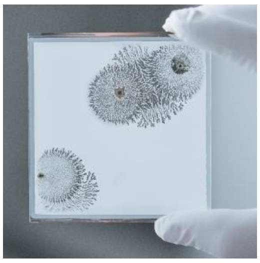
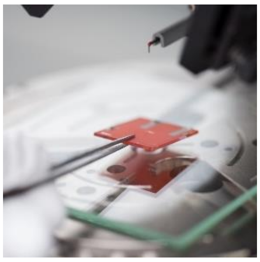
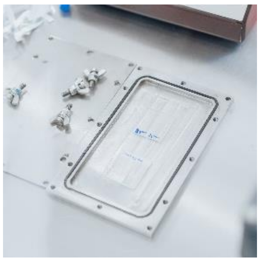
INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

RESEARCH PROGRAMME
2021 - 2024 - 2027

Riga

2021-2024

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).

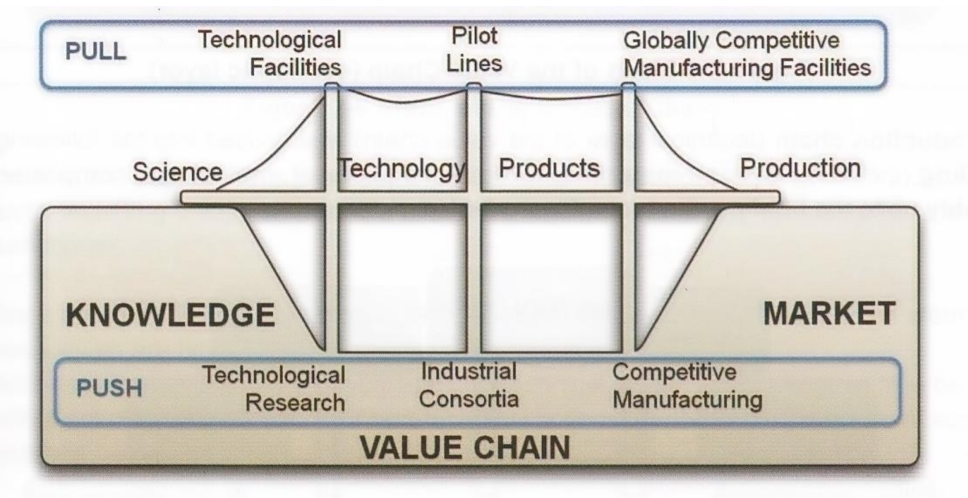


Fig.1. The scheme of the value chain.

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

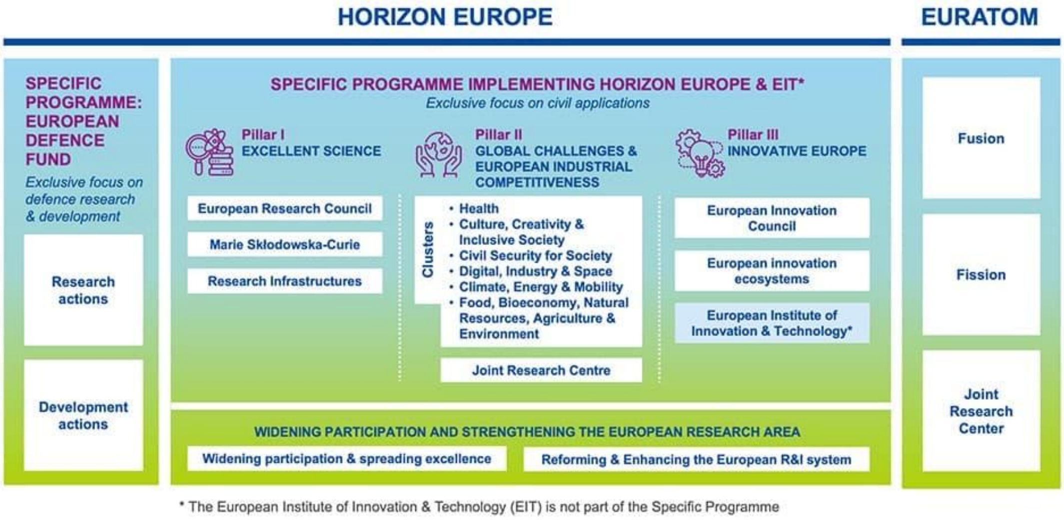


Fig.2. Structural outline of Horizon Europe programme.

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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FOREWORD TO THE UPDATED VERSION OF THE PROGRAM FOR THE PERIOD OF 2021-2024-2027

The long-term research program of the Institute of Solid State Physics, University of Latvia (ISSP UL) has been elaborated for 8-year period (2021-2027) and was launched at the beginning of 2021.

It was designed with an aim to chart the optimal course of the Institute in the multifaceted and rapidly changing research environment. Because of its long time span and the degree of uncertainty inherent to any research, and non-predictable external factors, like the COVID pandemic during 2020-2022, or the Russia's invasion of Ukraine, periodic updates are required in order to adjust the program to the current status quo and to the changing opportunities and challenges. The adjustments may range from small to significant ones; they must take into account a number of factors, like:

- The latest changes in the "state of the art" in the relevant research fields during 2021-2023.
- The results of our own research and further perspectives – or their absence- stemming from them.
- The changes in funding situation – completing projects and success or failure in competing for new ones. The changing priorities in new project calls.
- The possible deviations between the actually funded research directions and those planned in the research program – this is particularly actual for multi-partner projects, whose tasks cannot be exactly tailored to the research program(s) of each single partner.
- Changes in employment of key scientific staff members – departures and hiring of new ones.
- Establishing of co-operations with new partners.
- Actual or predicted future changes in key infrastructure and instrumentation.

The overall geopolitical situation has become more fragile during 2023: the continuing war in Ukraine, situation in Middle East, China-Taiwan tensions etc. This puts an additional focus on research fields, helping to reduce the dependence on fossil fuel energy and different raw materials (like rare earths, lithium etc.) imported from non-reliable or belligerent foreign partners. With a rapid development of solar and wind energy, energy storage, like batteries and hydrogen-based technologies become increasingly important.

An increased focus on research in different defense-related technologies is expected, in particular, in multiple technologies related to the evidently rising dominance of drone warfare: sensors, communications, lasers, computer control, robotics, artifical inteligence etc. Research and development of dual-use technologies for both military and civilian security will be intensified. The previously planned research topics of ISSP LU already have overlap with a number of these fields. Additional adjustment in these directions may be necessary in future.

Among the relevant developments having taken place during 2023, one can outline the renaissance of efforts towards nuclear energetics, largely motivated by the aim to reduce the CO_2 emissions and to mitigate climate changes. United Nations Climate Change Conference (COP28) took place in Dubai (UAE) in November-December of 2023. Its concluding statement, released on December 1 proclaims that "Resilient and robust nuclear power has the potential to play a wider role in the quest towards net zero carbon emissions, while ensuring the highest level of nuclear safety and security". The 1st Nuclear Energy Summit will be held in Brussels in March 2024, attended by industry leaders and high-level government representatives of more than 30 countries. It will discuss the role of nuclear energy in reducing the use of fossil fuels and enhancing energy security.

The renewed interest in nuclear energy requires studies of the various materials used in devices exposed to radiation environments. Scientists of ISSP LU have significant expertize in this field, since it has been traditionally one of main research directions of the institute, as reflected by the participation in EUROFUSION program, and by the fact that a significant fraction of all published research papers concerns irradiation effects in materials. Evidently, the shift of focus to nuclear energy will be reflected by increased activity in acquiring projects and research in this direction.

The updated version of the research program for 2021-2027 includes these adjustments in planning of each research domain. The necessary changes are made directly into the respective sub-sections of the domain descriptions: "State of the art", "Our position", "Future activities", "Networking", and "References". To make the annual changes more discernible within the program text, they are marked by red-colored font for changes in planning for 2024. Additionally, a short summary of the main changes titled "Summary of planned updates" is added at the end of each domain plan. The program updates are introduced to maintain a good balance between the basic and applied research.

KEY HIGHLIGHTS FOR 2024

The research activities and their organization in 2024 are largely dominated by the four now implemented Horizon Europe projects and a new European Space Agency project related to sensors/robotics, energy conservation and storage:

- Horizon CL4 project Sestosenso – "Physical Intelligence for smart and safe Human - Robot Interaction (SestoSenso)", started at 2021, ends 2025
- Widening participation and strengthening the European Research Area (WIDERA) Era Chair project “Smart Windows for Zero Energy Buildings (SWEB) ” has started on January 2023 for duration of 5 years;
- Horizon CL5 Europe Research and Innovations Action project “Eliminating VOC from Battery Manufacturing through Dry or Wet Processing (NoVoc)” has started on January 2023 for duration of 4 years;
- Horizon CL5 project "Atomic layer-coated graphene electrodes for micro-flexible and structural supercapacitors (ARMS)" implemented together with Tampere university has started on January 1, 2024 with duration of 4 years.
- European Space Agency project ESA RPP "Development of Low-Temperature Ionic Liquid-Based Li-Ion Battery Cells" will start on January 1, 2024 with funding of 96 k€.

Eight new Fundamental and Applied Research Projects (FARP), funded by Latvian Science Council start on January 1, 2024 for 3 years duration with funding 100 k€/project/year:

- New generation of piezoelectric materials for active vibration control (Leader R. Ignatans);
- Development of new advanced phosphors for lighting and non-contact optical thermometry (Leader E. Kotomin);
- Unlocking the secrets of multicomponent alloys and related compounds using X-Ray absorption spectroscopy and atomistic simulations (Leader A. Kuzmin);
- Modelling celiac disease on a chip (Leader G. Mozolevskis, in collaboration with Latvian Biomedical Center);
- Predicting the long-term tolerance of functional materials for use in extreme radiation conditions (Leader A. Popov);
- The entropy-driven approach to enhance the thermoelectric performance of chalcogenide-based compounds (Leader I. Pudza);
- Advancing Sustainable Thermoelectric Hybrid Systems Utilizing Glass- Forming Low Molecular Weight Compounds (Leader K. Pudzs);
- Light activated 4D printed materials for vascular tissue engineering (Leader V. Vitola).

Alongside with the 8 new FARP projects started in 2024, 15 FARP projects, started in years 2022 and 2023 will continue:

- Development of carbonic anhydrase IX test biosensor for cancer screening (Leader A. Anspoks);
- Defect control in novel UV-C long-lasting luminescence materials (Leader A. Antuzevics);
- Computer modelling, synthesis and characterization of modified TiO_2 nanoparticles for disinfection applications (Leader D. Bocharov);
- Raising critical temperature in MgB_2-based superconductive nanowire systems via internal strain engineering (Leader E. Butanovs);
- Non-destructive investigations of interfaces of multilayer organic materials for high-performance OLED development (Leader J. Butikova);
- Advanced atomistic studies on Ruddlesden-Popper phases for protonic ceramic electrolysis cells (Leader D. Gryaznov);
- Development of ternary organic solar cells by employing original indacene-tetraone based non-fullerene acceptors (Leader R. Grzibovskis);
- Non-contact nanothermometry based on X-ray absorption spectra (Leader A. Kalinko);
- Topological semimetals towards low-dissipation electronics (Leader G. Mozolevskis);
- Cross-luminescence engineering for picosecond time-of-flight gamma- and X-ray imaging for medical applications (Leader V. Pankratovs);
- Large-scale computer modelling of defective ternary chalcopyrites for photovoltaic applications (Leader S. Piskunovs);
- Research of microbiota derived extracellular vesicle role on breast cancer by using gut-breast cancer axis on a chip (GBA-OC) (Leader R. Rimsa);
- Multifunctional hybrid metal oxide nanowire arrays for simultaneous green power generation and CO_2 reduction (Leader A. Sarakovskis);
- Interstitial molecules and point defects in silicon dioxide-based materials for photonics, radiation-related and photochemical applications (Leader L. Skuja);
- Novel metal hydride-based thin films for electronics and energy technologies (Leader M. Zubkins).

- In 2023, 2-year project for Innovation Fund project "Smart materials, photonics technologies and engineering ecosystem (MOTE)" was started to establish co-creation ecosystem to foster scientific breakthroughs and further research commercialization in Latvia. The project is implemented by ISSP UL as coordinator together with partners, Riga Technical University, University of Latvia, Institute of Electronics and Computer Science, Rezekne Academy of Technologies, Latvian Biomedical Research and Study Centre, Latvian State Institute of Wood Chemistry and Institute of Mathematics and Computer Science.

  The objectives of the Innovation Fund project are:

  - Increase cross-sectoral scientific activities
  - Promote open science approach
  - Support early stage researchers
  - Supportive environment for innovation commercialization
  - Create new methods, technologies and prototypes with commercialization potential.

- The Institute continues to participate in the 3-year (2023-2025) Latvian National Research Program "High Energy Physics and Accelerator Technologies" aimed to support collaboration with CERN. Within this program, the institute works on nuclear energy–related materials.

- ISSP UL finalizes the work on thermo electronic generator (TEG) technology that has been developed for a high-speed electromagnetic radiation sensor that can characterize the shape of very short light pulses in a wide spectral range (UV-VIS-IR). It is around 1000 times faster than the ones currently in use. The technology can be used, for example, in laser surgical equipment, where it will provide precise control of the applied radiation energy and thus allow more safe and efficient manipulations. Sensor, based on this technology is now listed among the new products of Thorlabs Company.

- ISSP UL spin-off company CellBox Labs (https://www.cellboxlabs.com/) continues to work on polydimethylsiloxane (PDMS)-free gut-on-chip, suitable for anaerobic conditions necessary for microbiota cultivation controlled by integrated biosensors and user- friendly cultivation system, low molecule absorption, suitable for drug testing and compatible with mass manufacturing methods.

THREE MAIN ACTIVITY AREAS OF ISSP UL

The activities of the Institute can be roughly grouped in three partially overlapping areas:

- Research in the field of physical sciences
- Development of novel functional materials
- Technology, devices and applications

The research plans and their updates for scientific teams working in these 3 areas are detailed here below.

RESEARCH IN THE FIELD OF PHYSICAL SCIENCES

While all the research work performed at ISSP UL aims at practical applications as one of the most important targets, it yields also more general, fundamental results, which contribute to the general knowledge and go beyond single application or application class. This section presents research plans of both theoretical and experimental studies in this group.

THEORETICAL MATERIAL SCIENCE AND MODELLING

STATE OF THE ART

Computer large-scale 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 ones. They are performed, in particular by 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. band engineering of band gaps for water splitting, photovoltaics and in materials 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 defects in 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], water splitting [13] , *p*-type conductors [14], optics for fusion reactors diagnostics and plasma heating [15], photostimulated hydrogen production upon perovskite nanoparticles [16,17].

