion-doped PersL oxides belonging to alkaline earth silicates, germanates and stannates; (II) IIIrd element group nitrides doped with the same type ions. This second group of materials includes AlN nanoparticles (AlN NP) doped with ions of transition metals and rare-earth elements. These nano materials are prospective for biomedical applications.

The following activities are foreseen:

- Processing of the materials. It includes elaborating the synthesis methods of the first group oxide materials and their synthesis. Doped AlN NP belonging to the second group materials will be synthesized by activation of commercial AlN nano-powders.
- Analysis of the structure, morphology and defect content of the new materials.
- Investigation of spectral and temporal luminescence characteristics of PersL oxides and AlN NP materials.
- Investigation of the afterglow of photo- and X-ray excited materials, which directly characterizes the PersL properties.
- Special emphasis will be paid on the structural studies of the luminescence and carrier trapping centres using electron paramagnetic resonance (EPR) methods.
- Analysis of results ensuring close feedback between the material optical properties and its processing.

NETWORKING

The group has active domestic and international collaborations with research and commerce groups in:

- Latvia. Riga Technical University, Latvia. Dr. J. Grabis. Research collaboration, agreement on production of doped AlN nanopowders, mutual publications.
- Estonia. Dr. Arvi Freiberg. University of Tartu, Estonia. Material spectral characterization.
- France. Dr. Cr. Ramseyer. Universite de Bourgogne-Franche-Comte, Besancon, France. Luminescent nanomaterials applicable in biomedicine.
- Ukraine. Dr. Galina Dovbeshko. National Academy of Sciences of Ukraine, Institute of Physics, Department of Physics and Biological Systems. Luminescent nanomaterials applicable in biomedicine.

- Latvia. SME Lumini-Nights, Riga, Latvia. Elaboration and research of red light shining PersL coatings for metallic objects.

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MATERIALS FOR ENERGY HARVESTING AND STORAGE

MATERIALS FOR BATTERIES

STATE OF THE ART

European Long-Term Climate Strategy aims for European Union (EU) to be climate-neutral by 2050. Batteries play an important role in providing decarbonization of EU economy and enabling sustainable electrification, both for the transport sectors and grid-scale energy storage [1–3].

Current state-of-the-art batteries are largely based on lithium-ion chemistry, but the demand for higher energy density and performance requires short- to medium-term improvements, together with more radical changes towards a new generation of post-Li-ion batteries based on new advanced materials [4].

Development of lithium-ion batteries (LIB) has come a long way since their first implementation in 1991, with LIB gravimetric energy density more than doubling [5], the research and development of LIBs is ongoing. We are currently approaching widespread use of what is called generation 3b of

LIBs [6], with Nickel-Cobalt-Manganese (NCM) ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, proportion of nickel increasing over time from NCM 111 to NCM 811 and beyond) cathode in most advanced batteries along with Si-supplemented graphite anode and liquid electrolyte. Subsequent developments are widely believed to be related to high energy NCM or high voltage spinel (HVS), with first commercial Li/S and Li/O_2 technologies appearing within the next 10 years [6].

Other emerging battery types are Na-ion, Mg-ion, Ca-ion, Al-ion, metal-sulphur, anion shuttle, metal-air, semi-solid flow and redox-flow batteries. Out of these, Na-ion battery technology is the most mature and has high potential for further growth, especially when considering the increasing needs for stationary energy storage [7]. With sodium being the 6th most abundant element in Earth's crust, the raw material costs are expected to be significantly lower. Moreover, the high rate capability, stability and recyclability of sodium-ion batteries (SIBs) are considered to be very attractive [8]. However, cycle life, energy density and rate capability still need to be improved [9]. This can be done by both optimizing the existing materials and developing new ones – the latter strategy along with developing fundamental understanding of the solid-state electrochemistry of Na intercalation is often considered to be the more efficient approach [10].

For SIBs specifically, traditional liquid electrolytes produce solid electrolyte interphases (SEIs) that are often not sufficiently stable and are likely to cause severe polarization [11]. This along with decreased fire hazard has spun new ventures into developing ionic liquid (IL) -based electrolytes for SIBs. A new class of materials is created when ionic liquid (IL) molecules are integrated into polymer chains. These are called polymeric ionic liquids (PILs) and provide an added benefit of mechanical and design flexibility and of the possibility to be fabricated into desired thickness and shapes, albeit at a cost of decreased ionic conductivity [12]. A mixture of PIL and sodium salts can be classified as solid polymer electrolyte (SPE) [12].

Currently most of the applied research is focused on developing new materials and improving specific power and energy densities of existing materials [13,14] as well as evaluating cycle life (service life) of battery electrodes, cells and modules [15–18]. Developing of solid state and polymer electrolytes is also a recent topic of interest. On a the fundamental level, characterizing mass transport and related electrochemical reactions on a nanoscale is recently receiving increased attention from scientific community [19,20], and further improvements in materials is expected at least in part to stem form a deeper understanding of these issues.

OUR POSITION

Development of electrodes and electrolytes for Li-ion and Na-ion batteries

Mix between applied and fundamental research:

- Electrode development current focused on $LiFePO_4$, reduced graphene oxide, other carbon nanostructures, transition metal oxides [14,21–23], polyanionic compounds ($Na_2MP_2O_7$ and Na transition metal oxides $NaMO_2$ (M – Fe, Mn)), spinel-type Na_2MO_3, Na_2MO_3-$NaMO_2$ (M = Mn, Ru, Ir, etc.).
- Electrolyte research focuses on advanced polymer – ionic liquid composites sodium-ion electrolytes [24, 25].

Cycling stability of Li-ion battery materials and cells

Mix between applied and fundamental research:

- Structural and compositional changes of electrodes as a function of cycling;
- SEI as a function of cycling and cell composition;
- Electrochemical and structural analysis techniques for fast cycle life estimation;

- *In-situ* and *in-operando* characterization of battery materials for assessing ageing mechanisms in lithium and sodium ion batteries;

This is highly relevant problem for industry and also good grounds for subsequent more fundamentally directed research.

Mass transport within electrodes and across interfaces

Fundamentally oriented research:

- Lithium and sodium transport within electrodes (ionic and electronic conductivity, transport mechanisms);
- SEI stability and ionic transport across SEI;
- Thin film deposition as means of characterizing mass transport and forming artificial interfaces.

FUTURE ACTIVITIES

Our key competitive advantage will be *in-situ* and *in-operando* characterization techniques of battery materials, currently in development. Besides that, we aim that good knowledge in battery ageing characterization will be our second key advantage. Along with this, a significant investment in technological capabilities is needed:

- Electrode materials for Li and Na-ion materials. Cathodes – $NaMP_2O_7$, layered oxides, Na-rich and Li-rich layered oxides; anodes – metal oxides, 2-dimensional carbon structures; electrolytes – development of solid-state electrolytes using thin film technology, ionic liquids, polymer-ionic liquid composites; nanostructured and high-surface area additives (e.g. carbon-based additives – graphene, few-layer graphite, etc.).

- *Battery cycle life*. Development of measurement techniques: electrochemical measurements as a function of structure/composition and their changes, ventures into big-data and machine-learning techniques for data processing and statistical analysis.

- *Interfaces and mass transport.* Solid-electrolyte interphases and interphases within electrodes as a function of composition, structure, and cycling history. Mass transport within ionic and mixed ionic/electronic conductors and across interfaces, characterized by standard techniques as well as *in-situ* and *in-operando* measurements.

- *Services to industry*. Electrochemical characterization, prototype assembly (coin-cells, pouch-cells C < 0.1 Ah), cycle life analysis, consulting.

Material development is a general research topic that enables us to: a) build internal collaborations with fellow research groups strong in materials synthesis and; b) get publishable results relatively quickly in comparison with more fundamental research directions. The potential scientific impact of this research, however, is relatively low.

In order to increase our scientific impact, we plan to devote part of the work to interfaces and mass transport in battery materials. This is a purely fundamental research direction that allows building deeper insights into how battery materials function.

Recently, techniques based on processing large amounts of data (machine-learning, AI, big data, etc.) have been demonstrated to be of good use in predicting cycle life and future performance of battery cells. We are venturing in this territory with a national 3-year project starting in 2021 and another submitted project proposal together with a machine-learning expert from University of Latvia and a commercial partner manufacturing electric vehicles.

In terms of laboratory equipment, in the coming years the material treatment technologies (vacuum and other drying processes, sintering, inert gas environment and environment excluding water and oxygen in a glove-box) as well as the characterization unit will be finalized, involving thermal analysis of materials coupled with a gas chromatography, the mass-spectrometry and IR spectrometry, pyrolysis equipment. Such combination will be unique in Latvia and will, firstly, help us develop strong research in the aforementioned research directions and, secondly, can attract the interest of academia and industry from Latvia and neighbouring countries.