FUTURE ACTIVITIES

Labs future activities will be focused on understanding of chemical and physical material properties in the photocatalytic processes and design of new effective photocatalysts for water splitting with 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 other 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);
- Dr R.Merkle, Max Planck Institut für Festkörperforschung, Stuttgart, Germany
- Prof. R. Dovesi, University of Turin, Italy (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. M. Maček Kržmanc, Jožef Stefan Institute, Ljubljana, Slovenia
- Prof. T. Scherer, Karlsruhe Institute of Technology (KIT), Germany
- Dr. R. Vila, CIEMAT, Madrid, Spain
- Prof. K. Exner, Faculty of Chemistry, University Duisburg-Essen, Essen, Germany
- Dr. M. Krack, Paul Scherrer Institute, Switzerland

- Prof. J.C.S. Wu, Taiwan National University

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SUMMARY OF PLANNING UPDATES

- The improvement of water splitting on faceted surfaces of perovskite nanoparticles.
- Oxygen and hydrogen production mechanism, kinetics and thermodynamics upon water splitting.

- The role of defects and dopants in epitaxial growth of thin perovskite films.
- Calculations of the excited states of insulating materials.
- The properties of defects in the bulk, thin films and surfaces of fluorites and oxides.
- Advanced materials for photovoltaics, halide perovskites.
- Modelling and improvement of proton ceramic fuel cells.

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 Material development and Technology/devices/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 is 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, and 17 of them are located in the EU Member States. A coherent and strategic vision for 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 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 machine learning methods [7], is a hot topic of current research activities, also implemented at ISSP.

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 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 the reverse Monte Carlo (RMC) modelling. The Laboratory has world-level competence in the use of synchrotron radiation X-ray absorption spectroscopy (XAS) – an analytical tool to study the local atomic and electronic structure of materials. 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 (Hamburg), MaxIV (Lund), SOLEIL (Paris), ELETTRA (Trieste), ALBA (Barcelona), and ESRF (Grenoble) synchrotrons, resulting in more than 120 peer-reviewed publications. The results of these experimental projects have been used in the implementation of 16 international and national research projects (10 projects have been directly related to the use of the XAS method). The high level of laboratory research has been reflected by the inclusion of its recent results in the Highlights 2022 of the MaxIV synchrotron radiation centre. 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 its 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 an RMC part dedicated to disordered materials. The international group including the teams from ISIS, the University of Cambridge, the 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, high-entropy materials, and information technologies.

An increase in energy consumption and limited natural energy resources are the main challenges to address by our society. The EXAFS Spectroscopy Laboratory continues to be involved in the investigation of oxide dispersion strengthened (ODS) alloys and related materials, 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 studies of multifunctional materials for X-ray sensing, thermochromic, electrochromic, photocatalytic, thermoelectric, and other energy applications [11, 12, 13, 14, 15].

Materials science at extreme conditions such as ultra-high pressures and temperatures provides a promising route toward 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 in collaboration with two synchrotron centres at SOLEIL (Paris) and ESRF (Grenoble) [16, 17].

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, thin-film thermoelectric materials, hybrid organic-inorganic systems), which we plan to realize at PETRA-III and future PETRA-IV facilities [12, 13, 18, 19, 20]. 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 and promote their application in the future. 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”, are included in the PETRA IV beamline portfolio in 2021. 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 a high signal-to-noise ratio, exceptional reproducibility of the energy scale, and beam stability at the sample 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, to study the influence of spin-orbit coupling and the effect of crystal-field splitting on the electronic structure of functional materials based on 5d transition metals [11].

The new direction of our research aims at the understanding of multicomponent alloys, known also as high entropy alloys (HEAs) or complex concentrated alloys (CCAs) [21]. The concept of maximization of configurational entropy by using five or more elements in nearly equiatomic composition has revolutionized the field of alloy design [21]. HEAs show better mechanical, oxidation, corrosion, and irradiation properties compared to commercial alloys due to five key effects: high-entropy effect, severe lattice distortion, sluggish diffusion, short-range order effect and “cocktail” effect [21]. The understanding of these phenomena in homogeneous and heterogeneous HEAs at the atomic level requires detailed knowledge of the composition dependence of the short-range order, which can be probed by XAS combined with advanced atomistic simulations [22, 23, 24]. Complementary studies were performed on the high entropy oxides [25].

The development of the methodology of EXAFS data analysis is one of the pillars at ISSP. The next breakthrough is expected in the application of machine learning technologies to provide researchers with a tool for rapid decision-making and real-time control of experiments. This approach will contribute to the improvement of the efficiency of conducting experiments at synchrotron centres and will open new possibilities in the future. The laboratory plans to develop this technology within its activity in the COST Action CA22143 "European Materials Informatics Network" (2023-2027).

The sustainability strategy of the Laboratory is based on four 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; 4) 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 are available to the community from the website of the lab. They are used also for teaching purposes at 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 centres 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 centres such as PETRA-III (DESY, Hamburg), MaxIV (Lund), SOLEIL (Paris), ELETTRA (Trieste), ALBA (Barcelona), and ESRF (Grenoble). 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, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) (Berlin, Germany), Bundesanstalt für Materialforschung und - prüfung (BAM) (Berlin, Germany), Karlsruhe Institute of Technology (Karlsruhe, Germany), Centre of Physics, University of Minho (Braga, Portugal), Department of Chemistry, Stony Brook University (Stony Brook, USA), Paul Scherrer Institute (Villigen, Switzerland), and Wigner Research Centre for Physics (Budapest, Hungary) and Center for X-ray Spectroscopy, University of Helsinki (Helsinki).

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

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Summary of planning updates

- Explore the combined use of X-ray absorption spectroscopy and reverse Monte Carlo simulations for the understanding of short-range order phenomena in high-entropy alloys and oxides.
- Explore the lattice dynamics and interlayer coupling phenomena in 2D layered materials using X-ray absorption spectroscopy coupled to atomistic simulations.
- Develop the methodology of X-ray absorption spectra analysis and interpretation based on artificial neural networks.
- Started a new collaboration with international partners.

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. 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 electron and ion microscopy systems (SEM-FIB) equipped with nano-manipulators, gas injection systems and other 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. The SEM FIB systems also ensure quality specimen preparation for volumetric studies: cross-section lamella preparation and slice and view approach for 3d reconstruction.

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 UL; 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 and can be used for 3d reconstruction of material [1]. 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 high resolution and low voltages of ion beam column allows high quality lamella preparation even for challenging materials like polymers and porous nanostructured ceramics [5]. 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. Both SEM-FIB systems are equipped with electrical and optical inputs for in-situ electrical and optical properties measurements.

II. X-ray diffraction (XRD) is one of the most used characterization methods at ISSP UL. 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).

III. 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. To achieve this goal, the laboratory should consider using correlative microscopy, which combines multiple characterization techniques to study materials at different length scales. This can be accomplished through the use of in situ microscopy, which allows for the simultaneous observation of materials under working conditions. In situ microscopy can provide valuable information about material behavior and can be particularly useful in industrial research and development.

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 Tunnelling Microscopy, Scanning Tunnelling 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. At the moment we are working towards custom implementation of optical light detection/injection simultaneously with imaging in SEM. This approach could be beneficial to the whole ISSP-UL, as there are many initiatives considering photonics. 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 (wavelength-dispersive spectroscopy) system. With this configuration, a full analysis will be possible inside the same setup, thus providing an extensive data-set.

Similarly, the TEM system should be expanded with electron energy loss spectrometry (EELS) detectors or replaced with a newer generation TEM with probe correction for ultimate STEM resolution and monochromator for high energy resolution for electron energy loss spectroscopy. Such a system can be more successfully used in combination with an X-Ray absorption spectroscopy setup.

A rather fresh initiative is to introduce in situ mechanical properties probing stage in XRD. Such approach links macroscopic properties of the materials with the inner workings at the atomic level.

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.

In addition to traditional characterization techniques, the laboratory should also consider using machine learning and artificial intelligence to analyze and interpret data. Machine learning algorithms can be trained to recognize patterns and trends in data, allowing for the automation of data analysis processes and the identification of previously unrecognized relationships. Artificial intelligence can be used to simulate complex systems and optimize processes, leading to more efficient and effective research and development. By incorporating machine learning and artificial intelligence into their workflow, the laboratory can gain a deeper understanding of materials and improve the quality and efficiency of their research.

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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SUMMARY OF PLANNING UPDATES

- No updates to the initial program (January 2021) are planned (as of January 2024)

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. (technical names used: "fused silica", "quartz glass"). 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 for radiation environments. Devices made from SiO_2 are among the most resistant to radiation damage off all glass-based devices, they are widely 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 high density, multi-terabyte ultra-stable "5D" data storage by fs-laser writing in silica glass was demonstrated [11].

A key phenomenon, crucial for all these applications, is the presence or generation of optically active point defects in the material. It 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. During the years 2021, and in particular 2022, a number of research and review papers, e.g.,[14-17] have delineated a new trend, related to densification of silica-related glasses and engineering the size of nanovoids inherent to their structure. This has become a hot topic in the quest to further increase the transparency of the long –range optical communication fibers. At the presently reached glass purity level, the main cause of attenuation in optical fibers is Rayleigh scattering on fluctuations of glass density. It has been discovered that these fluctuations can be reduced by hot-pressing silica glasses [14], and this path is now pursued by a number of research groups. Apart from this new trend, a strong activity continues towards femtosecond laser writing in silica glass for Bragg-gratings and data storage [17-19, 21,22].

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). More recently, this group has tackled the problems of chlorine, a "technological impurity" in synthetic SiO_2 made from $SiCl_4$ [7,12], 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 has identified a number of up-to now not understood carbon-related defects in silica, demonstrating that they are due to interstitial polycyclic hydrocarbons [13]. A PhD student works now on closely related topics. Most recently, in 2023, the group has identified the first paramagnetic defect in fluorine-doped silica, directly associated with fluorine [23]. The group is well-qualified in optical, vibrational and magnetic spectroscopies. It can make use both of the 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 and is further developed.

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 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 [7,12], the nature and optical properties of carbon dopants are much less understood.
- Based the results of the recent (2021) work [13], particular activity will be focused on polycyclic hydrocarbons as optically active dopants in silica glass and on their possible role as precursors to other carbon-related defects and carbon nanodots.
- 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. Relying on the recently discovered electron paramagnetic resonance (EPR) evidence for fluorine-related defects [23], their optical properties and the nature of their precursors will be studied. 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. Performing of contract works on optical fiber spectroscopy.
- In view of the perspective of using nanoscale defect structures in silica for long-term information storage [11], it is planned to focus on studies of the properties of defects in silica induced within internal nanovoids, created by laser damage or high energy nuclear irradiation.
- Defects created by ion implantation of silica (in collaboration with prof. A.Hallen, KTH, Sweden)
- The studies of the effects of densification of silica on defect creation, in collaboration with Dr. N. Ollier, Ecole Politechnique, France (see ref.[20], this direction will be continued.

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);
- United Kingdom: Prof. Peter Kazansky (Southampton University);
- The group collaborates with Latvia-based fiber-optics industrial companies, Ceram Optec and Light-Guide Optics.
- A collaboration with prof. Andres Hallén (KTH) on topics of ion-implantation and carbon-doping of silicon dioxide, will continue in 2024 with an emphasis on finding possible correlations between 3 different application fields, all related to carbon in SiO_2: silica glass as optical material; SiO_2 insulating layers obtained by oxidation of SiC; and organics-modified silica ("organosilicas") developed for low-k materials.
- Topics of further collaboration with Dr. Nadege Ollier (Ecole Polytechnique, University of Paris-Saclay) are outlined as (i) properties of pressure densified silica glass and (ii) MeV electron irradiation-induced defects in SiO_2 materials. Parts of this collaboration will be assisted by samples from Prof. K. Kajihara (Tokyo Metropolitan University).
- Collaboration with prof. Peter Kazansky (Southampton University, UK) will be focused on studies of defects in femtosecond-laser modified silica and their role in modification of glass for information storage

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SUMMARY OF PLANNING UPDATES

- Studies of correlations between paramagnetic defects in fluorine-doped silica glass and radiation induced optical absorption bands
- Studies of defects in femtosecond-laser-modified silica glass.
- Defects in fast electron-irradiated sol-gel silica glasses.

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 ongoing 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 the 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, and 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 the origin of optical absorption bands in materials. Advanced complementary spectroscopic techniques are also accessible at ISSP UL.

The EPR group of the 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 analyze 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. A prospective collaboration with the Institute of Chemical Physics, University of Latvia has been initiated to investigate thermal properties of radiation-induced paramagnetic defects in potential solid-state candidate materials for tritium breeding in future thermonuclear fusion reactors. First-principle calculations have been implemented to explain the experimental EPR data of an X-ray induced center in $LiYF_4$ single crystal [23]; it is planned to extend this approach on other single crystal materials, *e.g.*, $Gd_3Ga_5O_{12}$.
- 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. Recent results provide valuable insights into paramagnetic defect contribution to optical properties of complex materials [16-18]. A methodology for correlated EPR and luminescence (decay kinetics, thermally stimulated luminescence) measurements has been implemented within the group. The methodology will be further developed. Defect engineering of persistent phosphors emitting in the short-wave ultraviolet (UV-C) range is planned based on the recently published results on persistent luminescence mechanisms [24,25].
- 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. Joint investigations have expanded the knowledge base of substitution mechanisms of impurity ions and creation of radiation-induced defects in calcium phosphate materials [19-22]. The group at ISSP UL has obtained know-how in advanced EPR methodology and spectra simulations. Insights into radiation-induced defect formation and properties have been obtained in different polymorphs of calcium pyrophosphate [26], and it is planned to expand the studies on other complex calcium phosphate hosts, *e.g.*, brushite and monetite.
- Nanomaterials and nanocomposite materials ranging from nanoparticles, thin films to multiphase functional materials.

NETWORKING

There are several ongoing 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.
- Laboratory of Radiation Chemistry of Solids, Institute of Chemical Physics, University of Latvia; Dr. Gunta Kizane; radiation-induced defects in tritium breeding materials.

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

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SUMMARY OF PLANNING UPDATES

- Local structure analysis of radiation-induced defects in functional single crystals
- Defect engineering of UV-C persistent phosphors
- Comprehensive analysis of paramagnetic centers on complex biomaterials

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].

In the wide field of luminescent materials, couple of promising directions can be outlined – mechanoluminescence [5] and electroluminescence [6], with subsequent studies of mechanisms as well as materials and production methods. Naturally, the interest for luminescence effects with such prominent practical applications is exceptionally high; however, the lack of understanding of underlying mechanisms often slows down the search for novel materials. Recently, a large increase of popularity was experienced by the field of additive manufacturing, where a range of challenges can be solved using optical properties of different materials, especially mechanoluminescence. The ever-increasing interest in improvement of the manufacturing, use cases and long-term quality assurance motivated scientists to look for ways to use existing luminophores (especially, doped metal oxides and complex oxide compounds) and develop new, application-tailored materials.

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 [7,8]; a new mechanism of long-lasting luminescence involving electron tunnelling has been proposed [9]. The work of this and other international groups on mechanisms of long-lasting luminescence mechanisms is summarized in our recently published topical review paper [10].

Additionally, mechanoluminescence is extensively studied combining the previous knowledge on the electronic processes in persistent luminescence materials with the newly developed experimental setup for mechanoluminescence tests. Studies on various production methods, host materials and spectroscopic properties are performed with a row of publications in the making.

Not only the experimental setup for mechanoluminescence measurements was published in detail in year 2022 [14], but also a completely new data analysis protocol was developed and published for automated 2d image analysis of mechanoluminescence while the parts are deformed [15]. This allows the use of our developed materals to be used in a form of paint for real practical applicaitons

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 [11]. The time constant determined for the decay of this luminescence was ≈17 ps [12] and it is very close to the present best result 15 ps found by M. Kano et al. [13].

Thermostimulated luminescence investigation of Al_2O_3:C layer on metallic aluminium was conducted [14] 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. An article on the improvement of Plasma Electrolytic Oxidation on aluminium surface was published in the year 2022 outlining an inexpensive, reliable and energy-efficient way to create flat, large surface area dosimetric coatings with the composition Al_2O_3:Cr, with TRL4 demonstration of the technology. [16]

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.

In addition, the knowledge on alumina-based dosimetry is applied to create dosimetric coatings using Plasma Electrolytic Oxidation. With efforts to produce alumina coatings on metal surface, the research can not only lead to the creation of a very promising method and material for practical applications, but also give an insight on alumina ceramic behaviour under ionizing radiation.

The work on mechanoluminescence will be continued further, as initial feedback from companies working with additive manufacturing methods (Baltic 3D) was very positive, and the possibilities for joint projects or commercialisation are outlined.

NETWORKING

- Prof. P.Rodnyi (Peters the Great Saint Petersburg Polytechnic University, Russia)
- Dr. P. Boutachkov (GSI Helmholtzzentrum für Schwerionnenforschung, Germany)
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SUMMARY OF PLANNING UPDATES

- New directions (mechanoluminescence and electroluminescence) are outlined.
- Recent developments on alumina dosimetry now include coatings.
- Updates are partly based on new projects or achievements.
- Work on persistent luminescence temperature dependence continues.
- Mechanoluminescece setup and data analysis methods are developed
- Electroluminescence field is expanded with the search of new luminophores and dielectric layers
- Plasma electrolytic oxidation for production of dosimetric coatings is greatly improved with future research plans

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 about nonlinear refractive index of material absent from the previously mentioned Optical Kerr spectroscopy works. Recently much attention has been given to application of Laguerre–Gaussian vortex beams in NLO studies [9]. While most of literature has been focused on third-harmonic generation studies scientists are slowly exploring possibility to use vortex beams in Kerr studies [10]. 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 as well as wider exploration of vortex beam applications.

To employ for practical applications third-order effects like Optical Kerr effect (OKE) and two-photon absorption (TPA) effect [11] -, various material groups as NLO media are being studied with different pros and cons. These include:

- ***Metamaterials*** that allow 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 [11], 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 [12]. 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 [13]. 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 [11]. Current state-of-the-art includes few examples of devices using graphene for optical switching [14] or polariton opto-optical devices using organic materials [15]; 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 [16], waveguide MZIs [17] and photonic crystal cavities [18] 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- [19–21] and third-order [6,22] 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 [23,24] and third-order NLO [6,25,26] properties. Development of polarization-resolved Z-scan measurements [27] 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 [17] as well as all-optical gas sensor [28].

Recently we have begun to study NLO properties of nanoparticles and quantum dots. This includes both silver nanoparticles [26] as well as more complex materials such as HgTe [29], HgS [30] and Bi_2Te_3 [31]. These researches have also extended to studies about silver nanoparticle influence on reorientation Kerr effect of organic chromophores have been published [26]. Recently we have also started to study near-zero-epsilon materials with main focus on ITO nanoparticles and their usage for NLO applications [32].

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).

.

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.

We have established both Polarization-resolved Z-scan method for spectral measurements and Beam-deflection method. First experimental results regarding spectral Z-scan measurements have been published [23,24]. Next planned measurement methods are:

- ***Third-harmonic generation*** will allow to extend characterization of NLO properties to study correlation between different third-order effects.
- ***Vortex beam application in measurements*** will be evaluated to study NLO effects in more fundamental studies.

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 to 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 [33];
- ***Raman scattering intensities and frequency,*** which allows us to calculate the vibration contribution [34];
- ***Second-order hyperpolarizability*** values, which allows us to calculate the electronic contribution [35].

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 three 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. First results about silver nanoparticles influence on organic chromophores in solution have been shown [26]. Next step will be focusing more on thin films.
3. ***Study of Near-Zero-Epsilon NLO properties***. This type of materials exhibits high-efficiency NLO properties.

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
- Rashid Ganeev from Laboratory of Nonlinear Optics, UL
- Janis Alnis from Quantum Optics Laboratory, UL
- Kaspars Leduskrasts – Latvian Institute of Organic Synthesis

Europe:

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

Additional:

- Kevin Chiou - National Sun Yat-sen University

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SUMMARY OF PLANNING UPDATES

- Collaboration with Kevin Chiou from National Sun Yat-sen University to study NLO properties of their nanowire samples,
- Build stronger collaboration with people in institute that synthesize different nanomaterials,
- Third-harmonic measurements and vortex beam NLO studies of thin films made from guest-host systems containing organic dyes and polymers.

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. 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 UL 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" that has been launched to strengthen the development of the Latvian scientific community in cooperation with CERN. In December 2022 this program was continued for another three years (2023-2025).

In the framework of EUROfusion activities, 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 50 papers were published in the last 5 years, some of them are referenced in refs [5-12].

Currently, we participate in the consortium within the framework of EUROfusion Enabling Research Project ENR-MAT.01.UT-T002-D001 jointly with Karlsruhe Institute of Technology (KIT) and University of Tartu: "Investigation of defects and disorder in nonirradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis". This project is focused on the development of diamond windows and related dielectric materials for DEMO reactor. More precisely, the project aims to find out how the purity of diamond ceramics, various protective layers and other technological innovations affect the radiation resistance of such windows. We also want to know how and for how long the properties of the window persist under radiation. According to the tasks planned for 2022, Raman, IR, EPR, PL (including via synchrotron radiation), EBSD characterization of different-size diamond windows (pristine/ irradiated), silica and alumina were performed. Furthermore, comparative 2D mapping of the oversized virgin and irradiated CVD diamond disks via CL spectra was carried on. Stepwise annealing of radiation-induced optical absorption in CVD diamonds exposed to energetic iodine ions was investigated and simultaneous decay of complementary Frenkel defects was detected, while a total loss of transparency and strong swelling of the samples gradually took place at pre-heatings above 650 °C. The first principles calculations of the atomic/electronic/vibronic spectra and basic radiation defects in diamond (N, single vacancies) were implemented.

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;
- neutron spectroscopy (inelastic and small angle neutron scattering) of pristine/irradiated samples

- detailed understanding of the optical degradation of irradiated CVD diamonds at high temperatures

Another consortium, we are participating, is HORIZON 2020 - RISE – RADON Project "Irradiation driven nanofabrication: computational modelling versus experiment“, where are partner and principal investigator - MBN Research Center GmbH, Frankfurt-M, Germany), where our main goal is deep understanding of how different nanostructures are formed under irradiation.

NETWORKING

The group has active international collaborations with research groups in:

- France: Dr. Martin Boehm (Institut Laue-Langevin, Grenoble);
- Germany: Prof. Dr. J. Maier (Max-Planck Institute, Stuttgart), Prof. Dr. T. Scherer (KIT, Karlsruhe), Dr, G. Pintsuk (Forschunzentrum Julich GmbH); Prof. Dr. Andrey V. Solov'yov (MBN Research Center GmbH at FiZ - Frankfurter Innovationszentrum Biotechnologie)
- Spain: Dr. Rafael Vila, (CIEMAT, Madrid);
- Sweden: Prof.Dr. Helmut Schober (ESS, Lund), Dr. Kirill Chernenko (MAXIV, Lund)
- Switzerland: Dr. Etiennette Auffray, K. Dreimanis (CERN)
- Estonia: Prof. A.Ch. Lushchik (University of Tartu).

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SUMMARY OF PLANNING UPDATES

- No updates to the initial program (January 2021) are planned (as of January 2024)

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). Modelling and design of new optical sensors using CompleteEASE® [22].

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

Research on innovative metal-oxide, -oxyhydrate and -hydrate thin films and effects of deposition parameters on thin film development in co-operation with Thin Films Laboratory.

To continue collaboration with Nonlinear and Quantum Photonics Group of Prof. Katia Gallo in KTH on dielectric tensor determination of domain walls (DWs) and to understand the optical contribution of DWs of different periodically polled LiNbO3 (PPLN) crystals and to investigate their optical properties and phonon modes.

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)
- Semiconductor interphases: Prof. A. Hallen, Prof. M. Hammer (KTH)
- Optical anisotropy in periodically polled $LiNbO_3$ thin films and crystals: Prof. K. Gallo (KTH)
- SiO_2 and SiC: Dr.phys. S. Karlsson (RISE AB)

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SUMMARY OF PLANNING UPDATES

- Temperature controlled hot stage integrated to the ellipsometer: system ready for thermo-optical investigations.
- Complex dielectric dispersion curves, optical band gap and optical depth profile as a function of the sputtering pressure obtained for the HiPIMS sputtered YHO thin films [23].

- Theoretical modelling of enhanced reflectivity change and phase shift of polarized light for double parameter multilayer sensor development: biomedical applications.
- Optical anisotropy study of epitaxial β-Ga_2O_3 thin films sputtered on *c*-, *a*-, and r-sapphire substrates.
- Evaluation of the optical band gap, complex dielectric curves and optical depth profile variation in ZnMgO thin films with different Zn content [24].
- First determination of refractive index and extinction coefficient for reactive pulsed DC magnetron sputtered narrow band gap semiconducting yttrium oxide thin film [25].
- Evaluation of the Cu diffusion in WO_x layers in antipathogenic multilayer structure PET/WO_x/Cu/WO_x.
- Simulation of complex dielectric function for domain walls in PPLN crystals (collaboration with KTH).
- Determination of complex dielectric function for irradiated and non-irradiated $MgAl_2O_4$, YAG, PbF_2, GGAG, and other crystals for fusion diagnostic applications.
- New project application submitted in May 2023 about development of 2D materials on periodically poled lithium niobate platform for novel applications in opto- and nano-electronics with enhanced functionalities. Project received good evaluation (13.5 from 15) but did not receive founding. The project description will be improved and resubmitted in 2024.
- Interphase layers simulations for OLED systems using CompleteEASE (LZP-2022/1-0331 project started on January 2023).
- Thermo-optical investigations of VO_x thin films: direct observation of the phase transition at 68°C for main ellipsometric angles (SWEB project started on November 2022).
- Automated rotation stage installed to the ellipsometer: system ready for high precision sample rotational experiments highly necessary for anisotropic studies.
- Spectroscopic ellipsometry investigation of the oxidation and migration of Cu in WO_3 films over time in three-layer antibacterial and antiviral WO_3/Cu/WO_3 transparent and counting coatings (ERDF project No. 1.1.1.1/21/A/050). Optical property modelling is used to optimize the thickness of the three-layer coatings to obtain the highest figure-of-merit for a transparent electrode. A structure of glass/WO_3 (70 nm)/Cu (10 nm)/WO_3 (45 nm) gives a sheet resistance of 14 Ω/sq. and a light transmittance of 65% at 600 nm [26].
- The time-dependent optical and structural change investigations occurring in a photochromic YHO thin film during the transition from a transparent to a dark state. The study revealed the expansion and contraction processes and change in optical properties taking place within the photochromic YHO film under UV illumination (paper draft prepared).

DEVELOPMENT OF NOVEL FUNCTIONAL MATERIALS

This section comprises research plans of studies having their primary focus points at creating new materials for photonics; nuclear energy; radiation detection and conversion; for energy storage and harvesting.

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, 54, 56].

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.) [42-50]. 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.

The three main accomplishments during the last year, which have an impact on the future planning, are:

- Published an original research work on stress induced reversible kink formation in CuO nanowires [52]. This work reports for the first time the post-synthesis formation of such defects, achieved by exploiting a peculiar plasticity that may occur in nanosized covalent materials. Specifically, in this work the authors found that single-crystal CuO NWs can form double kinks when subjected to external mechanical loading. Both the microscopy and atomistic modelling suggest that deformation-induced twinning along the $(\bar{1}10)$ plane is the mechanism behind this effect. In a single case the authors were able to unkink a NW back to its initial straight profile, indicating the possibility of reversible plasticity in CuO NWs, which is supported by the atomistic simulations. The phenomenon reported here provides novel insights into the mechanisms of plastic deformation in covalent NWs and offers potential avenues for developing techniques to customize the shape of NWs post-synthesis and introduce new functionalities.
- Published a critical review article on ZnO nanowires Young's modulus determination by experimental and theoretical methods [53]. Main attention was focused on a widespread problem related to the vast disagreement in elastic moduli values reported by different authors for nanostructures made of the same material (in this case ZnO nanowires). The most of works consider the same growth direction and wurtzite crystal structure, reported values of Young's modulus vary drastically from author to author ranging from 20 to 800 GPa. Moreover, both – diameter dependent and independent – Young's modulus values have been reported. In this work, the authors provide a critical overview and perform a thorough analysis of the available experimental and theoretical works on the mechanical characterization of ZnO NWs to find out the most significant sources of errors and to bring out the most trustable results. A special attention was paid to clarification of strong discrepancy between theory and experiment in regard of size effect dependence for Young's modulus of ZnO nanowires.
- Published a research work dedicated to comparison of Ag, Cu, Cu-Ag nanomaterials functional parameters for conductive coating applications. Spray deposition and inkjet printing of various nanostructures are emerging complementary methods for creating conductive coatings on different substrates. In comparison to established deposition techniques like vacuum metal coating and lithography-based metallization processes, spray deposition and inkjet printing benefit from significantly simplified equipment. However, there are number of challenges related to peculiar properties and behaviour of nanostructures that require additional studies. In present work, we investigate electroconductive properties and sintering behaviour of thin films produced from

nanostructures of different metals (Ag, Cu and Cu-Ag) and different shapes (nanowires and spherical nanoparticles), and compare them to the reference Ag and Cu magnetron deposited films. All nanowires-based films provided high conductivity and required only modest thermal treatment (200 ∘ C), which make them very attractive for large area transparent conductive electrode applications using spray deposition. To achieve sufficient sintering and conductivity of nanoparticles-based films, higher temperatures are required (300° C for Ag nanoparticles and 350 ∘ C for Cu and Cu-Ag nanoparticles). Nanoparticle based inks are ideal for precise deposition of conductive patterns using functional ink-jet printing.