NETWORKING

- Max Planck Institute for Solid State Research (Germany), prof. J. Maier: specialized in solid state ionics, defect chemistry and related fundamental research fields;
- Institute for Energy Research / University of Oslo (Norway), A. Koposov: development of battery materials, cells and battery modules, largest battery testing facilities in Norway;
- Norwegian University of Science and Technology (Norway), Prof. A. Svensson: development of Li-ion battery electrode materials and electrolytes;
- Vilnius University, Faculty of physics (Lithuania), Tomas Salkus' and Linas Vilciauskas' research groups: specialization in Broadband High Temperature Impedance Spectroscopy of ionic and mixed ionic-electronic conductors;
- University of Tartu – Taivo Raud, Kaido Tammeveski on metal-organic synthesis of catalysts;
- State Research Iinstitute Center for Physical Sciences and Technology (Vilnius) –Gintaras Valušis, Rasa Pauliukaitė on sensors and fuel cells, graphene based electrodes;
- University of Iceland – Jón Atli Benediktsson, Egill Skúlason on catalysts.

Local academia:

- Latvian State Institute of Wood Chemistry, G.Dobele, A.Volperts: wood-based materials (combusted carbon structures) as materials for Li-ion batteries and supercapacitors.
- Institute of Chemical Physics, University of Latvia, D. Erts, R. Meija: carbon-based nanostructures for application in batteries and other energy harvesting devices.
- Institute of Solid State Physics, University of Latvia, Theory group (see Section "Theoretical material science and modelling" in this document).
- University of Latvia Faculty of Physics and Mathematics – Dr.phys. Guntars Kitenbergs on magnetic and other nanoparticles.
- University of Latvia Faculty of Chemistry – Prof. Andris Zicmanis on ionic liquid synthesis, tritium diffusion in a graphene membranes and separation from proton using fuel cell technology.

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HYDROGEN ENERGY

STATE OF THE ART

European Long-Term Climate Strategy aims for European Union (EU) to be climate-neutral by 2050. It identifies renewable energy harvesting and storage as its cornerstones. Along with a rapid growth of EU's electric vehicle fleet, hydrogen is also an essential element in the energy transition and can account for 24% of final energy demand and 5.4m jobs by 2050 [1].

The main industrial hydrogen production processes are electrolysis and thermolysis, but technology to obtain biohydrogen from biomass by fermentation is under development. For hydrogen technologies new materials are needed, e.g. effective, stable and cheap catalysts to replace precious metals as platinum in water electrolysis, in microbial and proton exchange membrane fuel cells, and in storage (hydrogen bonding in solids or on the surface) [2]. Potential substitute for Pt and noble metals in electrocatalytic electrodes could be substituted by N-doped nanostructured carbon (graphene, etc.) [3].

Energy harvesting with the lowest environmental impact is another key element for cleaner future. Out of a wide variety of methods to combat pollution, the catalytic reduction of pollutants is considered as prominent one. Electrocatalytic CO_2 reduction into hydrocarbons such as methane or ethylene and photocatalytic CO_2 reformation can lower carbon footprint and pollution; both technologies are considered as prominent methods. Thus, extensive research of CO_2 reformation is being done to find the right materials that hold crucial properties and qualities [4]. Recent research in CO_2 reformation has shown that high faradic efficiency (FE) can be achieved by doping Cu with I, Br, Cl with FE maximum of 72.6%, pointing to the necessity of further modification of electrode material [5]. Investigation of various dopants and cell designs for CO_2 reduction is being researched. Not only the FE has to be improved, but also the stability of electrode, addition of N-G could improve lifetime and efficiency in combination of base electrode doping.

Photocatalytic hydrogen production, as well as pollution treatments such as wastewater treatment, antibacterial surfaces and gas treatments, can be viable solution for remote locations and for long term passive component in the cycle. In case of hydrogen production in light-induced water splitting process recent results reported as 9.8 $\mu mol \cdot mg^{-1}h^{-1}$ on Pt-TiO_2 [6]. Investigation and improvement of efficiency and composition of electrode for example by production of ternary systems increasing charge carrier separation and sensitivity to visible light region must be performed.

OUR POSITION

System Integration for Hydrogen Energy

- Collaboration with energy production companies for local implementation of hydrogen as grid balancing and off grid solutions
- Assessment of Latvian (and Baltic) resources for hydrogen technologies and implementation prospect – preparation of legislative suggestions.

Material development and investigation

- Carbon materials for hydrogen generation and catalytic reactions

  Carbon materials have proven to be versatile for various energy applications. Recently, we have obtained a few-layer graphene sheet stack powder via electrochemical pulse exfoliation of graphite [7]. This is a versatile material not only for gas sensing, battery, and supercapacitor applications, but also for electrolysis of water (hydrogen generation) and other catalytic reactions involving hydrogen.

- Investigation of advanced nanomaterials for hydrogen production: experimental and computational studies

  Hydrogen production becomes more important, as the renewable energy produced needs to be stored sustainably. We plan to keep developing both carbon materials as well as metal oxides [8] and carbon-metal composites [9].

FUTURE ACTIVITIES

Development of new materials and techniques for hydrogen production, storage, transport and use:

- H_2, CO_2 solid state storage materials – near RT applicable materials, no cryogenics. Increase of capacity and applicability estimation;
- Material retrofitting for hydrogen energy in large scale systems – theoretical and experimental leak test studies;
- Improvements in reduction efficiency. Development of materials and composites and techniques for reducing air pollution (CO_2, organic molecules, etc.) in electro- and photo-catalytic processes.

Carbon-based catalysts:

- Carbon-based catalysts as the actual active component and as a matrix. Further investigation of noble metal as Pt substitution as catalyst;
- Materials for hydrogen sensing – graphene-based, resistive, frequency scanning or photonic sensors.

  Carbon based material use in energy harvesting and storage is a promising field due to the wide use of Pt group metals. It is not yet clear would graphene be applicable to high or low temperature fuel cells best, but the possibility to replace Pt in PEM has been briefly tested within students' scientific work and has shown a promising basis for testing of larger sample batch. This would be a good field for a bachelor’s/master's thesis.

  Defective single layer graphene has been shown to be a good and sensitive H_2 sensor, which could replace Pt in sensing needs. Currently graphene isn’t selective to be standalone H_2 sensor however introduction of defects, surface doping and combination of AC resistive behaviour can lead to H_2 or pollutant sensor.

Computer simulation on discharging, refuelling and transporting natural gas and hydrogen via pipelines:

> Discharging and refuelling gas cylinders of large volume is characterized by temperature changes of the gas that, in turn, heats up or cools down cylinder and valve bodies. For a lot of cases thermodynamical computer simulations provide useful results, allowing to predict and to avoid overheating or freezing in inspected nodes. Regarding the gas blending transport via pipelines, the computer simulation accounts for laminar, turbulent and mixed regimes. The preferable software is Matlab (including Matlab Simulink) and Solid Works with its various add-ins. For some special computer simulation tasks the use of Comsol Multiphysics is considered. Besides that, with the given software the storage of gas blendings in a porous media and aquifers can be modelled.

Our key competences and capabilities are synthesis, thin film deposition, gas analysis and electrochemical characterization of materials. 17+ channels available for electrical characterization, gas adsorption, mass spectroscopy and gas chromatography equipment are also available. Equipment available at ISSP UL essential but not exclusive to this research direction include XRD, SEM-FIB, TEM, Raman spectroscopy, FTIR, XPS.

We are open to industrial collaborations in material characterization and prototype assembly. This includes developing materials for energy harvesting, storage, and use, such as fuel cells (primarily hydrogen), H_2 electrolysis – two-electrode (in various setups) and membrane electrolyzers and models demonstrating electrolysis.

NETWORKING

- Vilnius University, Faculty of physics (Lithuania), Tomas Salkus' and Linas Vilciauskas' research groups: specialization in Broadband High Temperature Impedance Spectroscopy of ionic and mixed ionic-electronic conductors
- Laboratory of Hydrogen Technologies and Materials of Lithuanian Institute of Energy, Laboratory of Hydrogen materials, Šarunas Varnagiris
- Latvian State Institute of Wood Chemistry, G.Dobele, A.Volperts: wood-based high surface area materials (combusted carbon structures) as materials for catalytic reactions

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THERMOELECTRICS AND HYBRID PHOTOVOLTAICS

STATE OF THE ART

The use of renewable resources and the use of smarter and more efficient devices are key principles in tackling the energy crisis.

Wasted heat is a potentially large source of energy that has not been fully utilized. It is estimated that mankind wastes ~ 20% of the 15 terawatts required annually for global power consumption as low-level heat (<200°C). The wasted energy could be harvested by thermoelectric generators (TEG) which directly converts heat into electricity. With effective TEG, a number of problems are addressed at a time: the wasted heat for electricity generation is used reducing global warming and dealing with the energy crisis. The identification of these conditions has stimulated extensive studies in the field of thermoelectric materials, including organic materials [1-5]. In low temperature range organic materials are able to show equivalent and better properties compared to classically used inorganic materials [6, 7].