FUTURE ACTIVITIES

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

(1) Development of 1D core-shell nanowire heterostructures based on charge density wave (CDW) materials ($TaSe_2$, $TiSe_2$, VSe_2); (2) Development of superconducting MgB_2 thin films and 1D core-shell nanowire heterostructures with superconducting MgB_2 shell; (3) Development of nanomanipulation setup for nanotribological and nanomechanical experiments with 0D, 1D and 1D / quasi 3D (e.g., ZnO tetrapods) nanomaterials. Development of MEMS device for 1D nanostructures simultaneous stretching and electrical conductivity measurements.

1. We are investigating 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.

2. We are developing technology of superconducting coatings based on MgB2 material and hybrid superconducting nanowire synthesis with goal to create nanomaterial suitable for photodetection in broad wavelength range. It is planned to experimentally investigate the effect of strain in MgB2 nanocoatings on its superconductivity transition temperature using various approaches of strain engineering in a core-shell nanowire (NW) configuration, including epitaxial mismatch strain, interstitial impurity strain and nanomechanical tensile tests of individual NWs in situ cryostat.

3. Nanomanipulation setup for nanomechanical experiments with 0D, 1D and 1D / quasi 3D nanomaterials is under development. There are several possible configurations depending on application: a) set Kleindiek "robot-arm"nanomanipulators, suitable for controllable deformation of 1D nanostructures, measurement of electrical properties and electrical excitation of mechanical oscillations; b) quartz tuning fork based sensor mounted on SmarAct 3D orthogonal nanomanipulator for force detection in nano-range. This configuration needs smooth piezo-scanners and controllers to make possible line or raster scanning like in AFM.

NETWORKING

Five Laboratories of ISSP UL 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 ISSP UL 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: Institute of Physics and Institute of Technology, University of Tartu (Estonia), Royal Institute of Technology KTH Stockholm and RISE Research Institutes of Sweden, Daugavpils University (Latvia), Riga Technical University (Latvia).

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SUMMARY OF PLANNING UPDATES

- New method of core-shell nanowires preparation is under development, where 2D shell is produced from transition metals in quartz ampoule at low pressure at elevated temperature using sulphur or selenium precursors.
- Alternative method of core-shell nanowires preparation is under development, where 2D shell is produced from soluble transition metals salts in quartz tube in inert atmosphere of glovebox at elevated temperature using sulphur or selenium precursors.
- Development of MgB_2 thin film deposition using direct magnetron deposition of Mg and B precursors using dual magnetron sputtering and following annealing in inert atmosphere.
- Nanomanipulation setup, based on Kleindiek and SmarAct nanopositioners equipped with quartz tuning force sensor, is under construction. Sharp W or AFM tip is glued to tuning fork and can be used for nanomanipulations of 0D, 1D and 1D/quasi 3D nanostructures.
- Silicon based MEMS actuator for simultaneous 1D nanostructures stretching and conductivity measurements is under development. Such MEMS device can be inserted into SEM microscope for in-situ experiments, and more advanced version of the device can be inserted in Liquid Helium cryostat for experiments at low temperatures.

MATERIALS FOR PHOTONICS APPLICATIONS

ELECTROLUMINESCENCE AND ORGANIC LIGHT-EMITTING DIODES

STATE OF THE 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) are 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 2207 publications in year 2021 (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 (ΔE_{S1-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. Recently Cu-based organic materials were used in the OLED. [15]

Nowadays, there are two more generations of OLED. The fourth generation (G4) is related to the combination of G1 and G3 molecules, where electrically excited states from G3 molecules move to G1 molecules via Forster resonance energy transfer. This process is known as superfluorescence. The latest generation of OLED materials (G5) consists of molecules with inverted singlet-triplet states. This means that electrically excited triplet states can transition to the singlet state and emit light.

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 and has investigated carbene–metal–amide (CMA) type organic emitters for OLED.

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. Recently bought thermal evaporator in glovebox will be used to prepare high quality OLED structures.

- 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-situ* 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.

- Degradation mechanism investigation by ellipsometry

Investigation physicochemical properties of the interfaces, and their dependence on the deposition conditions and their role in the performance and degradation kinetics of organic electronic devices is very important. Interfaces between thin films of different organic materials and multilayer structures should be investigated to understand the interface contribution to interfacial transport of electrons and the degradation of OLEDs, and to explore the possibilities of interfacial tuning with the aim to improve the OLEDs performance. Advanced spectroscopic ellipsometry (SE) technique can be used to study layered polymer/molecular glass systems tailored to the parameters of the film deposition and post-deposition treatments, and analyse in-situ the degradation kinetics of the OLEDs device under the thermal and electrical load.

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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SUMMARY OF PLANNING UPDATES

- OLED degradation

LIGHT AMPLIFICATION AND ORGANIC SOLID-STATE LASERS

STATE OF THE 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 μJ/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 μJ/cm^2) [3]. The same is for green emitters (around below μJ/cm^2) [4]. A yellow emitter has around 10 μJ/cm^2 [7], a red emitter has around 24 μJ/cm^2 [8], and for infra-red emitter it is 20 μJ/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 ones in the red spectral region (24 μJ/cm^2). This value is still one order of magnitude higher in infra-red spectral region (165 μJ/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].

New type of organic solid state lasers were developed that can be excited by organic light-emitting diode.

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 μJ/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 methyl 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 μJ/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 μJ/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.

- ASE 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.

- Investigation of NIR emitters.

Organic compounds have been widely used in dye lasers and the same or similar compounds can be found in organic solid-state lasers. Most of the compounds have emission in the visible spectral region with the amplified spontaneous emission or laser emission excitation threshold energy below 1 $\mu J/cm^2$. Organic near infrared emitters have higher threshold energies, but they are more competitive compared to inorganic infrared lasers. Inorganic III-V semiconductor has low exciton binding energy (around 6 meV) which partially is the reason of low photoluminescence quantum yield of these materials. Additionally, a specific three or mostly a four-level system should be made to get population inversion. Organic materials exhibit the four-level energy system in the molecule and no additional modifications should be done. Organic compounds have higher Frenkel exciton binding energy (more than 200 meV), which increases the recombination possibility of the excitons. Organic materials that form thin films from solution would additionally benefit due to the possibility to make lasers by simple wet casting methods. Thus, such properties could increase the applications of lasers in telecommunication, bioimaging and lab-on-chip

- 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, technology and experimental setup should be developed:

- 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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SUMMARY OF PLANNING UPDATES

- Investigation of NIR emitters
- CW laser

MATERIALS FOR RADIATION CONVERSION

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. TL materials have been used in personnel, environmental and clinical dosimetry for many years. Key issues to consider when selecting a radiation dosimeter are: What is the application? What are the anticipated radiation fields? What are the anticipated dose levels? The main groups for dosimetric materials studied are fluorides (LiF:Mg,Ti; LiF:Mg, Cu,P; CaF_2:Mn; CaF2:Dy), sulphates ($CaSO_4$:Mn; $CaSO_4$:Dy: $CaSO_4$:Tm), borates ($Li_2B_4O_7$:Mn; $Li_2B_4O_7$:Cu), oxides (Al_2O_3:C; Al_2O_3:Mg,Y; BeO, MgO) and others. Among the prospective materials for the new clinical dosimetry and space exploration areas the nanopowdered materials and optical fibres with different dopants are being studied [12, 13]. 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 for medical needs, 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. In 2D and 3D dosimetry, the main challenge is development of dosimetric OSL materials with fast luminescence lifetimes (much less than 1 µs), to allow the fast readout of films using laser-scanning techniques such as those used in computed radiography. 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.

Different TLD materials in the form of glass, microcrystalline, nanocrystalline phosphors have been studied in search of new prospective TL/OSL materials. It was concluded that studies on TL dosimetry materials should be focused fundamentally on the development of more efficient phosphors, compared with existing materials. The search for new TL materials should aim for simplicity of glow curves, a high range of TL response linearity and very low fading. Furthermore, the TL mechanism is also very important and must be considered before developing new efficient materials for different applications.

OUR POSITION

Researchers of the dosimetry group (L. Trinkler, B. Berzina, A. Zolotarjovs) 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 data, e.g. ref. [5, 14] indicate that dosimetric properties of Al_2O_3 the form of 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. In future we plan the investigation of the material using mainly the OSL method.

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 of AlN with transition metals and rare earth ions. AlN ceramics samples, pure and doped with Y_2O_3, Eu_2O_3 and GaN were studied for photoelectric effect, photoluminescence spectra and kinetics and thermoluminescence under irradiation with UV light from above- and below- bandgap spectral region [15]. The additional studies of materials are planned using mainly the OSL method.

Wide band gap dielectrics, on the example of $LiGaO_2$ (LGO). LGO is a wide band gap (E_g=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 and OSL. The further investigations have shown that, although this material provides only a weak response to ionising radiation and UV light and hardly can be applied as a dosimetric material, the TL/OSL methods used are very useful instruments for elucidation of the energy transfer and luminescence mechanisms, which allows revealing and characterization of pyroelectrical luminescence in LGO [16, 17].

Novel approaches under development include two and three-dimensional dosimetry for radiotherapy applications, dosimetry for new radiotherapy modalities, such as laser-induced particle beams, FLASH radiotherapy, and magnetic resonance-guided radiotherapy; accident dosimetry and neutron dosimetry using fluorescent nuclear track detectors. The need for new TL and OSL materials exists, it is limited to specific applications; any new material must satisfy the requirements for those applications. Research of new materials should substantially advance the understanding of a physical process and demonstrate that these materials have advantages compared to the existent materials or technologies. The models must be developed that provide a deeper understanding of the defects involved and the role played by them. Investigating and elucidating the roles and predominance of defect clustering and localized transitions in high-sensitivity TL/OSL materials may also play a key role towards a more guided "defect engineering" of new material. The main challenge for luminescence dosimetry is in materials engineering. Of importance is a more efficient and systematic development of new TL/OSL materials, potentially offering properties currently not available in the existing ones. Some of these properties may not only satisfy the presently identified needs, but perhaps can open the possibility of new, not-yet-envisioned applications of TL/OSL materials [18,19]. A better understanding of the influence of synthesis parameters and methods on the final luminescence and dosimetric properties is required.

TL/OSL investigation of wide band-gap dielectrics, including oxides single crystals, polycrystals, powders and ceramics, optical glass fibres will give new insights in luminescence mechanisms and estimate applicability of new materials for dosimetry of ionising and UV radiation in the fields of medicine, radiation safety, environment, industry and space flights.

There are many commercial dosimeters available for use in radiation dosimetry, but these are applicable only within a specific range of radiation doses. Although researchers have suggested the use of high intense phosphor as SO_4:Dy, this phosphor is not accurate due to variation in the glow peaks at high doses. Moreover, another limitation was saturation of the TL signal in many materials at higher doses. Therefore, there is a need to explore more sensitive materials that show linear TL responses over a wide range, materials that are energy independent, thermally stable and have low fading. Research is progressing rapidly to develop new TL materials. One of such new materials is AlN, studied in our works.

There is continuous demand for efficient TL dosimeters for monitoring high-dose levels of swift heavy ion (SHI) radiation. This demand is growing daily, as these ions are used extensively in medical applications. The significance of SHI ion therapy over photon radiotherapy is that it delivers a better mean energy per unit length at a particular depth. SHI irradiation also modifies the luminescence properties of the material. Moreover, SHI-exposed phosphors can be used for high energy space dosimetry, ion beam dosimetry for personnel applications, radiotherapy, or diagnostic purposes, etc. Therefore, there is considerable scope for work on SHI dosimetry. [20]

Studies on nanomaterials have reported high sensitivity and saturation at very high doses. Therefore, they have potential application in dosimetry of ionizing radiations for measurements of high doses, at which conventional microcrystalline phosphors saturate. Therefore, future work may focus on developing nanomaterials based on their wide linear range. The use of personal neutron dosimetry currently grows rapidly. Recently, $CaSO_4$:Dy and MgB_4O_7:Ce, Li were synthesized to study neutron dosimetry. Moreover, materials containing Li, or Li and B simultaneously, were found to be more sensitive to neutrons. If these materials were enriched in ^{6}Li and B, isotopes became sensitive to thermal neutrons [20]. Therefore, future work may be focused on developing a thermoluminescent material sensitive to neutrons.

Another prospective area of luminescence dosimetry is OSL dosimetry for case of high energy physics (HEP). The specifications to be met by a radiation monitor in this environment should be 1) a total dose measurement range of 10 kGray and 2) with reset capabilities it should be able to measure short radiation bursts. The main advantages of the OSL materials are: 1) a dynamic range that covers seven orders of magnitude; 2) a very high sensitivity (100 µGy) that depends on both the amount of material in the sensor and the photosensor used to collect the luminescence; 3) a 50-µm resolution when used as silk-screen printed films. [21]. Different examples of OSL dosimetry already used for HEP can be mentioned:

- The SrS:Ce,Sm phosphor suitable for operation in harsh radiation environments where real-time dosimetry measurements. The advantages of this system are the combination of OSL and optical fibers, immediate readout, simplicity of use, low cost, reliability, flexibility, and robustness. The applications targeted are the measurement of the dose delivered during a treatment in radiation therapy and the monitoring of the dose or dose-rate around or in nuclear reactor and accelerator facilities in high energy physics [22 2008].
- To characterize the hadron environment of Large Hadron Collider (LHC) the OSL material based on kapton foil was used and an OSL sensor produced. To enhance the sensitivity of the material to neutron irradiation it was mixed with polyethylene or doped with boron [23 theses]

Further experiments are still to be conducted in order to fully characterize the system and evaluate the feasibility of each application mentioned.

Furthermore, TL/OSL methods have a fundamental role in research on luminescent materials, including scintillators and persistent phosphors. TL is extremely sensitive to small concentrations of defects and can be used to detect defect energy levels or to investigate phenomena such as tunnelling between defects. This will help to engineer new luminescent materials for a variety of applications.

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 accessory, allowing an additional sample irradiation UV light. The TL, OSL and radioluminescence signals can be spectrally analysed using an additional spectrometer and CCD camera. Development of the OSL experimental setup is planned using LED sources of different wavelengths. Additionally, the dosimetric studies are complemented by photoluminescence emission and excitation spectra measurements. Therefore, there is a need to enhance the experimental basis for the PL/TL spectral measurements by acquisition of Andor Spectrograph Kymera with 4 gratings, with ICCD IStar 320 and accessories), and closed cycle cryostat (5.5- 800 K) for optical spectroscopy.