Solar energy is a second source of energy, the more efficient use of which can help solve today's energy crisis and challenges. The use of organic materials has the potential to create lighter, flexible and more efficient solar cells for widespread use of them. Great attention is paid to hybrid organic-inorganic material perovskite solar cells [8–13]. In combination with thermoelectricity solar cells could show very high efficiency reaching more than 23% [14]. Organic solar cells (OSCs) based on fullerene acceptors demonstrated significant growth over the past two decades with power conversion efficiencies (PCE) exceeding 13%. But it has reached its theoretical maximum. New generation of OSC has been proposed where fullerene is substituted with other organic compounds as electron acceptor. Such electron acceptors has it specific name – non-fullerene (NF) acceptor. The advent of non-fullerene acceptors with superior optoelectronic properties, tuneable morphology, and absorption characteristics, have resulted in a scenario where the NF OSCs have demonstrated higher PCE of over 14% in single junction and over 17% in tandem OSCs incorporating NF OSCs which is relatively higher than conventional fullerene-based counterparts.

Novel devices for sensor application, like thermoelectricity based radiation sensors and novel hybrid organic-inorganic X-ray detectors could reduce the consumed energies in related application, due to lower working voltages and more effective sensitivity and detection process [15–22]. Current X-ray detector sensitivities are limited by the bulk X-ray attenuation of the materials and consequently necessitate thick crystals (~1mm–1 cm), resulting in high operational voltages and rigid structures. The development of new radiation detectors, in particular, based on nanomaterials[18], is an active field of research. In the last two decades, organic semiconductors have received increasing attention for thin film photovoltaics, optical sensing and recently been proposed also for Xray detection as promising alternatives to inorganic semiconductors [23,24]. They are relatively inexpensive and easy to produce, can be flexible, operated under low voltage (<10V)[25], may have a large area, and demonstrate promising sensing properties, despite their lower carrier mobility and low X-ray radiation absorption coefficient compared to inorganic semiconductors[23]. In order to improve the absorption of X-rays in thin films, recently active study has been carried out on hybrid cells in which inorganic high-Z nanomaterials are placed in a flexible matrix of organic materials. Therefore, organic materials in combination with high-Z nanomaterials have high potential to be employed for radiation detection purposes, allowing unprecedented devices architectures and functionality[16, 22]. The X-ray detectors can be divided into two types: (i) *direct*, which convert incident X-ray photon into current, and (ii) *indirect*, which convert X-ray photon into visible photons further detected by a photodetector. Both types of detectors could be realized by using hybrid organic-inorganic systems, moreover superior properties could be developed, such as flexibility, lightweight, increase sensitivity and registration rate [15–20, 22, 35].

OUR POSITION

Laboratory of Organic Materials is the main place in Latvia with all necessary equipment and competence to produce and investigated organic thin film devices. Laboratory has long time experience in investigation of electrical properties of organic materials which is essential in applications such as thermoelectricity and organic solar cells and also sensor application. In recent years, experience in device prototyping has also been actively developed and accumulated.

Electrical properties and charge carrier transport play a key role in the organic electronics, so their research is the basis. Therefore, laboratory pays great attention to the investigation of energy structure and electrical properties of organic semiconductors. Energy levels of the compounds have been studied by photoelectron emission spectroscopy (PES) and spectral dependence of intrinsic photoconductivity [26–28]. It gives information about molecule ionization energy (IE) and the second method gives a good estimation of the energy bandgap between IE and electron affinity (EA) energy. Local trap states in the bandgap have been investigated by temperature modulated space charge limit current method. Charge carrier mobility has been obtained by Time of Flight (ToF) or Charge Carrier Extraction by Linearly Increasing Voltage (CELIV) techniques [29]. In Laboratory of Organic Materials full spectra of thermoelectric properties could be investigated, including Seebeck coefficient measurements in a lab-made Seebeck measurement unit, thermal conductivity measurements by 3ω technique and electrical conductivity measurements by 4 probe method [30], [31]. In the future, the measurement of thermal conductivity in thin films will be improved, achieving the possibility to determine the thermal conductivity in different directions in a thin layer [32].

Flexible organic−inorganic hybrids are promising thermoelectric materials to recycle waste heat in versatile formats [1–3, 33]. Besides, thermoelectric effect can be used to create light sensors. For example, thermopile detectors have long been known. Using thin films of organic materials with unique properties, prototypes of thermoelectric radiation sensors with superior properties such are created, achieving broad spectral range as thermopiles and high-speed performance as photodiode.

Recently laboratory has started investigation of hybrid system organic-inorganic X-ray photo-detectors [34].

FUTURE ACTIVITIES

Further development of energy harvesting device field will be divided in two parts. One will be performed in close collaboration with chemists from other academic institutions. Second is related to investigation of the energy conversation system in relation to the morphology.

Research into new original compounds in collaboration with chemists may open possibilities to discover new origin materials with superior properties and create high-efficiency devices from them.

By continuing to study previously investigated materials and exploring the effect of morphology on energy conversion, it is possible to optimize the properties of thin films made from these materials, thus opening the possibility to create devices with higher efficiency.

Future directions:

- Investigation of organic-inorganic nanoparticle hybrid systems thin films.

One of the first and main further steps is the high-quality incorporation of inorganic nanoparticles into organic material systems. Achieving a homogeneous distribution of nanoparticles in the thin film is a key for successful further development of a hybrid system X-ray detector and organic -inorganic hybrid system thin films for thermoelectricity and solar cells.

In order to create efficient organic and hybrid electronic devices, such as a TEGs, OSCs or light or X-ray radiation sensors, it is necessary to know the charge carrier transport and energy levels in solids. This is particularly important in hybrid systems, where charge carrier transport can be hampered by trap levels that result indirectly from structural defects and due to incompatibility of energy levels of systems components. Up to now, the most of the necessary investigation methods that includes UPS, XPS, PYS I-V-L curve measurement, TM-SCLC, AFM, SEM, thin film thickness and profile measurements and available at the Institute. One of the most important parameters for OSCs and sensors are charge carrier mobility and recombination process. Charge extraction with linearly increasing voltage (CELIV) is suitable for studies of both processes. The method is valid for thin films and can be used to investigate charge carrier recombination and determinate charge carrier mobility. Thermal conductivity is one of the key parameters to determine figure of merit ZT for thermoelectric materials, however measurements for thin film is complicated. 3W method will be developed and established for thermal conductivity measurements in thin films. Fully established method gives opportunity to measure thermal conductivity in both directions of thin films – laterally and to the normal. A system for X-ray detector research will also be set up. The system includes an X-ray lamp with all safety measures, as well as a part for reading electrical signals from samples.

- Development of hybrid system X-ray detector.

The X-ray detectors can be divided into two types: (i) direct, which convert incident X-ray photon into current, and (ii) indirect, which convert X-ray photon into visible photons further detected by a photodetector.

The direct conversion of ionizing radiation into an electrical signal within the same device is usually a more effective process than the indirect one, since it improves the signal-to-noise ratio and reduces the device response time. Both types of detectors could be realised by using hybrid organic-inorganic systems, moreover superior properties could be developed, such as flexibility, lightweight, increase sensitivity and registration rate. While the low atomic number (Z) of the component atoms in the organic (typically C and H with O, N or S) make them almost transparent to X-rays, high-Z nanoparticles offer high cross-sectional area for X-ray interaction, thus enhance the absorption efficiency and sensitivity and hopefully retain the advantageous physical properties of the host polymer, such as mechanical flexibility.

- Development of organic -inorganic hybrid system thin films for thermoelectricity.

Good thermoelectric material should exhibit low thermal and high electrical conductivity. Organic material has low heat conductivity but at the same time it also has low electrical conductivity. Hybrid organic-inorganic materials have been considered as a new candidate in the field of thermoelectric materials from the last decade due to their great potential to enhance the thermoelectric performance by utilizing the low thermal conductivity and high Seebeck coefficient of organic materials, and high electrical conductivity of inorganic materials. However, current organic/inorganic hybrids suffer from inferior thermoelectric properties due to aggregate nanostructures. To overcome this issue high-quality incorporation of inorganic nanoparticles must be achieved. Incorporation of thermoelectric active inorganic nanoparticles or low dimension carbon structures, such as carbon nanotubes or graphene, in the matrix of organic materials could increase the electrical conductivity and Seebeck coefficient of the system, meanwhile reducing thermal conductivity, realising "phonon-glass, electron-crystal" principle resulting with higher Figure of Merit ZT values. The alternative approach to overcome this issue is to define the localisation of inorganic nanoparticles by lithography methods [1–3, 36–39]. Polymer nanowires prepared by electro-spun method in combination with inorganic nanoparticles could be the first approach for preparation of hybrid thermoelectric systems.

- Investigations of electro-spun polymer-based nanowires.

Nanowires or nanofibers could be of a great use in high sensitivity sensors and nanoscale electronic devices due to their high surface to volume ratio, tuneable characteristics and mechanics behaviour. Electrospinning has been identified as a straightforward and viable technique to produce nanofibers from polymer solution as their initial precursor. These nanofiber materials have attracted attention of researchers due to their enhanced and exceptional nano-structural characteristics [40–45]

- Development of non-fullerene organic solar cells.

A new non-fullerene acceptor for organic solar cells will be investigated. The best and most appropriate donor compounds will be selected based on the original acceptors studied previously. The OSC will be optimized for the best performance.

- Development of Thermoelectric generators (TEGs) and OSCs on flexible substrate.

Organic material-based thin film deposition on flexible substrate by making flexible devices is one of the biggest advantages of organic materials. Nevertheless, several issues should be addressed before it is possible to deposit a multilayer system on the flexible substrate. Structuring of electrodes should be mostly done by lithography method. Thermal deposition of compounds should be done in low temperatures. The thermal properties of flexible substrate should be considered during thermal treatment of the layers. Investigation of bending radius and cycles should be performed.

Prototypes of investigated systems will be made to confirm commercial potential of the devices.

NETWORKING

Latvia:

- Institute of Organic Synthesis
- Riga Technical University, Institute of Applied Chemistry, Prof. Valdis Kokars, Dr. habil. chem. Valdis Kampars
- Research Laboratory of Functional Materials Technologies, Dr. sc.ing. Andris Šutka,
- Institute of Technology of Organic Chemistry, Prof. Dr. chem. Māris Turks
- Daugavpils University, Institute of Life Sciences and Technologies:
    - Department of Technology, Prof. Dr. phys. Edmunds Tamanis
    - Department of Applied Chemistry

Europe:

- Kaunas University of Technology
- Vilnius University
- Julius-Maximilians-Universitat Wurzburg, Experimental Physics vi, Pflaum group, Prof. Dr. Jens Pflaum, https://www.physik.uni-wuerzburg.de/ep6/pflaum-group/
- The University of Nottingham, School of Chemistry, GSK Carbon Neutral Laboratories for Sustainable Chemistry, The Woodward Selective Synthesis Group, Dr. Simon Woodward
- Institute of Organic Chemistry with Centre of Phytochemistry - Bulgarian Academy of Sciences, Dr. Vladimir Dimitrov

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FERROELECTRIC MATERIALS FOR ELECTROMECHANICAL AND ELECTROCALORIC APPLICATION

STATE OF THE ART

Ferroelectric materials are an integral part of the modern technological world.

Lead zirconate titanate (PZT)-based solid solutions presently dominate in applications of ferroelectric materials, as they exhibit excellent electromechanical properties. However, use of lead-containing materials is being limited during the last decades due to environmental and health considerations, which are regulated by RoHS directive of the European Union. Scientific society is stimulated for research of alternative lead-free ferroelectrics.

For that reason, intensive efforts are devoted to studies of lead-free ferroelectrics [1]. One of the most promising lead-free compositions is $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and different solid solutions based on it. There are discovered NBT-based solid solutions with improved electromechanical properties, already able to compete with PZT-based ferroelectrics. It is shown that for some specific applications NBT and its solid solutions are even more suitable than PZT, for example, in ultrasound transducers [2].

<u>Technological aspects</u>

Despite the intense research of modification of properties of NBT-based compositions and wide discussion on possible applications of these materials, the development of their production technology is left without appropriate attention. At the same time, a lot of discrepancies appear in literature regarding various experimentally measured parameters for the same NBT-based compositions, therefore reducing the quality of interpretation of such results. It is obvious that properties of these materials depend on the production process, and it is impossible to implement them in manufacturing without clarifying the relation between their production parameters and properties.

In respect of development of production technology, the following experimental findings should be taken into account:

- *Stoichiometry in NBT composition*. As Bi is volatile, in order to improve quality of the ceramic material, it is reasonable to produce Bi-excess compositions. Results obtained in [3] indicate that this dramatically influences conduction mechanisms in NBT and reveal that, in such a way, it is possible to tune properties of NBT ceramics to suppress leakage conductivity for piezoelectric and high temperature capacitor applications. Surprisingly, a measurable deviation of Bi concentration from stoichiometric was not found;

- *Grain growth mechanisms.* In the case of NBT and NBT-based solid solutions, anomalous grain growth (AGG) is a common mechanism for grain growth, wherein only a small fraction of grains grow rapidly and the microstructure is characterized by a bimodal grain size distribution. AGG occurs in systems with faceted (atomically ordered) grain boundaries and is controlled by interface reactions and diffusion [4]. In [5] it was shown that in particular case of NBT, excess Bi, as well as two-step sintering and hot pressing during the production process are effective inhibitors of abnormal grain growth;

- *Stability of ferroelectric state in dependence on grain size.* The role of nonstoichiometry on depolarisation temperature is demonstrated [6]. According to recent suggestions, the nonstoichiometry has only indirect role through its influence on grain size [7]. In rather specific composition, NBT-ST-PT, relevant role of grain size on domain structure is also observed [8].

<u>Electrocaloric effect.</u>

Electrocaloric affect (ECE) is of great interest for designing active cooling elements, especially in micro- and power-electronics, environmentally friendly air-conditioning and cooling systems. Unfortunately, the prospects of practical realization of such idea were unclear for a long time, due to the limited values of temperature change ΔT, especially in the temperature range actual for cooling devices.

The situation has significantly changed with the first publications, where ECE in thin films was evaluated by the Maxwell relation or indirect method [9]. Intensive studies, inspired by these pioneering works, revealed compositions with extremely large ΔT range, where the upper limit reaches even 45°C (the latest review in [10]). In spite of more than ten years of intensive research, attempts to create working cooling prototypes are scarce. Moreover, even a general picture of the perspective for application of particular FE compositions does not exist. There are several reasons for that:

- Wide scattering or even contradictions in the results, mostly obtained by the indirect method, which, at the same time, is the dominating method in determining of ECE;

- The most promising results are obtained in thin films, which are complicated to apply due to low heat capacity;

- Insufficient understanding of the nature of ECE and polarization in high electric field E values range.

Application of Maxwell relations requests clear understanding of the nature of measured polarization, since they are applicable only for temperature dependence of homogeneous intrinsic polarization.

This requirement is usually left without attention, which leads to unconvincing results, where not only the value, but even the sign of the calculated Δ*T* is disputable [11].

Therefore, looking for materials, which could be promising for application in cooling devices and to get reliable results, at the present stage of research direct measurements at high fields on bulk samples and thick films are very important. As it follows from the values of *Δ*T available from publications and corresponding to such requirements:

- High-*E* is a relevant condition to expect high *ΔT* values;
- Among the studied compositions, Ba(Ti,Zr)O_3 solid solutions in the concentration range of morphotropic phase boundary, where all three FE phases merge together, look the most promising (T up to 6^{o}C at E=150 kV/cm [12]);
- Available results are very limited and contain remarkable scattering of Δ*T* values for the same or similar compositions.

Cooling efficiency is dependent on heat capacity and therefore from the volume of the working body of cooling device. At the same time, their thickness should be reduced in order to reduce the voltage of ECE-based working body, maintaining high values of electric field, which are necessary to reach large value of *ΔT*. To satisfy both requirements which are partly contradicting, research should be focused on thick films and multilayers. Just such approach is implemented in [13,14].

Electromechanical properties.

Wide research of electromechanical properties in NBT-based compositions creates impression that competitive with PZT values of piezoelectric coefficients cannot be expected in these lead-free materials. At the same time in some NBT-based compositions sufficiently large mechanical quality factors are found, which are key performance indicators for application of electromechanical properties in resonance mode. Moreover, the values of mechanical quality factors are much less deteriorated at high powers, what is a clear advantage compared to PZT in high ultrasound power applications [2].

One of most widely studied properties of NBT-based compositions is electric field induced strain. Reason of such focusing is possibility with appropriate dopants reduce ferroelectric-nonferroelectric phase transition temperature (depolarisation temperature T_d) in the range of room temperature and below. It allows to implement a field-induced reversible phase transition into ferroelectric state and to utilize the strain, created by this phase transition. Indeed, strains achieved in such a way, exceed 0.6% [15]. Research in this direction is almost completely focused on compositions in concentration range of morphotropic phase boundary (MPB). Taking into account that main reason of large deformations in this case is shifting of depolarisation temperature in the range of room temperature and getting contribution in field induced strain from field induced phase transition, restriction regarding the solid solution concentration range corresponding to MPB does not look convincing. Therefore, range of compositions which could be promising in respect of large field induced strains can be remarkably extended. It is especially important taking into account that in searching of compositions for practical application besides large strains crucial features are limited hysteresis and fatigue resistance.

The first ultrasonic devices based on MEMS technology were able to deliver the acoustic pressure to ambient medium. They were fabricated by combining silicon micromachining and thin piezoelectric films on thin ZnO/Si composite plates. These devices can be considered as the pioneers of piezoelectric micromachined ultrasonic transducers (PMUT) today [16,17]. The advantage of PMUT compared to traditional bulk ceramic and single crystal lead zirconate titanate (PZT) based piezoelectric transducers are higher acoustic coupling coefficients and smaller form factor [7]. The absence of high bias voltage makes PMUT a better candidate for biocompatible and ultrasonic devices than its relative capacitive micromachined ultrasound transducer (CMUT). Attempts to create PMUT, where lead-free ferroelectric materials are applied, are not yet published.

OUR POSITION

The scientific team in the Laboratory of Ferroelectric Materials has wide experience in producing and studies of ferroelectric ceramic materials, including fabrication of ceramic using hot uniaxial pressing. Laboratory has been one of leading research centres in producing and research of transparent $(Pb,La)(Zr,Ti)O_3$ ceramic [19], which was synthesized by wet chemical method and hot pressed at sintering stage. Hot pressing was applied also in sintering of other lead-containing perovskites [19, 20].