FUTURE ACTIVITIES

- Development of Al2O3 and AlN-based dosimetric materials in the form of ceramics using mainly the OSL method.
- TL/OSL Investigation of wide band-gap dielectrics, including oxides single crystals, polycrystals, powders and ceramics, optical glass fibres for application in medicine,

radiation safety, environment, industry, space flights 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; -upgrade of the set-up for PL/TL spectral measurements with a new spectrograph and CCD camera; - upgrade of the Lexsyg research TL/OSL reader by installing a Peltier cooling element in the device, thus enabling TL/OSL measurements at temperatures below RT (beginning from -50 C).

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. Benabdesselam).

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, Vilnius, Lithuania Dr. R. Nedzinskas and Dr.S. Tumenas, Dr.Jurga Juodkazyte).
- Institute of Applied Research, Vilnius University, Lithuania (Dr. S. Miasojedovas, Dr. P. Scaev).
- Technological group of Riga Technical University (Dr. I. Steins)
- Company Freiberg Instruments, Freiberg, Germany (Dr. M. Richter).

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SUMMARY OF PLANNING UPDATES

- Dosimetric properties of Al_2O_3 and AlN related materials will be studied focusing mainly on OSL method. Development of the OSL method using of the Freiberg Legxyg equipment.
- TL/OSL investigation of wide band-gap dielectrics is planned, including oxides single crystals, polycrystals, powders and ceramics and optical glass fibres placing the main emphasis on materials luminescence mechanisms and dosimetric properties for application in medicine, radiation safety, environment, industry and space flights.
- Upgrade of the experimental set-up is planned with Andor Spectrograph Kymera and Closed Cycle Cryostat (totally 5.5- 800 K).
- Upgrade of the Lexsyg research TL/OSL reader by installing a Peltier cooling element in the device, thus enabling TL/OSL measurements at temperatures below RT (beginning from -50 C).

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 resolution 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 well-supported 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, 5] and FINESTLUMI endstation [6, 7]. 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 [8], BaI_2, BaBrI [9], YAG:Ce nanocrystals [10], cryogenic scintillating material CsPbBr [11], complex oxides $SrBO_4$ [12]. 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 [13-15]. Moreover, radiation defects and damages induced in GGAG:Ce by swift heavy ions have been studied for the first time [16].

Furthermore, using advantages of the photoluminescent endstation (FINESTLUMI) installed at MAX IV synchrotron facility we have recently carried out unique experiments in double activated fluoride single crystals. Excitation spectra in VUV spectral range of rare-earth ions in fluorides with meV spectral resolution have been successfully measured and deconvoluted [17-18].

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.

- Development of red and infrared scintillators based on rare-earth doped fluorides. The main attention will be focused on the fundamental properties of rare-earth ions in vacuum ultraviolet spectral range with meV spectral resolution and the relaxation processes resulting to the infrared luminescence.
- 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.
- Expand the studies of luminescence characteristics as well as radiation defects by means of synchrotron based methods to optical materials having practical interest in nuclear physics and fusion applications. These materials ($MgAl_2O_4$, Ga_2O_3, $Gd_3Ga_5O_{12}$, Al_2O_3, MgO, Si_3N_4, etc.) do not belong to the scintillators, however the approach utilized to the study of scintillators perfectly fits for such non-luminescent materials as well.
- Development of ultrafast scintillator materials based on cross-luminescence phenomenon. Both theoretical and experimental engineering of fluorides to obtain cross-luminescence materials with time resolution down to 10 ps.

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 (Photon Science Division at DESY)
- Sweden: Dr. K. Chernenko and Dr. K. Klementiev (MAX IV Laboratory, Lund University)
- Estonia: Prof. A. Lushchik and Prof. M. Brik (Tartu University)
- Ukraine: Prof. A. Voloshinovskii and Dr. V. Vistovskii (Lviv University)
- Russia: Dr. R. Shendrik (Vinogradov Institute of Geochemistry, SB RAS, Irkutsk)
- Kazakhstan: Dr. Z.T. Karipbaev (Gumilyov Eurasian National University)
- Poland: Prof. A. Kaminska and Dr. Y. Zhydachevski (Warsaw University)

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Summary of planning updates

- The study of luminescence properties of rare-earth doped fluorides in vacuum ultraviolet spectral range with meV spectral resolution.
- Extension of the research utilizing advanced synchrotron methods to optical materials.
- The study of ultrafast cross-luminescence in novel fluoride materials by means time-resolved luminescence spectroscopy using pulsed synchrotron radiation excitations.

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 covers 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 the PersL light with colours from blue to yellow spectral regions are the best investigated, whereas there is considerably less information on the red and infra-red light emitters, which are essential for biomedical applications. Development of new prospective PersL materials is actual and there are numerous studies in this field (see papers [1-4] and references therein). Among the main problems are elaboration of new materials and understanding the PersL mechanisms, which would help to increase 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. [5-15]). The group is well-qualified in optical and magnetic spectroscopies as well as in material synthesis.

FUTURE ACTIVITIES

The proposed research includes synthesis and studies of luminescence properties and mechanisms in several prospective groups of materials: (I) Transition metal ion- and rare earth ion-doped PersL oxides, alkaline earth silicates, germanates and stannates; (II) third element group nitrides doped with the same type ions; (III) materials, emitting red – infra red light, selected during experiments. The second group of materials includes AlN doped with ions of transition metals and rare-earth elements such as Mn^{2+} and Eu^{2+}. The nano-sized structures of these 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 materials and their synthesis. For this purpose, the common high temperature methods are actual.
- Elaboration of low temperature synthesis methods for processing of the materials from the II and III groups.
- Manufacturing of nano-size particles from the synthesized materials above.
- Analysis of the structure, morphology and defect content of the synthesized materials.
- Investigation of spectral and time-dependent luminescence characteristics of PersL oxides, nitrides and other materials.
- Investigation of the luminescence afterglow of photo- and X-ray excited materials, which directly characterizes the PersL properties.
- Special emphasis will be paid to the structural studies of the luminescence and carrier trapping centres using electron paramagnetic resonance (EPR) methods. A methodology for correlated EPR and luminescence (decay kinetics, thermally stimulated luminescence) measurements has been implemented and will be further developed.
- Investigation of the thermoluminescence properties, which directly characterize the PersL properties.
- Analysis of results ensuring close feedback between the material optical properties and its processing.

Two new projects related to the planned activities have been submitted: (1) Latvian – Ukrainian Joint Programme of Scientific and Technological cooperation Project Proposal. ”Novel prospective long-lasting luminescent materials for biological applications”. (Dr. B.Berzina) Partner: Institute of Physics of National Academy of Sciences of Ukraine. (Dr. Galyna Dovbeshko); (2) Latvian Council of Sciences project: “Novel persistent luminescent solid-state nanomaterials for biological application” Nr. lzp 2023/1-0488. (Dr. B. Berzina). The project was evaluated above the threshold, however, was not approved due to lack of funding.

NETWORKING

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

- 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. Dr. Anna Zajakina. Biomedical Center at University of Latvia (BMC UL). Application of luminescent nanomaterials for testing of biomaterials.

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SUMMARY OF PLANNING UPDATES

- A methodology for correlated EPR and luminescence (decay kinetics, thermally stimulated luminescence) measurements will be further developed.

- In-depth study of the thermoluminescence characteristics together with the luminescence spectra, which allow detailed characterization of the PersL (persistent luminescence) properties are planned.

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. However, the demand for higher energy density and improved electrochemical performance in general require short- to medium-term improvements. In parallel, sustainability-related issues (i.e. material availability and toxicity) drive the development of post-Li-ion batteries [4].

Development of lithium-ion batteries (LIB) has come a long way since their first commercial implementation in 1991. Since then, with the gravimetric energy density of LIBs more than doubling [5], the research and development of LIBs is ongoing. We are currently in generation 3b of LIBs [6], with Nickel-Cobalt-Manganese oxide (NCM) ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, proportion of nickel is increased from NCM 111 to NCM 811 and is already advancing 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), all-solid-state batteries, and Li/S or Li/O_2 technologies further out in the future [6] while a parallel track of $LiFePO_4$ and alternatives to Li-ion have emerged, dictated by sustainability and material availability related questions.

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, sodium-ion battery (SIB) technology is the most mature and has a high potential for further growth, especially for application in grid-level energy storage [7] and budget EVs. With sodium being the 6th most abundant element in Earth’s crust, the raw materials are more readily available and costs – significantly lower. While the high-rate capability, stability and recyclability of SIBs are considered very attractive [8], cycle life and energy density 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 prompts for developments in electrolyte or artificial engineering of SEI via coatings. Another interesting approach is ionic liquid (IL) -based electrolytes for SIBs. In this case, 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 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

- Electrode material development focused on reduced graphene oxide, other carbon nanostructures and transition metal oxides [14,21–23] for LIBs; polyanionic compounds ($Na_2MP_2O_7$ and Na transition metal oxides $NaMO_2$ (M – Fe, Mn)) as cathodes for SIBs, their stability in aqueous electrolytes
- Cross-functional LIB and SIB electrode improvements: electrolyte additives (FEC), electrode binders (focus on sustainable aqueous electrode processing), electron-conductive additives, inert protective coatings for active electrode materials
- Electrolyte research focused on advanced polymer – ionic liquid composite sodium-ion electrolytes [24, 25]

Cycling stability of Li-ion battery materials and cells

- Ageing of LIB cells as a function of temperature, C-rate and other parameters
- 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

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

Mass transport within electrodes and across interfaces (longer-term perspective)

Fundamentally oriented research:

- Lithium and sodium transport within electrodes (ionic and electronic conductivity, transport mechanisms);
- SEI stability and ionic transport across SEI;

FUTURE ACTIVITIES

We aim at good knowledge in battery electrode development, processing and testing, strengthened through contacts with local and European battery industry. Our competitive edge will be the availability of advanced material characterization techniques, including *in-situ* and *in-*

operando methods currently in development. For this, further investments in human and material resources are planned:

- *Materials for Li and Na-ion materials:*

- SIB cathodes: finalizing studies on $NaMP_2O_7$, layered oxides, layered oxides for Na-ion batteries; initiating new studies on next-generation layered SIB cathodes, protective coatings for SIB cathodes (three project proposal submitted)
- LIB electrodes: leveraging existing developments of carbon-based and nanostructured materials in ISSP, screening and optimizing these for use in LIBs; sustainable and industrially feasible electrode preparation for LIBs; inert protective coatings for LIBs; development of anodes optimized for low-temperature performance, continued studies of 2-dimensional carbon structures; overlap and collaboration with developing materials and electrodes for supercapacitors is planned
- Electrolytes: development of solid-state electrolytes using thin film technology (one project proposal submitted), ionic liquids, polymer-ionic liquid composites (one project proposal submitted); nanostructured and high-surface area additives (e.g. carbon-based additives – graphene, few-layer graphite, etc.), novel primarily water-based binders (one HE project proposal has been funded recently), conductive additives, protective electrode coatings (two proposal submitted), leveraging the strength of ISSP in thin film deposition techniques.
- *Battery cell cycle life*. Continued 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.
- *Development of in-situ and in-operando characterization capability* of battery materials for assessing ageing mechanisms in LIBs and SIBs by leveraging strengths of ISSP in optical microscopy, Raman spectroscopy, XRD, synchrotron X-ray, gas mass chromatography, mass-spectrometry
- *Services to industry*. Electrochemical characterization, prototype assembly (coin-cells, eventually 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) produce publishable results relatively quickly and address more fundamental research questions, subsequently generating more impactful fundamental results via in-depth studies of the materials developed.

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 that started in 2021 and already has 2 publications with collaboration partner Centre for Solar Energy and Hydrogen Research Baden-Wurttemberg (ZSW).

Personnel development. Continued development of personnel is needed, increasing the proportion of PhD students and young researchers relative to undergraduate students. Gradual involvement in preparation of project proposals is encouraged starting PhD level to ensure continued funding of the personnel. Preparation of high-quality (Q1) research articles is prioritized.

Existing facilities. ISSP's facilities currently include basic laboratory equipment, equipment for electrode coating (mixer mill automatic coater, vacuum oven, high-precision balance), battery cell assembly (Ar-filled glovebox) as well as 75 channels for cell characterization. There are also good synthesis capabilities (syntheses in air and inert atmosphere are possible), equipment for basic structural and compositional analysis (XRD, SEM-FIB, TEM-EDX, XPS) is available.

Facilities – outlook. Expansion in electrochemical testing channels is needed along with climate chambers ensuring constant conditions during the measurements of electrochemical cells. Small equipment for mixing electrode slurries, calendaring and drying electrodes is needed and will be ordered within next year, provided at least one battery-related project application submitted in 2022 is funded. Longer-term plans and needs include equipment for pouch cell assembly (~80k Eur). Continued renovation of laboratory and office space is also needed to ensure both safety of the personnel and comfortable and motivating working conditions.

NETWORKING

- ZSW: Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Margret Wohlfahrt-Mehrens, focuses on applied research of battery materials and cells;
- 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;
- Kaunas University of Technology, Faculty of Chemical Technology – Agne Sulciute, Metal oxide composites and nanomaterials for energy storage
- University of Tartu – Alar Janes, materials for Na-ion batteries and supercapacitors;
- 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 protons using fuel cell technology.

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SUMMARY OF PLANNING UPDATES

- Minor updates to state-of-art specifying advances in NCM Li-ion cathode and parallel sustainability-based development track (LFP Li-ion cathode and Na-ion batteries).
- Clarification of our current position based on the funded projects.
- In future activities applied research and industry-related activities have been prioritized. This is a consequence of the successful networking with battery industry and applied research institutions, as well as the funded project portfolio – applied projects on low temperature Li-ion batteries, inert coatings for Li-ion battery electrodes and materials for supercapacitors have been funded by European Space Agency, M-Era.net and Horizon Europe at ISSP in 2023.

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 [1a]. That includes small- and large scale pilot project in various regions, which opens an opportunity for Latvia and ISSP UL to be a focal point of hydrogen technology research in various areas.

Research and industrial innovation in hydrogen applications is an EU priority and receives substantial EU funding through the research framework programmes. Hydrogen projects are managed by the Fuel Cells and Hydrogen Joint Undertaking (FCH JU), a public-private partnership supported by the European Commission. Almost all EU Member States recognise the important role of hydrogen in their national energy and climate plans for the 2021-2030 period. About half have explicit hydrogen-related objectives, focussed primarily on transport and industry [1b].

The main industrial hydrogen production processes are electrolysis and thermolysis, the technology to obtain bio-hydrogen from biomass by fermentation is under development. Global capacity of electrolysers, which are needed to produce hydrogen from electricity, doubled over the last five years to reach just over 300 MW by mid-2021. Around 350 projects currently under development could bring global capacity up to 54 GW by 2030 [2a]. In addition, it is projected that by the same year methane conversion to hydrogen (with carbon captures) could reach 14 million tonnes. In addition, Latvia has multiple companies that work in the industry, which sets us at a good position for catalyst development and possibly device development.

Studies of hydrogen application in transport sector and decarbonisation of gas networks with hydrogen-enriched biomethane in Latvia are performed [2b, 2c]. Municipal and national enterprises (Rīgas Siltums, Latvenergo, Conexus) announced their interest to involve hydrogen as energy carrier to support decarbonisation plans in national economics. Companies, such as Latvenergo, have started training its engineers for hydrogen technologies and is exploring ideas for possible projects. Other local companies have shown interest in Hydrogen on a smaller or larger scale, a new entity Hydrogen Alliance has been established with many new industry participants.

Electrochemical hydrogen–water conversion is an ideal energy system that can produce fuels via sustainable, fossil-free pathways. However, the energy conversion efficiency of two functioning technologies in this energy system—namely, water electrolysis and the fuel cell—still has great scope for improvement. For hydrogen production efficiency increase and further development of technologies, new materials are needed, e.g., effective, stable and cheap catalysts to replace precious metals like platinum in water electrolysis, in microbial and proton exchange membrane fuel cells, and in storage (hydrogen bonding in solids or on the surface) [2d]. Potential substitute for Pt and noble metals in electrocatalytic electrodes could be substituted by N-doped nanostructured carbon (N functionalized graphene (N-G), activated carbon, and others) or other scalable catalysts, such as copper, iron-nickel composites and others [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. Collection from exhausts and electrocatalytic CO_2 reduction into hydrocarbons such as methane or ethylene, as well as photocatalytic CO_2 reformation, can lower carbon footprint in addition to other types of pollutants; 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, and 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 solutions for remote locations or for passive catalytic component in the cycle. In case of hydrogen production in light-induced water splitting process, recent results reported as 9.8 μmol·mg^{-1}h^{-1} on Pt-TiO_2 [6] and 100 000 μmol·mg^{-1}h^{-1} of hydrogen production on carbon materials [6d]. Investigation and improvement of efficiency and composition of electrode for example by production of binary systems (TiO_2/nanocarbon structures [6b], TiO_2/WO_3 [6c]) increasing charge carrier separation and sensitivity to visible light region were started and preliminary results reported.

Currently, waste management and energy production are recognized as an essential field for world sustainability assurance. Aluminium (Al) is a very important strategic material in Europe with wide variety of application areas. Unfortunately, this invokes huge amount of waste Al generation. Despite part of waste Al being recycled, there are plenty of landfilled Al, which pollutes environment. Therefore, we will initiate scientific and engineering activities revealing innovative ways for waste Al application in electricity generation using hydrogen produced after waste Al-water reaction. Obtained reaction by-product can be further recycled back to Al via carbon free electrolysis or used as a precursor for other valuable materials production [7].

Hydrogen storage and transport in displaced storage medium i.e., aluminium, methane, methanol etc. is perspective direction with appropriate catalyst. In all these reaction additional heat and other by-products can be produced, which in turn, can be utilized further. New insights into reaction kinetics and pH changes have been elaborated combined with hydrogen production from aluminium . [7a, 7b]

OUR POSITION

Running project AliCE-Why has opened new directions and opportunities in the areas of Carbon capture, hydrogen production, aluminium industry and circular economy.

New project has started on catalyst development for hydrogen production from methane pyrolysis.

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 [2b, 2c].
- Participation in hydrogen-related decarbonisation activities in line with national legislation and guidelines [8, 14].
- Investigation and development of CO_2 capture and utilization and closed carbon cycle development.

MATERIAL DEVELOPMENT AND INVESTIGATION

- Nanostructured doped carbon materials for hydrogen generation and catalytic reactions

Structure and composition of carbon materials can be engineered to be versatile for various energy applications. Recently, we have obtained a few-layer graphene sheet stack powder via electrochemical pulse exfoliation of graphite [9,10,11]. 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. Such as recently defended bachelor's thesis "Synthesis and application of functionalized carbon materials for energy storage" Riga, RTU 2022 or continued work in the same direction for master's thesis.

- Investigation of advanced nanomaterials for hydrogen production: experimental and computational studies [12, 15].

Hydrogen production becomes more important, as the renewable energy produced needs to be stored sustainably. We plan to keep developing carbon materials as well as metal oxides [11], carbon-metal composites [12] and utilization of aluminium scraps [13] for environmental and hydrogen production researches. The collaboration with theorists to fit theoretical models to experimental results, the progress in development advanced catalysts can be more rapid. Alternative electrolysis cells and materials for displaced electrolysis are envisioned and project with Dr. Andris Šutka is being carried out, our role is gas analysis.

- Nanostructured catalyst development for photocatalytic and electrocatalytic reactions i.e., CO_2 reformation and photocatalytic pollution degradation on materials as TiO_2 NT with various dopants.

- Direct and displaced Hydrogen storage in metal hydrides, carbon-based materials, aluminium.
- Gas analysis with MS and GCMS, ability for detailed analysis of produced and collected gas samples.
- Research of hydrogen and valuable material production from waste aluminium in Al-water reaction.
- Theoretical/modelling investigation of aluminium – water reaction and process efficiency.
- Computer simulation on discharging, refuelling and transporting natural gas and hydrogen via pipelines
- 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.
- Catalyst investigation for methane pyrolysis for hydrogen production, catalyst regeneration and cleaning of deposited carbon for further use in pesticide sensors.
- Methane pyrolysis and catalyst investigation for increasing the efficiency of the process, catalyst regeneration and new developments.

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;
- Catalyst efficiency testing for gas reforming in the field of Hydrogen production in collaboration with Lithuanian researchers;
- Material retrofitting for hydrogen energy in large scale PtG 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.
- Hydrogen storage in various nanostructured materials, such as activated carbon, functionalized graphene, hydrides, aluminium etc.

- CO_2 capture and reformation catalysts and systems for efficient carbon cycle development.
- Theoretical investigation of systems and processes for hydrogen technologies
- Updating and developing teaching materials in hydrogen technologies (FC, storage, electrolysis, blending, etc.)
- MFC development for power and hydrogen production
- Further development of nanostructured TiO_2 for environmental cleaning such as Pb filtering.
- In situ CO_2 reduction reaction investigation on large surface area base for single atom catalyst development.
- Activated aluminium hydroxide investigation for carbon capture technologies.
- Collaboration with local industry for e-fuel investigation as well as hydrogen testbed development.

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 of oxygen reduction reaction in fuel cell, supercapacitors and microbial fuel cells;
- 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.

Our key competences and capabilities are synthesis, thin film deposition, gas analysis and electrochemical characterization of materials. From research instruments the 70+ channel battery tester is available for electrical characterization, equipment for gas adsorption/desorption, for gas composition analysis the mass spectroscopy and gas chromatography are also available. Equipment available at ISSP UL essential but not exclusive to this research direction includes 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

- University of Iceland, prof. Christiaan Richter, Iceland
- IceTec (Innovation center of Iceland) Dr. Chem Guðmundur Gunnarssonr, Iceland
- Prof. Dr. Danjela Kuscer Jožef Stefan Institute, Slovenia
- 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
- Institute of Power Engineering of Riga Technical University (Ass.Prof. Laila Zemite): decarbonisation aspects of Latvian Gas Network Infrastructure
- Latvian Hydrogen Association (Dainis Bošs): Legal aspects of the concept of "hydrogen in the natural gas network"
- Dr. Ewa Wierzbicka

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SUMMARY OF PLANNING UPDATES

- The production of hydrogen gas from aluminium waste by aluminium-water reaction at various conditions has been researched as sustainable and cheap technology.
- CO_2 capture from flue gases via activated aluminium hydroxide and synthesis of aluminium hydroxide
- Calculations show that the introduction of hydrogen into the Latvian gas network can decarbonize the gas network if the HCNG mixture is used by final consumers. Increasing the hydrogen content from 0.1% to 20% reduces carbon dioxide emissions by 20%.
- Municipal and national enterprises (Rīgas Siltums, Latvenergo, Conexus) announced their interest to involve hydrogen as energy carrier to support decarbonisation plans in national economics, consultation and development of hydrogen energetics and e-fuel investigation
- Update on the current situation in laboratory in terms of hydrogen technologies and current project as well as development of previously proposed directions

THERMOELECTRICS AND HYBRID PHOTOVOLTAICS

STATE OF THE ART

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

Wasted heat is a potentially significant source of energy that has not been fully utilised. It is estimated that humankind wastes ~ 20% of the 15 terawatts required annually for global power consumption as low-level heat (<200°C). Thermoelectric generators (TEG) could harvest the wasted energy, which directly converts heat into electricity. With effective TEG, many problems are addressed: the wasted heat for electricity generation is used to reduce global warming and deal with the energy crisis. Identifying these conditions has stimulated extensive studies in the field of thermoelectric materials, including organic materials [1-5]. In the low-temperature range, organic materials can show comparable and better properties compared to classically used inorganic materials [6, 7]. Recently synthesis of TE nanoparticles with a high figure of merit (ZT >1) has been reported [46, 47]. The incorporation of such nanoparticles into suitable polymer matrices can lead to valuable hybrid TE materials for example for Photovoltaic-Thermoelectric hybrid systems [48].

Solar energy is the second energy source, 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. 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%. However, it has reached its theoretical maximum. A new generation of OSC has been proposed where fullerene is substituted with other organic compounds as electron acceptors. Such electron acceptors have a specific name – non-fullerene acceptor (NFA). The advent of NFAs with superior optoelectronic properties, tuneable morphology, and absorption characteristics have resulted in a scenario where the NFA OSCs have demonstrated higher PCE of over 18% in single junction and over 19% in tandem OSCs incorporating NFA 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 applications due to lower working voltages and a 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. They have recently been proposed also for X-ray detection as promising alternatives to inorganic semiconductors [23,24]. They are relatively inexpensive, 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, a 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, in combination with high-Z nanomaterials, organic materials have a 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 photo-detector. Both types of detectors could be realised using hybrid organic-inorganic systems. Moreover, superior properties could be developed, such as flexibility, lightweight, sensitivity, and registration rate [15–20, 22, 35].

OUR POSITION

Laboratory of Organic Materials is a prominent place in Latvia with all necessary equipment and competence to produce and investigate organic thin-film devices. The laboratory has a long experience investigating the electrical properties of organic materials, which is essential in applications such as thermoelectricity and organic solar cells and sensors. In recent years, experience in device prototyping has also been actively developed and accumulated.

Electrical properties and charge carrier transport play a vital role in organic electronics, so their research is the basis. Therefore, the laboratory pays attention to investigating the 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 ionisation energy (IE) and the second method gives a reasonable estimation of the energy bandgap between IE and electron affinity (EA) energy. The bandgap's charge carrier local trap states have been investigated by the temperature modulated space charge limit current method (TM-SCLC). Charge carrier mobility has been obtained by Time of Flight (ToF) or Charge Carrier Extraction by Linearly Increasing Voltage (CELIV) techniques [29]. In the Laboratory of Organic Materials, full spectra of thermoelectric properties can be investigated, including Seebeck coefficient measurements in a lab-made Seebeck measurement unit, thermal conductivity measurements by 3ω technique and electrical conductivity measurements by four-probe method [30], [31]. In the future, the measurements 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].

The hybrid materials concept, where inorganic TEs are coupled with polymers, has gained much attention, enabling harvesting low-grade heat otherwise lost, even with a lower ZT than the inorganic counterpart. Flexible organic−inorganic hybrids are promising thermoelectric materials to recycle waste heat in versatile formats [1–3, 33]. Besides, the thermoelectric effect can be used to create light sensors. For example, thermopile detectors have long been known. Prototypes of thermoelectric radiation sensors with superior characteristics are created using thin films of organic materials with unique properties, achieving broad spectral range as thermopiles and high-speed performance as a photodiode. ISSP UL has patented technology as WO/20202/095126 and EP3811043 "A High-Bandwidth Thermoelectric Thin-Film UV, Visible Light and Infrared Radiation Sensor and Manufacturing Method Thereof", which have been sold to the multinational company Thorlabs. Licensing and technology transfer contract with Thorlabs GmbH was signed on 11.10.2021.

Recently laboratory has started to work on studies of hybrid system organic-inorganic X-ray photo-detectors [34].

FUTURE ACTIVITIES

Further development of the energy harvesting device field will be divided into two parts. One will be performed in close collaboration with chemists from other academic institutions. The second is related to the investigation of the energy conversion system concerning morphology.

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

By studying previously investigated materials and exploring the effect of morphology on energy conversion, it is possible to optimise 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 foremost 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 the 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 TEGs, OSCs or X-ray radiation sensors, it is necessary to know the charge carrier transport and energy levels in solids. It is crucial 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. 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 measurements are available at the Institute. One of the essential parameters for OSCs and sensors is the charge carrier mobility and recombination process. Both processes could be studied by Charge extraction with linearly increasing voltage (CELIV). The method is valid for thin films and can investigate charge carrier recombination and determine charge carrier mobility. Thermal conductivity is one of the critical parameters to determine the figure of merit ZT for thermoelectric materials. However, measurements for the thin film is complicated. 3W method will be developed and established for thermal conductivity measurements in thin films. The fully established method allows measuring thermal conductivity in both directions of thin films – laterally and along 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 and reading part of 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 photo-detector.

The direct conversion of ionising radiation into an electrical signal within the same device is usually more effective than indirect. It improves the signal-to-noise ratio and reduces the device response time. Both types of detectors could be realised using hybrid organic-inorganic systems. Moreover, superior properties such as flexibility, lightweight, increased sensitivity, and registration rate could be developed. 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 a high cross-sectional area for X-ray interaction, thus enhancing the absorption efficiency and sensitivity and (hopefully) retaining the host polymer's advantageous physical properties, 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 typically 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 thermoelectric materials from the last decade due to their great potential to enhance the thermoelectric performance by utilising 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. High-quality incorporation of inorganic nanoparticles must be achieved to overcome this issue. Incorporating thermoelectric active inorganic nanoparticles or low dimension carbon structures, such as carbon nanotubes or graphene, in the matrix of organic materials could increase the system's electrical conductivity and Seebeck coefficient of the system, meanwhile reducing thermal conductivity, realising the "phonon-glass, electron-crystal" principle resulting with higher Figure of Merit ZT values. The alternative approach to overcoming this issue is defining the localisation of inorganic nanoparticles by lithography methods [1–3, 36–39]. Polymer nanowires prepared by electro-spun method combined with inorganic nanoparticles could be the first approach for preparing hybrid thermoelectric systems. In collaboration with Prof. M. Toprak group from KTH we have started to study $Bi_{2-x}Sb_xTe_3$ TE nanoparticles and we are planning to form hybrid structures and develop TE devices. We plan to expand our research also with copper chalcogenides nanoparticles possibly other TE nanoparticles that can be obtained by efficient microwave-assisted synthesis developed by the professor Toprak group.