During the last decade laboratory is focusing on lead-free, especially NBT-based ferroelectrics. Phase transitions in these compositions, which are still not sufficiently understood, are studied in a number of NBT-based solid solutions including NBT-$BaTiO_3$, NBT-$CaTiO_3$, NBT-$CdTiO_3$ [21-23]. Preliminary results on the role of sintering conditions, nonstoichiometry and dopants on microstructure are also obtained [5].

Laboratory has significant experience in ECE studies as well. The laboratory staff has synthesized and studied $Pb(Zr,Sn,Ti)O_3$ composition with the largest known ECE ΔT value in medium E range [24], has revealed large values of ΔT in $PbSc_{1/2}Nb_{1/2}O_3$ and especially in $PbSc_{1/2}Ta_{1/2}O_3$ [25] and has studied ECE at the 1st order phase transition between the relaxor and FE states in $(Pb,La)(Zr,Ti)O_3$ and $PbMg_{1/3}Nb_{2/3}O_3$. Recently, studies of ECE in NBT-containing solid solutions were performed, again, exceeding ΔT values of 1°C in the medium E range [26]. The studies were also devoted to ECE in pure NBT in medium E range [11].

Three financed projects are running now to contribute in development of planned activities, described in the next part. They are:

Role of manufacturing process on structure and properties of NBT-based solid solutions (2020-2022).
Investigation and optimization of cutting-edge lead-free PMUT platform: from materials to devices (2020-2022).
Development of Lead-Free Ferroelectrics for Application of Electrocaloric Effect (2020-2021).

FUTURE ACTIVITIES

<u>Technology.</u>

Aim: to discover lead-free compositions and develop technology of producing of bulk materials and films of ferroelectric materials to participate in international projects with research centres, oriented on implementation ferroelectric materials in applications:

- Development of sintering at ambient atmosphere, evaluation of microstructure, porosity, deviations from stoichiometry;
- In cooperation with Vilnius University to develop producing of lead-free thick films and multilayers by tape casting. Such approach allows to reduce the driving voltage and is

important for such applications as actuators, electrocaloric cooling etc. Luminescence intensity modulation by electric field - will be also considered;

- Using of hot pressing (HIP, vacuum hot pressing) in sintering of lead-free ceramic. Expected result: optimizing of microstructure, reducing of porosity, improvement of chemical content. Important to improve electromechanical properties (piezoelectric coefficients, electromechanical coupling factor, mechanical quality factor) and increasing of breakdown field level. Later HIP is planned to implement in sintering of thick films and multilayers;

- Mechanical activation of particles to activate chemical reaction and sintering process.

- Lead-free (NBT and BT based) thin films, produced by PLD, for actuator, PMUT applications, luminescence intensity modulation by electric field;

- Microwave (MW) assisted hydrothermal synthesis of NBT to produce NBT nanopowders with different morphology (spherical particles, plates, nanowires). Particles of anisotropic shape are necessary to produce textured films by tape casting.

Application-oriented properties.

Aim: To study ferroelectric properties at high fields, intrinsic and extrinsic contributions in electromechanical properties, requirements for high values of ECE:

- Electromechanical properties - piezoelectric coefficients, electromechanical coupling factor, mechanical quality factor, field-induced strains. Searching of materials with a set of properties appropriate for practical application, including reduced hysteresis, weak dependence on temperature, improved breakdown and fatigue resistance;

- Electrocaloric effect at high fields, achieving values of $\Delta T = 5^{o}C$ and above, paying attention to increasing of breakdown fields and fatigue resistance. Important step will be a transfer from thin plates to thick films, allowing to extend the applied field range. Improvement of electrical breakdown strength and fatigue resistance;

- Modulation of luminescence by electric field in cooperation with Laboratory of spectroscopy;

- Electrical characterisation of thin films, obtained by pulsed laser deposition (PLD).

Fundamental research.

1. Nature of relaxor state in ferroelectrics.
2. Behaviour of ferroelectrics at ultra-high fields. Applicability of Ginsburg-Devonshire theory.

NETWORKING

- Vilnius University, Faculty of Physics, Prof.J.Banys:

  - study of dielectric dispersion, with focus on relaxor state;

  - developing of thick film producing technology by tape casting method.

- University of Duisburg-Essen, Institute for Materials Science and Center for Nanointegration, Dr.V.Shvartsman:

  - AFM, PFM..

- Kirensky Institute of Physics, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia, Prof.I.Flerov:

  - study of thermal properties.
- National Cheng Kung University, Department of Electrical Engineering,Prof. Chih-Hsien Huang:

  - creating of PMUT using lead-free ferroelectrics.
- Fraunhofer institute, Institute of Ceramic technologies and Systems, Germany, Dr.S.Gebhard:

  - creating of prototypes of ECE cooling device.
- Institute of Technical Acoustics, Belarussian Academy of science, Dr.V.Rubanik:

  - to implement optimised technology of manufacturing of ceramic for capacitors.
- Piezoinstitute, the European Institute of Piezoelectric Materials and Devices – hub of European expertise and resources on piezoelectric materials and their applications, (ISSP participates in this organisation), *piezoinstitute.univ-tours.fr*

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ANNEX

SWOT ANALYSIS

Strengths	Weaknesses
ISSP UL shows world-class performance in : • Theoretical material modelling; • X-ray absorption spectroscopy; • Optical spectroscopy; • Radiation defects in solids, particularly, in oxides, materials for radiation conversion and UV light dosimetry (up-conversion luminescence, persistent luminescence); • Organic material research and applications; • Radiation damage studies in scintillating materials for high-energy physics and medical applications. ISSP UL has established a cross-disciplinary and cross-laboratory system for idea harvesting and has developed a supporting process for preparation of complementary research-innovation (RIA) project proposal applications. Theoretical simulations at ISSP UL are locally supported by a high-performance computing (HPC) infrastructure (Linux Cluster) with a theoretical peak performance of about 150 teraflops. The Master and PhD programmes performed in the framework of CAMART[2] by ISSP UL scientists comprise the content related to fundamental problems of materials science, synthesis and characterisation of functional materials as well as the design and fabrication of micro- and nano-	A relatively high percentage of researchers in the age group of 65+ and a gap in the age distribution in the age group of 40 to 60. Attracting and training of qualified staff in the elaboration of the new initiatives (polymer photonics platform, 0D,1D,2D nanostructures, Organ-on-chip, Lab-on-chip devices) proposed in the ISSP UL Research Programme could take a long time (2-3 years, at least). Most of the implemented national projects are relatively small; research areas vary from project to project, causing the risk of a scattered development of research fields and making more difficult the infrastructure support and development. Relatively small numbers of scientific papers are published in high-impact journals. Number of EU project (e.g. H2020) applications selected for financing is relatively small compared to the main international competitors.

photonic and electronic devices. ISSP UL is one of the leaders in Latvia in attracting competitive research funding, both by national and international projects, e.g., EC-supported Teaming project CAMART[2], a number of projects on functional and diagnostic materials in EUROfusion Programme, and considerably above-the-average success rate in Latvian research grants. ISSP UL is the founder and organizer of International Functional Materials and Nanotechnology (FM&NT) conference series, recognized and attended by some of world's leading scientists. The meetings are cyclically hosted in turn by each of the three Baltic countries; the last one, the 13th FM&NT-2020 took place online at Vilnius University Nov. 23-25. ISSP UL is a co-publisher of the "Latvian Journal of Physics and Technical Sciences", indexed by SCOPUS. ISSP UL is supported by International Advisory Board, which consists of high-level scientists, science managers and industrial partners. ISSP UL has a wide network of co-operating universities, research consortia, institutes and individual scientists across the globe.	
Opportunities	**Threats**
Substantial development of research-innovation ecosystem, incl. up-to-date technological and research infrastructure and advanced research environment opens up new possibilities to improving the quality of the research and allows ISSP UL to become a more attractive partner in the formation of domestic and international consortia. Long-term investment in institutional development by the implementation of CAMART[2] project allows to raise further the scientific and administrative capacity and international visibility of ISSP UL. There is an opportunity in exploiting existing networks and expanding co-operation with strong partners, e.g. within RIX-STO platform, to increase ISSP UL visibility by increase of the volume and quality of co-operation projects, especially in the	There is a lack of young people studying STEM subjects in the country and their average out-of-school knowledge level tends to be too low to pursue scientific career in the world-class material science. Latvia stands out by one of the lowest state investments in R&D in EU; it is insufficient for competitive and sustainable growth. National funding for the research and innovation development has too high dependence on the EU social and structural funds. Latvian high-tech industry is still comparably small; therefore, the volume of industrial contracts is tiny.

interdisciplinary fields. Expanding collaboration with synchrotron centres, especially in Hamburg and Lund, which provide access to excellent infrastructure and guarantee the involvement of the ISSP UL team in the European research area. To sustain and develop “Materize” innovation hub at ISSP UL as a link between research and industry will expand for getting new local and EU co-operation commercial projects. Open access laboratory will increase the potential of Research & Development & Innovation activities by attracting external teams. Further increase of participation in EURO*fusion* Programme will raise recognition and reputation of ISSP UL and will open possibilities for additional funding (through limited competition within Enabling Research Projects). Technology transfer (including spin-off companies) can lead to the new sources of income and can help to expand the industrial customer base.	