- Investigations of electro-spun polymer-based nanowires

Nanowires or nanofibers could be of 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 the attention of researchers due to their enhanced and exceptional nano-structural characteristics [40–45].

- Development of ternary organic solar cells containing non-fullerene acceptor materials

We've started Latvian Council of Science project No. LZP-2022/1-0494 "Development of ternary organic solar cells by employing original indacene-tetraone based non-fullerene acceptors". The objective of this research project is the development of novel non-fullerene electron acceptors with one-dimensional charge transfer properties that will allow the construction of highly efficient ternary OSCs. In this project, novel non-fullerene acceptors for organic solar cells will be synthesized and investigated. Adding them to already used commercial donor and acceptor materials (electron donor polymers PM6 and PM7, as well as NFAs like Y6 and Y7), ternary organic solar cells will be developed. During the project, the most promising materials will be selected and from these, the OSC will be made and later optimized for the best performance.

- Studies of self-assembling monolayers (SAM) in semi-transparent solar cells

In the EEA and Norway Grant "Development of Semi-Transparent Bifacial Thin Film Solar Cells for Innovative Applications" novel self-assembling monolayers (SAMs) will be investigated. Here, SAMs work as a charge carrier transport layer for chalcogenide based solar cells. We will use our main strength in fundamental research: the vast variety of material characterization methods. Energy levels of SAMs and possible interface (metal- SAM, semiconductor- SAM) effects will be studied.

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

Organic material-based thin film deposition on flexible substrates by making flexible devices is one of the most significant advantages of organic materials. Nevertheless, several issues should be addressed before depositing a multilayer system on the flexible substrate.

1. Structuring of electrodes should be done mainly by the lithography method;
2. Thermal deposition of compounds should be done at low temperatures;
3. The thermal properties of the flexible substrate should be considered during thermal treatment of the layers;
4. Investigation of bending radius and cycles should be performed.

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

NETWORKING

Latvia:

- Institute of Organic Synthesis
- Riga Technical University, Institute of Applied Chemistry, Prof. Valdis Kokars
- Research Laboratory of Functional Materials Technologies, Dr. sc.ing. Andris Šutka,
- Institute of Technology of Organic Chemistry, Prof. Dr. chem. Māris Turks

Europe:

- Kaunas University of Technology
- Tallinn University of Technology
- Vilnius University
- Julius-Maximilians-Universitat Wurzburg, Experimental Physics vi, Pflaum group, Prof. Dr. Jens Pflaum
- 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
- KTH Royal Institute of Technology, Nanochemistry Lab, Professor Muhammet S. Toprak

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SUMMARY OF PLANNING UPDATES

- We will boost the study of organic-organic composite and hybrid (organic-inorganic) TE materials. In collaboration with our partners, we will study printable TE materials.
- We will study thermoelectrical properties of glass-forming low molecular weight compounds as promising candidates for novel hybrid thermoelectric materials. Our proposal "Advancing Sustainable Thermoelectric Hybrid Systems Utilizing Glass-Forming Low Molecular Weight Compounds" has been positively evaluated.

- We will study novel high entropy thermoelectric nanomaterials. Proposal "The entropy-driven approach to enhance the thermoelectric performance of chalcogenide-based compounds" has been positively evaluated.
- In collaboration with chemists from Riga Technical University, novel non-fullerene acceptors for ternary organic solar cells will be developed.

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].

Technological aspects

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*. Since 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 non-stoichiometry on depolarisation temperature is demonstrated [6]. According to recent suggestions, the non-stoichiometry 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 the range of high electric field E values.

Application of Maxwell relations requests a 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 ΔT 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 ΔT 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 (ΔT up to 6°C at E=150 kV/cm [12]);

- Available results are very limited and contain remarkable scattering of ΔT 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 an 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 the most widely studied properties of NBT-based compositions is electric field-induced strain. Reason of such focusing is the possibility to reduce with appropriate dopants ferroelectric-non-ferroelectric 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]. Study of sintering at ambient atmosphere, evaluation of microstructure, porosity, deviations from stoichiometry is completed [].

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].

Experimental equipment for study of electrocaloric effect at high fields (in range of 100 kV/cm) is created.

Experiments of ECE up to 100 kV/cm are performed in NBT-BT-CT and NBT-BT-NN solid solutions, allowing to evaluate prospects of application of these lead-free materials in cooling devices [27-28].

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).

In 2021 studies of optimisation of sintering atmosphere are finished, including ways of creating of intentional/non-intentional deviation from stoichiometry. Few conclusions: NBT is very stable against deviations from stoichiometry, an evaporation of Bi at high temperatures is possible only from the surface [29-31].

Studies of modulation of luminescence intensity by electric field are finished. Modulation is observed, modulation depth is around 10%. Problems with transparent electrodes and electrical breakdown were encountered.

Dielectric dispersion in frequency range up to 10 GHz is analysed in relaxor ferroelectrics NBT-$Sr_{0.7}Bi_{0.2}TiO_3$. Interpreting obtained results general concepts of relaxor ferroelectrics, freezing and appearance of nonergodic state, are questioned.

Deeper insight into phase transitions in NBT are obtained by PFM, comparing NBT ceramic with different average grain size and comparing structure and phase transition of NBT and NBT-CT.

0.9NBT- 0.1$Sr_{0.7}Bi_{0.2}TiO_3$ thick films were successfully produced and their structure and ferroelectric properties were characterized.

FUTURE ACTIVITIES

Technology.

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:

- To improve technology of freestanding thick film production, extending range of parameters, influencing film properties. Optimization of sintering conditions approaching application oriented requirements.
- 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 ΔT=5°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;
- 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 UL participates in this organisation), piezoinstitute.univ-tours.fr

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SUMMARY OF PLANNING UPDATES

- Development of lead-free thick ferroelectric films for application in actuators and electrocaloric cooling.

TECHNOLOGY, DEVICES AND APPLICATIONS

This section comprises research plans of studies with the main emphasis on creating devices and their creation technology, in difference to the previous sections, which had their main focus un material synthesis and properties.

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, 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 coatings (solar cells, 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, allows 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 the 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 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.

This direction positively contributes to the achievement of Sustainable Development Goals, European targets for Clean Energy for all Europeans, the Smart Specialisation Strategy of Latvia, and contribute to the European Research Area. This activity was financed by LZP FLPP Nr. lzp-2020/2-0291 and ERAF-073 HIPIMS projects.

The Thin Films Laboratory is 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). The 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 [10-17]. 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 a 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. On January 12, 2023 Latvian Academy of Sciences published the results of the competition in various fields of science, most outstanding in the nomination "Achievements in Applied Science" was the ISSP Thin Film laboratory's team represented by TF Laboratory: Dr.phys. Juris Purāns, Dr. phys. Ilze Aulika, Dr. phys. Boriss Poļakovs, Dr. phys. Mārtiņš Zubkins and Dr. Habil. phys. Smagul Karazhanov. The authors demonstrated a prominent photochromic effect and a light-induced resistivity change at room temperature and ambient presure, as well as demonstrated a superconducting filament effect in Y-O-H and yttrium hydrides.

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 in the deposition of new materials: Y-O-H, 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 an 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.

Magnetron HIPIMS sputtering cluster - **G500M** installed at ISSP UL (thin films laboratory) in 2020 is intended for research and development in the field of HIPIMS thin film technologies. The cluster comprises a HIPIMS MELEC power source and 3 deposition chambers. The pumping system consists of turbomolecular and mechanical pumps with and an adjustable gate valve; Ar, O_2, N_2, Ar+H_2, H_2 flows controlled by MKS mass flow controllers; 2 rectangular 150 x 75 mm (or 200 mm x 100 mm) co-sputtering magnetrons in each chamber; substrate temperature between 800^{o}C (chamber N2) and RT- Low T (- 150^{o}C); sputtering modes: DC, pulsed-DC, HIPIMS with unipolar pulses, MF and HIPIMS with bipolar symmetric and asymmetric pulses ES and voltage process control for reactive processes; substrate linear movement. The main goal of activity on the G500M is to develop vacuum thin film deposition technologies for the stable deposition of gallium oxide (Ga_2O_3) and $ZnGa_2O_4$ thin films by reactive pulsed-DC magnetron sputtering from a liquid Ga target.

Pulsed laser deposition (PLD) is a valuable tool for the 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 (AFM), in characterization of dielectric and electromechanical properties.

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 a 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, 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.

Moreover, ISSP Thin Film laboratory is full of confidence to continue research and ensure significant research excellence within the Horizon Europe financed ERA-Chair project "Smart windows for zero energy buildings" (SWEB)". This project kick-off will take place on 26th of January and implemented during next 5 years with overall budget of 2,4 million EUR focusing on innovative smart windows (SW) solutions, materials and products to foster market growth and address EU-wide climate challenges.

The aim of the Smart Windows for Zero Energy Buildings (SWEB) project is to develop world-leading research on functional materials and their SWEB applications, to advance teaching capacity and to foster institutional governance changes towards excellence and sustainability. Institute of Solid State Physics (ISSP) of the University of Latvia is the leader of Functional Materials and Coating research in Latvia. It concentrates significant resources in materials research, testing, advanced training, and innovation. ISSP key technologies are based on inorganic and organic thin film deposition on a wide variety of materials, using different advanced deposition techniques from existing and new tools. The deposition tools are operated by highly skilled staff, enabling the deposition of novel materials as required by internal research projects and external customers. Currently several ongoing research projects aim at the development of novel advanced materials and coatings for SWEB.

ERA Chair SWEB will establish high-quality researcher and expert team by synergistically merging chromogenic SW materials and complementary competencies at ISSP and bridging the gap between research and technology transfer. The knowledge gained will increase research excellence, visibility, and attractiveness of ISSP and Latvia in general, thus enhancing participation in ERA. Furthermore, these ambitious research and innovation goals targeting emerging next-generation chromogenic SW development will lay the foundation for further technical development and innovative production of SWEB in other regions of the EU. Ultimately, society as a whole will benefit from excellent job opportunities for specialists, more youths are drawn to prestigious technology and engineering-oriented higher education, a bridge between R&D and the public, and consumers will indirectly benefit from shorter prototype to market development cycles of targeted chromogenic SW.

Development of new energy saving and chromogenic materials and devices, developing scalable deposition methods, stability testing protocols for photochromic and thermochromic films, indoor and outdoor testing. Successful implementation of the project in terms of photochromic, thermochromic, and static energy saving coatings, developing scalable synthesis methods will open new possibilities for R&D activities at ISSP enhance industry-academic collaboration, and creating new start-up companies. It will improve such fields as energy-saving and SW, sensors, ophthalmic lenses, and medical devices. These achievements will possibly affect the innovation capability of the EU market on a long-term time scale.

The future market of SW and zero energy buildings (SWEB) will rely on a variety of innovative SW solutions and products in order to meet the market growth potential and address the grand environmental challenges faced by EU to achieve and sustain a zero energy buildings market. Development of non-toxic, earth abundant, long-term functional SW materials (photochromic, thermochromic, electrochromic, transparent conducting), along with implementation of cost-effective, robust and industrially scalable, rapid, resource saving technologies for fabrication of low-cost thin film SW and chromogenic devices with flexibility in design, such as photochromic, thermochromic and electrochromic SW, self-powered SW – the basis for zero energy buildings, smart cities and smart villages. The SWEB aims to recruit a Knowledge Developer and Manager to bring complementary knowledge to the existing core team, and thereby enhance scientific excellence, to increase visibility and attractiveness, and to bridge the gap between research and technology transfer. This will positively contribute to achievement of Sustainable Development Goals, European targets for Clean Energy for all Europeans, the Smart Specialisation Strategy of Latvia, and to the contribution to the European Research Area.

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*;*
- Liquid target (Ga) and off-centre HIPIMS growth of epitaxial ultra-wide bandgap gallium oxide and metal oxide (GaMeO) thin films and multilayers for deep UV optoelectronics and electronic applications;
- Reactive HiPIMS deposition of hydride-based (Y-O-H, RE-O-H) films for emerging energy technologies;
- MOCVD technology for epitaxial growths of 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 the 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, WS_2, 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.
- magnetron sputtering process for MgB_2-based thin film growth including epitaxially strained coatings on various material nanowires, solid solutions with co-sputtered interstitial impurities of various metals and few-atom-thick hydrogenated MgB_2 layers

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; (ii) 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 recently 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 strengthening of European industries.

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(a) **J.Purans**, EU Patent EP2881974B1 Method and device for controlling reactive sputtering deposition (18.07.2018 Bulletin 2018/29);
(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);
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SUMMARY OF PLANNING UPDATES

- Magnetron HIPIMS sputtering cluster - **G500M** installed at ISSP UL (thin films laboratory) in 2020 is intended for research and development in the field of HIPIMS thin film technologies. The cluster comprises a HIPIMS MELEC power source and 3 deposition chambers. The pumping system consists of turbomolecular and mechanical pumps with and an adjustable gate valve; Ar, O_2, N_2, Ar+H_2, H_2 flows controlled by MKS mass flow controllers; 2 rectangular 150 x 75 mm (or 200 mm x 100 mm) co-sputtering magnetrons in each chamber; substrate temperature between 800^{o}C (chamber N2) and RT- Low T (- 150^{o}C); sputtering modes: DC, pulsed-DC, HIPIMS with unipolar pulses, MF and HIPIMS with bipolar symmetric and asymmetric pulses ES and voltage process control for reactive processes; substrate linear movement. The main goal of activity on the G500M is to develop vacuum thin film deposition technologies for the stable deposition of gallium oxide (Ga_2O_3) and $ZnGa_2O_4$ thin films by reactive pulsed-DC magnetron sputtering from a liquid Ga target.
- Reactive HiPIMS deposition of hydride-based (Y-O-H, RE-O-H) films for emerging energy technologies

PROTOTYPING OF MICROFLUIDIC DEVICES

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 this laboratory – 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.

Recently, there has been a few attempts at producing alternative-material OOCs from Kang group [16] and Jeon group [17] (both in Korea) and George group (UC Davies, U.S., unpublished). However, there has not been a major publication showing PDMS-free OOC devices that have been utilized in conjunction with drug development studies. It is noteworthy that majority of the innovation within the alternative material field is likely coming in the form of various start-ups developing the technology under confidentiality.

Furthermore, particular focus in conferences – MicroTAS 2022, MPS World Summit 2022 and EurOOCs 2022 – three largest conferences in the field, all attended by ISSP UL members, have been on sensors aimed for understanding cellular metabolism. Of particular importance has been glucose and lactate sensor development in the field, which is now evidenced by recent publications in the field, as well as the large interest and poster presentation garnered within the conferences. [25, 26] In the field of gut on chip, there is still heightened interest in the O2 sensing to aid the gas environment understanding within the epithelial channels.