HUMAN RESOURCES

The practice of Human resources Management (HRM) is concerned with all aspects of the employment and management of the people. It covers activities such as strategic HRM, knowledge management, organization development, resourcing, performance management, learning and development, reward management, employee relations, work safety and employee well-being.

Key point for new HRM system is to raise the potential of the staff attracted and retained by seeking and being part of high-quality research projects, maintaining motivating work environment and supporting educational programs and multidisciplinary skills development, supporting excellent science and an innovation-friendly environment.

The human resource philosophy of ISSP UL is based on the general strategic goal to raise the potential of the staff, to support ISSP UL aims to improve its scientific outcomes, foster its capability in innovation and enhance its technology readiness levels, while adapting to and supporting the cultural and infrastructure changes. The human resource philosophy of ISSP UL declares that the people advance the success of ISSP UL and it is important to align corporate and individual targets putting the focus on the main research directions. ISSP UL gives particular importance to teamwork.

The key strategic goal for ISSP UL is to be able to constantly retain the existing and to attract new scientists from Latvia and abroad.

Recruitment.

The main recruitment target groups are:

- Doctoral, Master and Bachelor students, which could be attracted by opening positions and providing necessary environment for preparation of theses;
- Postdoctoral researchers (PR) – Latvian or foreign scientists; Doctors, mature scientists – from Latvia and abroad;
- School-age children - to create their interest in physical sciences as their career choice in the future.

Learning and development. The HRM instruments identify personal knowledge, skills and competencies of the employees, and organize several training programs during the year with the aim to change the scientific culture and mind-set within ISSP UL researchers, facilitating excellent science and closer collaboration with industry.

Talent management. The selected approach to future local talent development involves the application of key activities, which aim to support both the attraction and recruitment of new talent from outside of the ISSP UL and the identification and effective management of talent already residing within.

The HRM has defined the talent management as a systematic attraction, identification, development, engagement, retention and deployment of those individuals who are of particular value to the ISSP UL, either in view of their 'high potential' for the future or because they are fulfilling critical roles. It is defined that talent management programme should cover the heads of laboratories, Senior Researchers, some technical staff and key administrative positions.

Training management.

The scientific staff training strategy is elaborated with a number of strategic priorities:

- deliver training through schools, seminars and events based on identified needs, including cooperation with CAMART[2] project partners as a specific case;
- explore learning alternatives, such as external provision, workshops, mentoring and coaching;
- facilitate knowledge sharing throughout the scientists and technical staff from different research areas through the different internal communication canals on training events and material;
- facilitate exchange of experience and knowledge sharing among scientists through establishment of strong networks with academic institutions and industry;
- facilitate technical assistance to advance synergy between different Institutes Laboratories and institutional development of projects.

ISSP UL research culture is supporting creativity and innovation and is open to all staff members with their different backgrounds. Innovation process-related skills represent many cross-functional areas, and these skills will foster an open culture that facilitates idea creation and fulfilment.

Training programmes are planned to develop in-house, involving KTH, RISE and external training providers. Online courses and manuals as well as a series of live and pre-recorded webinars will be available for ISSP UL staff members as well new employees for self-development.

With the goal of driving talent and training management into the culture of ISSP UL, it will be integrated with critical processes like selection and recruitment, workforce planning and performance management.

Performance management. Performance management values of ISSP UL are based on the ethical principles of respect for the individual, mutual respect, procedural fairness and transparency-based performance.

Performance management contributes to the achievement of culture change and it is integrated with other key HR activities, especially talent management, learning and development and reward management. For each employee there is given a chance to inform their supervisor about their problems, on their requirements, on encouraging opportunities to increase their workflow efficiency. One other important aim of performance management is to hold employees to account for their performance by linking it to reward and career progression.

The policy of the ISSP UL is that performance conversations should not be one-way information, but rather open exchanges in which the employee is fully involved, and both share their hopes and concerns.

The annual performance conversation offers the opportunity to systematically discuss:

- work and performance of the past year – tasks, work conditions and cooperation;
- resolve problems and misunderstandings;

- discuss about actors that have helped or hindered performance and how employees can become more effective now and in the future;
- mutually voice acknowledgement and critique in a factual manner;
- agree on measures to boost development and further training;
- agreement on the long-term goals and focus points.

Feedback is a critical element in performance management, not only because it directs the focus on learning and improvement, but also because it allows individuals to monitor their progress towards goals and stay motivated. Because of that there is worked out form of Individual development plan which is not obligatory, but if supervisor and employee are interested to do regular evaluation of progress and/or achievements, this is like one additional tool for faster development.

Reward management is concerned with the strategies, policies and processes required to ensure that the value of the people and the contribution they make to achieving organizational and team goals is recognized and rewarded. Reward management is equally concerned with non-financial rewards such as recognition, learning and development opportunities and increased job responsibility.

EDUCATION

ISSP UL has always been deeply involved in the education process of students at different stages starting with the course work and continuing to PhD and postdoc activities. Latest developments of the Master and PhD programmes performed in the frames of CAMART^2 have raised the education process to considerably higher levels. A list of courses developed by the scientists of the institute comprises the content related to fundamental problems of Materials Science and Solid State Physics, synthesis and characterisation of functional materials as well as design and fabrication of micro and nano-photonic and electronic devices, signifying the applied nature of the programme and addressing the challenges set out by high-tech industry.

Group	Name of the course	Responsible	ECTS
Fundamental	Materials physics	Assoc. prof. Anatolijs Sarakovskis	3
	Nanotechnologies and nanomaterials	Asst. prof. Aivars Vembris	3
	Solid state physics	Prof. Uldis Rogulis	3
	Thin films and coatings	Juris Purans	6
	Semiconductor physics and devices	Prof. Uldis Rogulis	3
	Introduction to computational methods on materials research	Dmitrijs Bocarovs	3
	Introduction to symmetry, crystallography and group theory	Dmitrijs Bocarovs	3
Characterization methods	Structure characterization methods	Aleksejs Kuzmins	6
	Optical and magnetic spectroscopy	Prof. Uldis Rogulis	6
	Electrical characterization of materials	Eriks Birks	3
Fabrication	Micro and nanofabrication of electronic and photonic devices	Gatis Mozolevskis	6
	Synthesis, processing and applications of modern materials	Linards Skuja	3

The content of the courses has been developed in close collaboration between scientists of ISSP and KTH. More than 40 people including senior researchers, PhD and Master students have been involved in the preparation of the materials. The result of the work is electronic study materials (lecture notes) available for the students enrolled by the Faculty of Physics, Mathematics and Optometry, University of Latvia. All these courses have been included in the curriculum of the University of Latvia and are being taught within the new upgraded Master's programme. It is foreseen that some of these courses could be included in the curriculum of Riga Technical University as well.

In 2021, the newly developed Master's programme is expected to become officially international, thus increasing the number of enrolled students at the faculty and consequently those associated with ISSP UL.

Since 2009 a Doctoral school "Functional materials and Nanotechnologies" based at ISSP UL has been successfully operating. Weekly workshops with lecturers from Latvia and abroad are attended by more than 15 PhD students and 20 Master's students from University of Latvia and Riga Technical University mastering in Physics, Chemistry and Biology programs. In 2021, regular lectures in the Doctoral study programmes of Materials Science and Solid State Physics are planned to be organized for the PhD students, and will be given by dedicated lecturers from ISSP, KTH and RISE.

Since the foundation of the Institute in 1978, a series of annual conferences at ISSP UL has been organized. Nowadays, this tradition is still kept alive, and the conferences are usually held in February. These 3-4 days events gather more than 100 oral and poster presentations delivered by the staff members of ISSP UL and students. These events are particularly important for students and early stage researchers, providing the opportunity to deliver the results of the research in front of a broader audience and at the same time train their presentation skills.

Strong demand, both internal (ISSP UL) and external (industrial partners), for well-qualified students and young researchers requires special attention and extra efforts in the development and support of education activities within ISSP UL. These activities are in the list of the current priorities of the Institute and their place is certainly secured in future.

INNOVATION

Innovation is one of the pillars on which the sustainable development of ISSP UL is based. In order to integrate innovation into the daily ISSP UL routine, an innovation system has been developed that involves most of the ongoing processes in ISSP UL. A well-functioning innovation development system is a part of research development in ISSP UL.

In the research program, the innovation component permeates the entire research process, from the generation of ideas to the commercialization of research results, and innovation activities can be seen as a supportive mechanism for ensuring a successful scientific and research process.

The innovation component of the research process takes two forms. On the one hand, innovation activities play an engaging role throughout the research process. The innovation process is like a bridge between science and the world. By working closely with industry and external bodies, it is able to guide research activities, both by understanding needs and by actively monitoring emerging topics in the world and jointly developing industry benchmarks.

On the other hand, it has a supporting role in providing day-to-day activities, such as addressing intellectual property (IP) issues, providing support and training about innovation development in IP management, assistance in project definition.

The next step, which embodies the identified directions in competitive ideas, using various idea generation tools, is also important. ISSP UL has successfully integrated the hackathon principle into day-to-day processes, using it at various stages of the research process. During the research project, the innovation process ensures regular involvement, so that at an early stage of the research project, the possibilities to generate commercializable results in the future are considered. In turn, when the research project is completed, the innovation process ensures the evaluation of the results for commercialization readiness, attraction of further funding, as well as commercialization at the end of the process.

In general, the innovation component of the research program leads application-based development and is divided into three groups: ecosystem & partners, IP and funding, growth and support (*Fig. 5*).

Innovation in Research programme

Ecosystem & Partners	IP and funding	Growth and support
Outreach & Networking • Ecosystem mapping • Workshops • Conferences & Exibitions • Visits **Requirements** • Industry needs • Academia needs (research and education) • Emerging topics in world **Idea generation & identification** • Workshops • Hackathons	**Intellectual Property** • Identification • Protection **Technology transfer** • Idea identification • IDD, benchmarking • Proof of concept, prototype • Licencing, spin-off **Sales** • Expertise, Services • IP • Products/Technology	**Training** • Project writing • IP indentification and protection in research projects **Opportunities** • EU calls • National calls • Industry collaboration **Project support** • Proposal preparation • Project implementation (administration)

Fig. 5 The main activities of the innovation system in the research process.

Ecosystem & Partners mainly covers the overall situation. This identifies the needs of industry and academia through a variety of networking tools. ISSP UL is actively integrated into both the national and international ecosystems and holds regular discussions with industry, academia and government, thus being able to respond quickly to current trends. Industry surveys are conducted on a regular basis to identify research topics that are relevant and necessary for the industry. Efforts have been put into developing the capability of identifying the market pull and reducing the use of technology push in technology marketing and communication of research results, i.e., to develop and strengthen the capability of ISSP UL researchers and innovators to find solutions to industrial problems or needs. This section also includes an idea generation process that allows to formulate and develop ideas for future project calls. ISSP UL organizes regular events that bring together professionals from different fields, creating a breeding ground for the growth of interdisciplinary ideas.

IP & Funding covers everything related to IP protection and management, from the identification of a protected object in research projects to the selection and provision of its protection mechanism. As research commercialisation raises the importance of protection of intellectual property rights (IPR) and improved knowledge management, part of the support system is geared towards IP management. Further, an IP policy is formulated following the aims of the IP strategy to guide the decision on when and whether to apply for a patent.

In order to ensure a sustainable financing model, the technology transfer process is essential in finding potential customers and identifying their needs. The Innovation Due Diligence (IDD) method is used in this process. IDD is a method developed by LTU Business (Luleå University) to retrieve project and market information. The method is a working process that can be used to evaluate ideas, plan the commercialization or write project proposals. ISSP UL has purchased a license to use this method and the staff of the innovation team has been trained in the use of this method and have successfully used it since purchasing the license. It is essential to steer the decision points in various stages of the innovation development before new investments and it is critical to demonstrate successful proof-of-concept devices and prototypes meeting market benchmarks to attract investments for further commercialization. Sustainable funding is provided through the commercialization of research results in various forms, such as licensing or spin-offs, as well as through a sales process.

Growth & Support provides regular training of research staff on innovation-related topics - project writing, IPR process. Regular screening of various project calls is also provided in order to inform scientific staff about potential opportunities in a timely manner. Day-to-day support in project preparation and implementation is also provided.

Further changes in the culture of the ISSP UL are needed to handle a closer collaboration with industry, especially in the area of IPR and knowledge management, which is based on formulated policies and strategies and introduced as clauses in employment contracts at ISSP UL.

ISSP UL has also initiated the process of engaging qualified personnel within the organisation, and attracting individuals from outside, with skills for driving the process of innovation and aiming at the creation of new companies and technology transfer. Team must be strengthened with people having entrepreneurial spirit to ensure potential contributors in sustainability of activities.

Innovation development, R&D services for industry and technology transfer process requires access to extensive infrastructure and competences, which are provided using the Open Access Laboratory concept.

INFRASTRUCTURE DEVELOPMENT

The infrastructure development strategy and its implementation is organized in coordination with the ongoing and future fundamental and application-oriented projects performed at the Institute. The infrastructure development actions take into account that ISSP UL facilities become an “Open access laboratory”, which must serve the needs of students and also the needs of domestic public research institutions and entrepreneurs, and must be open for international partners.

The following instruments and systems have been installed during 2017-2020 at ISSP LU. Allocation of costs by each of infrastructure category in MEURO is illustrated in Fig.6 and listed in detail here below. A complete list of infrastructure items and a description of the corresponding equipment can be found at**: https: //www.cfi.lu.lv/en/services/all-services/full-equipment-list/**

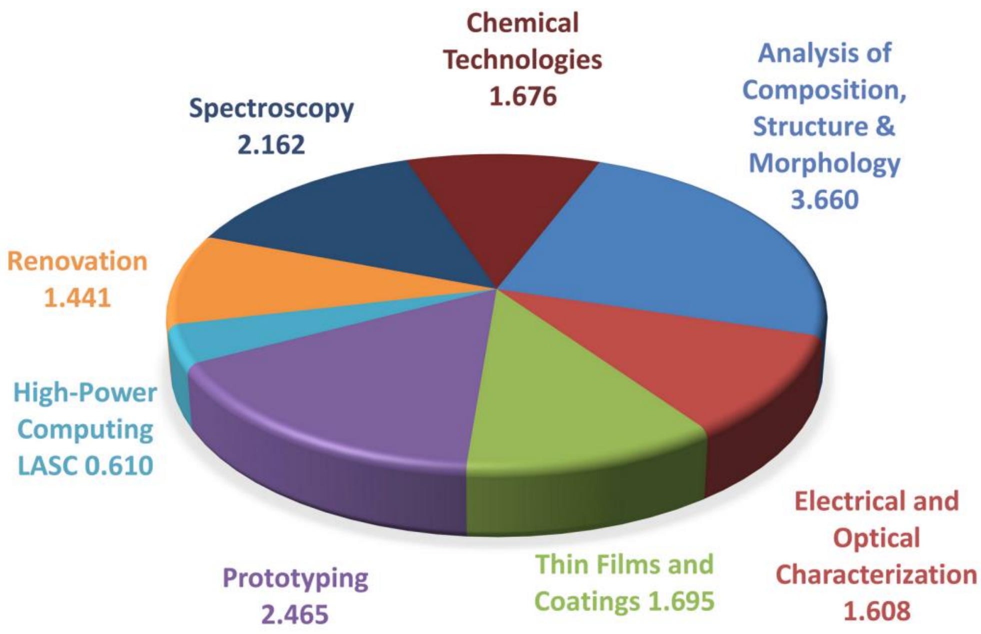

Fig.6 Allocation of costs (in millions of €) of different infrastructure categories.

The most important equipment by categories:

High-performance computing

- **La**tvian **S**uper**C**luster (LASC) upgraded to theoretical peak performance 150 Tflops

Thin film and coating technology

- Multifunctional cluster device for the production of vacuum coatings: *SAF25/50*
- MOCVD reactor: *Aixtron – AIX-200RF*
- Pulsed Laser Deposition (PLD): *Twente Solid State Technology*
- Atomic Layer Deposition (ALD): plant *Savannah S100*

Chemical technologies

- Isostatic hot press setup: *LAB HIP 200-77*150 G (EPSI))*
- Vacuum hot press furnace: *Model FR210-25T-M-200-04T*
- Muffle furnace with gas supply: *NABERTHERM HT 08/16*
- Tube furnace: Carbolite *Gero HTRH/HTRV*
- Planetary mill: *Pulverisette 5/4 Fritsch*
- Microwave Synthesis System: *SynthWAVE*
- Particle size analyser: *Anton Paar Litesizer 500*
- Differential calorimetry - thermogravimetric analyser: *Setaram LabSys Evo*

- Spin-coater*: Laurell WS650*
- 8 fume cabots for synthesis Doctor blade, ultrasonic bath;
- Thermal analysis *LABSYS Evo-1A (Setaram)*
- Spray-coater: *ND-SP*
- Centrifuge: *TBE-334*
- Membrane preparation module - installed, fully operational
- Glove-box*: Mbraun*
- Anhydrous synthesis and characterisation of materials for lithium and sodium batteries

Structure and Morphology

- X-Ray diffractometer for advanced measurements:
  - *PANalytical Xpert PRO MPD*
  - *Rigaku MiniFlex Benchtop*
- Transmission electron microscope: *FEI Tecnai GF20*
- High resolution SEM/FIB: *Helios 5 UX (ThermoScientific)*
- Nanoindentor: *Agilent G200*
- Profiler: *Dektak 150*
- Profiler: *Zygo 7100*