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 [18] and various gas and pH sensors [19]. 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.

Throughout the 2021, we have developed a novel OSTE/COC fabrication process, which allows to fabricate OOC devices with significantly improved small molecule and gas permeability properties. We also have shown the initial experimental data on TEER and oxygen sensor integration within the chips with a major publication expected to come in 2022.

Furthermore, as a part of LIAA project, we have submitted a patent for design elements of a novel GOC device that would enable large scale next generation device manufacturing.

In 2022, previously developed chips have been used to show full human microbiota culturing in gut on chip devices. Subsequent analysis of microbiome diversity via advanced sequencing has shown that >95% of the bacteria still present in the chip after more than 72 h are either strict anaerobic or anaerobic. This result confirms that the fabricated devices allow for superior gut microenvironment recapitulation on the ISSP-made chip. Throughout the 2022, experiments were done to show bacterial extracellular vesicle transfer across the gut-blood barrier. In 2023 multi-OOC experiments will be started, as a project for connecting kidney-liver-pancreas system has been won for the two years starting 2023.

The 2022 patent application has been turned into PCT application with the same priority date for priority retention. Furthermore, the EP patent application made in 2022 has been sold to Latvian spin-off company Cellbox Labs, which will commercialise this technology.

Regarding oncology-related biomarker work, our core interest is connected to Dr. A. Line group in BMC, where the 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 [21]. 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 [22, 23]. 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 UL 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.

Throughout the year 2021 we have performed the experimental work with EV separation devices with initial results presented in The 25th International Conference on Miniaturized Systems for Chemistry and Life Sciences MicroTAS 2021 conference. Further experiments are in progress to optimise device performance in use of large-volume samples. Subsequently, the TRL level for this technology so far is 3 on the way to 4.

In 2022 we presented the nanoparticle separation results from the aforementioned projects in MicroTAS 2022, and two publications relating to nanoparticle and EV-separation are in progress for submissions in Polymers (IF=5) and Journal of Extracellular vesicles (IF = 17).

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 UL. 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.
- Thermofisher
- Merck (we have engagement);
- Novartis (we have engagement);
- Janssen J&J Company (we have engagement);
- Abbvie
- Evotec
- Charles River laboratories (we have engagement);
- Covance/Labcorp (we have engagement);
- Eurofins (we have engagement);
- Agilent

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 [24].

NETWORKING

Cooperation partners:

- Biomedical research and study centre, J. Klovins group, (Latvia);
- K. Jaudzems group, Latvian Institute of Organic Synthesis
- 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;
- U. Beitnere, UC Davies
- D. Konetski, Oregon Health & Science University
- Y. Chen, University of Connecticut
- Massachusetts Institute of Technology Griffith Lab.
- Beatrise Berzina, Technische Universität Dresden

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SUMMARY OF PLANNING UPDATES

- Submitted PCT application for the EP patent covering the mass-manufacturable organ on chip devices
- Sold the EP patent application to startup Cellbox Labs that will commercialize the technology
- The previously shown GOC device can indeed create superior microenvironment, which allows to culture human microbiome in the chips. Publication will be submitted to journal Small.

- Refined the OSTE-COC fabrication process, developed internal process controls and optimised fabrication methods to meet the increasing demand for ISSP UL-made devices.
- EV-related activities will see 2 publications prepared and published concluding the first Latvian Council of Science project.

POLYMER PHOTONICS TECHNOLOGY PLATFORM

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 to 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;
    - E-beam 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 – polymers allow 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], polymers are very suitable for bio functionalization and biosensors [10].

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. Bio-polymers for green technologies can be introduced in this platform.

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 UL 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 UL: 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 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.

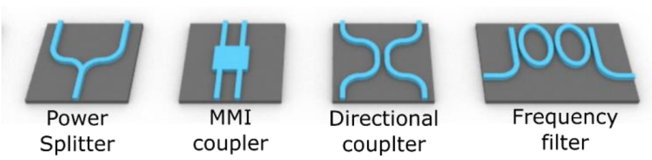

Fig. 3 Passive elements: waveguides, Y branch, crossings, coupler

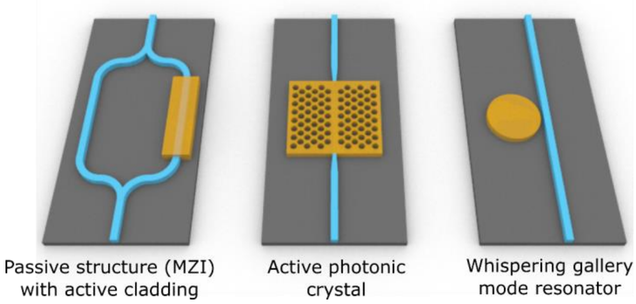

Fig. 4 Active elements: cladding layer that can be used for MZI or other modulators, photonic crystal, and ring resonator.

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].

Standard workflows for optical lithography and mask aligner have been established allowing to create SU-8 structures down to 1 um. Having achieved this, ISSP UL can look further in collaborations with chemists and biologists regarding polymer sensor development for specific applications.

COMSOL software packets are available in ISSP UL, and a team responsible for simulations is being established. First works regarding simulations of polymer waveguide sensors based on lossy-mode resonance have been published.

We are also working on photonic device fabrication using dry etching, EBL, and trench structures.

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. We have developed a procedure for waveguide polishing and fiber attachment to waveguide facets, but this procedure needs further optimization to yield lower coupling losses.

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 (n=1.57) and air, the 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 is 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 micro-ring 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.

A collaboration between ISSP UL and Institute of Atomic Physics and Spectroscopy (IAPS UL) of the University of Latvia regarding microresonator development and characterization has been initiated in 2021. As IAPS UL possesses infrastructure and experience in photonic device characterization, this collaboration will be beneficial for development of polymer photonic platform. The main focus on this collaboration is practical demonstration of polymer waveguide ring resonator sensor for environment monitoring.

Recently, a collaboration started with two European-level universities. They are Trento University and the University of Technology of Troyes. The research subject is related to the development of a polymer photonic technology platform for quantum photonic applications.

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SUMMARY OF PLANNING UPDATES

- Development of workflows for element fabrication through national research program initiative.
- Multiple projects regarding photonic device development have been submitted and in case of acceptance focus will be on specific device development.
- Increase of human resources with the main focus on COMSOL simulation team.
- New collaboration started.
- Explore applications in quantum photonics.

PHASE RETRIEVAL FOR ADAPTIVE OPTICS AND IMAGING

Note: the title of this domain has been changed starting from 2023. The previously used title was "VISUAL PERCEPTION AND IMAGE PROCESSING IN ADAPTIVE OPTICS AND AUGMENTED REALITY"

STATE OF ART

Physical, diffractive and adaptive optics, as also photo- and colorimetry are the main study areas to understand and to apply the advances in material science, optics, bioscience, environmental science, and communications to ensure optimal imaging and optical systems performance (including vision) [1-4].

Adaptive optics is an area in optics of large 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 in retinal imaging. 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 material 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].

Recently, the Laboratory of Visual Perception has focused attention to absorbing thin films finding many applications not only in optics and photonics, but also in energy harvesting, stealth technology, light sources etc. Such materials appear to be very promising for applications in waveguides and phase retrieval and provide opportunity to develop advanced technologies in wavefront sensors. The Laboratory of Visual Perception has also started to carry out research in his field together with the partners from KTH. [26]

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

1. A distinct goal of research is to develop and implement novel type of wavefront sensors. The new wavefront sensors foreseen for biomedicine and astronomy are based on phase retrieval approach from intensity measurements. This applies also to general optical applications, thus improving their performance and resolution of optical systems [22].
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, 23].
3. To develop advanced microoptics for applications in phase retrieval. Such microoptical elements are based on transparent waveguiding part with absorbing sidewalls. The sidewalls are typically fabricated using either plasmonic nanoparticles/nanostructures or stacks of thin films. Such stacks are formed by various metals and lossy dielectrics.
4. To increase the competitiveness in energy-saving and human-centric lighting, free from adverse effects to human circadian rhythm 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 an adverse impact [12-15, 25].

OUR POSITION

The Laboratory of Visual Perception of the ISSP UL has a strong background related to research in the following fields: adaptive optics (VIS, IR), optical phase retrieval algorithms; phase retrieval in a scattering optical media; developing of advanced micro-optical elements; fabrication of thin absorbing films; simulation of photonic structure in COMSOL; wavefront modulators technologies; tuneable optical elements and their use in virtual reality and vision appliances; smart human-centred illumination; hyperspectral imaging and analysis.

The Laboratory of Visual Perception has several doctors in Physics. The head of the laboratory is Sergejs Fomins who also is an assistant professor at the UL, Faculty of Physics and Mathematics, and Optometry, Department of Optometry and Vision Science. Two other employees of the laboratory are a professor Maris Ozolinsh who supervises diploma works every year and Dr. Phys. Varis Karitans working in the field of phase retrieval and micro/nano optics/photonics. Varis Karitans also teaches geometrical and physical optics at the UL.

Adaptive optics and phase retrieval is currently the most actively studied fields in the laboratory, and it 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 for control of optical aberrations. At the Laboratory of Visual Perception studies of phase retrieval based on unique modulation of the object under study have been carried out within 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, 22].

European Space Agency (ESA) project "Feasibility of phase retrieval adaptive optics for Satellite-Ground optical communication" is dedicated to extend the optical phase retrieval into IR range to be suitable for free space optical communication. The project aims to adapt the technologies of phase retrieval to improve communication between satellites and ground-based sensors. The project is realized in close cooperation with a Portugal company "Lusospace".

The scientific activities are also facilitated by a project "Implementing phase retrieval algorithms in embedded systems" supported by University of Latvia Foundation and a company "Mikrotik". Infrastructure and experience of the Laboratory of Visual Perception can also be improved by implementing these algorithms into embedded systems to make them applicable in compact and practical optical systems.

A number of novel project proposals were submitted to fundamental and applied research programm

- "***Study of light propagation control in scattering media for depth imaging in biophotonics***" (S. Fomins) proposes idea of imaging in scattered media. is problematic due to multiple elastic scattering phenomena moderate (biological tissue) process kinetics. Te input-output response of a scattering medium can be described by a so-called transmission matrix (TM), which relates free modes at the input to those at the output. The experimental measurement of transmission matrix is rather time-consuming because it requires both the scanning of incident waves in such a way to cover input free modes and the recording of complex field, i.e. amplitude and phase, at various output channels. To correct TM typically spatial light modulators or digital mirror devices are applied with phase retrieval techniques, which are slow and do not allow to progress to 3D correction in scattered samples/tissues. Fusion of our phase retrieval knowhow with innovative NIR assisted guide star method will allow to identify the right phase retrieval methods and transmission matrix identification techniques for set of classified scattering samples to implement 3D imaging in highly scattering samples. The aim is (1) to achieve the speed, quality, and penetration depth in scattering media for provision of 3D light control with choice of right PR algorithm; and (2) to provide guidelines for PR implementation within scattering media for biomedical and photonic applications.

- A project "***Phase retrieval of two-dimensional objects by processing of the diffraction patterns optically separated vectors***" (Fundamental and applied research projects) has also been proposed (V. Karitans). The project aims to develop a stack of modulated cylindrical microlenses for phase retrieval of 2D objects. The microlenses have thin absorbing sidewalls based either on interference or plasmonic nanoparticles. The absorbing sidewalls imitate free-space propagation of a wavefront encountered in coherent diffractive imaging (CDI). Until now, absorbing stack of Au/Ge/HfO_2 thin films has been fabricated and its optical properties have been measured. These stacks were fabricated in cooperation with Martins Zubkins from the Laboratory of Thin Films. In cooperation with Mattias Hammar and Olof Sjödin from Electrum Lab (KTH), such stacks have also been simulated in Matlab and COMSOL. These activities form a part of a demonstrator project, and were discussed in detail in April 2023. The progress of the demonstrator project has been reported in a conference "Optics and Photonics in Sweden 2023" [26]. Plasmonic Ag@SiO_2 core-shell nanostructures have also been synthesized in cooperation with Madara Leimane from the Laboratory of Optical Materials.

- "Determination and improvement of binocular vision functions using smart adapters with dynamically variable optical characteristics" (M. Ozolinsh) project is devited to implementation of variable focus optics in VR technology.

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, 25].

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 coronavirus disease risk; *culture* – hyperspectral imaging, spectroscopy of cultural heritage and data archiving; *climate, energy, industry* – human-friendly economic and ecologic material studies, prototyping and design of illumination devices.

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

- Theoretical development of visual information phase retrieval methods,
- Developing and optimization of adaptive optics systems with novel wavefront sensors;
- Optimizing and standardization of lighting using solid state materials, creating of human centric lighting;
- Development of prototypes using smart materials/devices with controllable optical properties anticipated in vision appliances and visual reality and augmented reality devices;
- Fabrication of absorbing thin films based on plasmonic nanoparticles/nanostructures and interference;
- Nanostructures for SERS applications;
- Tunable optical elements – adaptive optics deformable mirrors, tuneable lenses.
- Optical system metrology on macro and micro levels.
- Imaging in scattering media including tissue optics and underwater imaging.

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.

The Laboratory of Visual Perception plans to upgrade its infrastructure in near future. It is intended to upgrade imaging solution into IR range for studying phase retrieval of very faint light sources using high sensitivity cameras, light scattering and aberrations in biological tissue etc.

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); KTH Electrum Laboratory; 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); Lusospace (Lisbon, Portugal).

- 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 University College Dublin, Centre for Biomedical Engineering; Stockholm KTH Visual Optics research group (together with ACREO as partners within ISSP UL CAMART[2] project); KTH Electrum Laboratory; 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; multi-wavelength 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. University College Dublin (UCD), Laboratory of Optics and Advanced Optical Imaging (Dublin, Ireland). Contact person in UCD Prof. B. Vohnsen was adviser of current ISSP UL 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. 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.
- City University, Newcastle Universities – with good experience on visual perception, colour research, colour vision test development;
- 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, adaptive optics.
- Latvian Institute of Electronics and Computer Science (Riga), project proposals in Latvian Science Council project calls.

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 adaptive optics applications.

Industrial interest in the area, potential industrial partners

The 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 lighting; object multispectral diagnostics, analysis and data archiving; materials and designs for vision improvement; applications of adaptive optics for astronomers; 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), e-EYE.

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SUMMARY OF PLANNING UPDATES

- Advancements in phase retrieval approaches gained during ESA RPA project.
- Three Fundamental and applied research projects have been proposed.
- Plans to upgrade the infrastructure of the Laboratory of Visual Perception to enable high-resolution imaging in turbulent and scattering media. Update microscopic adaptive optics equipment for fibre optic and photonic applications.
- Cooperation with industry partners and new project proposals.
- Study the cooperation potential with Tartu Astronomic Observatory (EE) in adaptive optics for small-sized telescopes.