Spectroscopy

- High performance optical absorption/reflection spectrophotometer*: Agilent Cary 7000*
- Raman spectrometer: *TriVista CRS Confocal Raman Microscope (TR777)*
- Spectroscopic system for luminescence studies: *Edinburg Instruments FLS-1000*
- FT-IR system with microscope and helium refrigerator cryostat: *Bruker Vertex 80v*
- Electron paramagnetic resonance (EPR): *Bruker Elexsys-II E500*
- Optically detected magnetic resonance (ODMR): Upgraded to 93 GHz frequencies
- X-ray photoelectron spectroscopy (XPS): *ThermoFisher ESCALAB Xi*
- Streak camera with high temporal resolution: *Hamamatsu C10901-1*
- 3D scanning microscope with Raman spectrometer: *Solar Tii Nanofinder S*
- Spectroscopic ellipsometer: *J.A. WOOLLAM RC2-XI*
- Thermally and optically stimulated luminescent device: *Freiberg instruments Lexsyg research LMS*
- Spectroscopy methods and lasers: *Model Ekspla*

Electrical and optical characterization

- Dielectric spectroscopy equipment:
  - precision LCR meter: *HP 4284*
  - precision LCR meter: *MFIA, Zurich instruments*
- Hall measurement unit*: Ecopia: HMS-5000*
- Custom built setups for nonlinear optical effect characterization – *Z-scan, Maker-fringe, MZI*
- OLED parameter measurement system in GloveBox
- Scanning Kelvin probe system: *KP Technology SKP5050*
- *PYS* and intrinsic photoconductivity measurement system
- *TM-SCLC* measurement system
- Seebeck coefficient measurement system
- Sun simulator: *Sciencetech Inc., SS150W*
- 15-channel battery tester, portable battery tester racks: *Voltalab PGZ-301* and *Metrohm Autolab PGSTAT302N*
- *El-Cell OPTO-STD cell* for in-situ and in-operando measurements of batteries characteristics
- Mass Spectrometer, Gas Chromatograph
- Adaptive optics kit: *DM24 and DM19, SHAH-0620(A)*
- *Multispot-250* AO kit: *DM97, SHAH CMOS, ACE software*
- Spatial light modulators:
  - *HES 6001* for amplitude modulation
  - *PLUTO 2* for phase modulation
- Aberrometer;

Technology for prototyping

- Direct recording laser lithography system: *Heidelberg µPG 101*
- Electron beam lithography equipment: *Raith eLINE Plus*
- Mask exhibitor: *Suss Microtec MA/BA6 Gen4*
- Probe station: *Form Factor MPS 1500*
- Wire bonder for Au and Al wires
- Dry etching

Tentative wish list for further infrastructure development

- Time of Flight measurement system TOF-SIMS
- Thermoelectric properties (Seebeck-Coefficient / Resistivity / thermal conductivity of TEG and Peltier Modules / Thin Films) characterization Instruments
- gas sorption- analysis technique - PCT Pro2000 with RGA-100 mass-spectrometer
- dual HIPIMS magnetron vacuum chambers with plasma regulation and control by time-resolved Optical Emission Spectroscopy (OES) system
- Inside TEM SPM Scanning Probe Microscope
- Low temperature vacuum AFM STM
- SQUID

COMMUNICATION

The objective of outreach activities are aimed to promote ISSP as a well-established environment for research and innovation and as a modern and attractive partner for entrepreneurs, scientists, investors, and policy makers in Latvia and internationally.

Strategic outreach is based on a balanced communication strategy (CS) that is of main importance to strengthen the ISSP UL as an important player in research and innovation field by increasing awareness of the possibilities, knowledge, skills and excellence.

CS is a guideline to work with identified target groups by using tailored messages, actions, channels and tools, as well as to monitor expected outcomes, impact and relevance in accordance to the ISSP UL objectives. Effective CS can help ISSP UL to achieve overall organizational objectives, to engage effectively with stakeholders, to demonstrate the success of our work, ensure that people understand what the ISSP UL does and to change behaviour and perceptions where necessary.

On the whole, the main target audiences are local and international public bodies, private companies and consortiums, research and academic sectors, universities and schools, as well as the general public..

Communication objectives are specified for each target group, however, the unifying overarching objective for every audience is to build trust in ISSP UL and its research, to inform about scientific excellence, innovation and all kinds of achievements and capabilities as well as to increase awareness about how the ISSP UL research may relate to them.

Communication channels are specified for each target group, but they also can overlap, as one individual can belong to many identified target groups. Channels are as follows: ISSP UL (LV, ENG), CAMART², Materize internet portals; attendance and organization of conferences, scientific meetings and workshops; visits to the scientific institutions and industry; CAMART² strategic board and ISSP UL Advisory board meetings; direct meetings with society, industry members and with policy and decision making bodies; events for general public and school children (Physics Festival, exhibitions, Researcher’s Night, Career days, Solar Cup, children excursions at the ISSP UL, visits to schools; media – TV, press, radio, YouTube, Facebook, Twitter (other, if needed), LinkedIn, ResearchGate, Mendeley, Publons, SciTechEurope; printed materials (booklets/brochures/leaflets) as well as promotion materials, etc.

Target group (To whom?)	Reason to address the group (Why?)	Message (What?)	Channels and materials (How?)
Scientists covering researchers, research assistants and technicians that are involved in research and innovation work in fields related to ISSP UL research program, not ISSP UL employees as well as the **Academic and research community** meaning leaders who make decisions about the fields and directions of the research, collaboration and innovation as well as science communicators and involved personnel within universities and research institutions	Reputation of ISSP UL depends on the understanding, motivation and attitude of this target group	Great place where to work/make/prolong/foster a career; excellent scientists, modern equipment, trustful collaborators, opinion leaders	ISSP UP/CAMART²/universities webpages, social networks, matchmaking / brokerage events, EC project calls, conferences and workshops, media, meetings using prepared materials, such as: **booklets, leaflets, roll-ups, hand-outs, videos, press releases, ppts, giveaways, FB, YouTube, TW, LinkedIn, ResearchGate, Mendeley, Publons**
Industry meaning relevant business owners, investors and technology developers	The success of ISSP UL reputation as an industry partner depend on the target group's understanding of the current issues and needs of the industry	Science beneficial to business; expertise, excellence and experience**;** **a**vailability and flexibility for industry needs; **v**aluable intellectual property background relevant to the industry	Meetings, brokerage events, joining into industry related 'clusters', networks, Materize\ ISSP UL homepage, infrastructure and service provider networks, technology platforms, special events, ISSP UL employees and Alumni as a channel using the following tools - **ppts, hand-outs, prospects, roll-ups, giveaways, LinkedIn, FB**
Policymakers meaning policy officers and anyone who makes decisions or impact the shaping of national research and innovation policies, as	The support of other sectors and employers' organizations for the sector and the development of scientific processes depend on the target group's understanding of the	Trustful opinion leader; research driving force; right place to invest for new research and innovation, to boost new discoveries, industrial growth and	EC infopages, media, conferences, public meetings, CAMART² and ISSP homepage, information on the Cordis data, meetings with EU/LV decision makers (Latvian parliament commissions, government), boards using prepared information in S**ciTech-**

well as EC commissioners and officers	current issues and needs of the sector	economy	**Europe, brochures, roll-up, hand-outs, video, ppts, TV, radio and engaging in advisory boards**
Students covering both high school and university learners and school youth	An important group in the long run - potential employees, researchers, scientists	Great place to build an impactful career; your research can help to trigger important changes; it is cool to be a physicist; good place to develop yourself for future start-up idea or relevant position in industry	ISSP UL/ CAMART² Web page, universities homepages, EC project calls, conferences, media, public events, study programs/lectures, social networks, e-klase, excursions, visits to schools, special events (Solar Cup), work with career consultants, work with teachers reaching the group by well-prepared **roll-ups, hand-outs, videos, ppts, giveaways, status updates on FB, YouTube, Twitter and press releases, TV and radio broadcasts (for parents who may belong to any other of the mentioned target groups)**
General public meaning all society that are not related with research fields of the ISSP UL and not covered in previous points	An important group for several reasons - potential employees, potential business partners, potential promoters of their children for careers in physics and science	Great discoveries, innovation and new technology development happen here; your tax investments bring great value thru us to economy and quality of life; we are known abroad and successful; we work for your future.	Media and social media, ISSP & CAMART² homepages, public events, decision making bodies using **roll-ups, hand-outs, videos, giveaways, press releases, TV and radio broadcasts, FB, YouTube, Twitter, TV discussions, engagement in advisory boards, booklets, ppts**
Media (traditional, business, lifestyle, regional), electronic and social**; information intermediaries and partners**	A communication channel to reach the general public as well as to provide support in public for the information provided to stakeholders; providers of information in the field of physics and materials science (companies in the field), leaders of public opinion (in science, education, etc.)	Physics and materials science are an important field of science in the development process of society and national economy. The Institute of Solid State Physics, University of Latvia is an excellent place for research and innovation. Science and discoveries live here.	Media and social media, ISSP & CAMART² homepages, public events, decision making bodies conferences, press releases, interviews, public events, ISSP UL employees and Alumni as a channel and also as experts using **all the above mentioned tools as necessary**