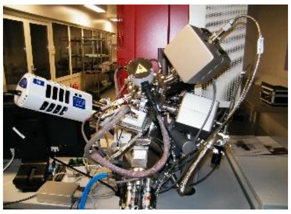
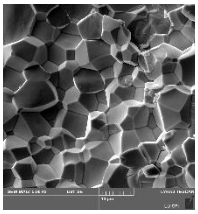
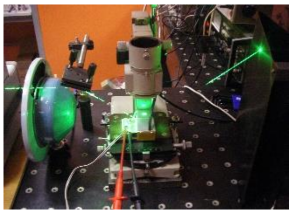
INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

RESEARCH PROGRAMME 2020







Riga
2020

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Executive Summary

The Institute of Solid State Physics, University of Latvia (ISSP UL) is an internationally recognized leader in the materials sciences and cross-disciplinary topics in Baltic Sea Region. ISSP UL aims to **transfer excellence** in materials science and solid-state physics into highly educated people and into innovative products, processes and services. Important challenge for the Institute is to translate the new knowledge coming from fundamental research into real innovations with a potential of principally new solutions, disruptive to the existing ones. It requires a new approach: **change of mind-set** that fundamental research should also be directed towards the technological needs and challenges of industries. ISSP UL has created and continues to improve **a suitable ecosystem** that allows new ideas to be feasible.

680 m^2 of ISO class 7-8 **cleanroom facility** is established and laboratory infrastructure is upgraded, including equipment for:

- basic technological methods: thin film fabrication and parameter control, chemical synthesis, nano- structuring;
- analytical methods: XRD analysis, electron microscopy (SEM, TEM), X-ray photoelectron spectroscopy (XPS), morphology analysis, optical and EPR spectroscopy, spectral ellipsometry;
- prototyping of photonic and electronic devices. A new dedicated prototyping cleanroom laboratory was newly established.

This development increases research capabilities and enables application-oriented development needed for innovations and technology transfer.

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

Well-developed research infrastructure and technological facilities in conjunction with highly trained and qualified personnel are indispensable conditions for successful advancement of materials science. To augment the local research capabilities, to improve the expertise of researchers and to foster international cooperation, studies at world-leading **large-scale research facilities** (e.g. PETRA III, ILL, Max-4, ESS, European XFEL, ELI) are of crucial importance. The present Research Programme 2020 formulates the practical implementation of the mission of the Institute. The Research Programme of ISSP UL puts emphasis on four top **Priority Directions**:

I. Theoretical and experimental studies of materials structure and properties;

II. Nanotechnology, thin films, nanocomposites and ceramics;

III. Functional materials for photonics and electronics;

IV. Materials for energy harvesting and storage, clean energy transformation.

These Priority Research Directions have been strategically established to increase the scientific capacity of the Institute, ensure scientific excellence and to heighten the international visibility of the Institute. These directions will be further elaborated and implemented within interdisciplinary cross-laboratory collaboration. Research will be structured towards the application-driven Research& Innovation (R&I) **domains,** where research outcomes will initiate and establish the value chain. Realization of the Priority Research Directions will be based on implementation of a number of measures and activities within R&I domains.

Strategic Context

ISSP UL Research Programme uses the instructions and recommendations of “Europe 2020” strategy:

- priority "For Smart, Sustainable and Inclusive Growth", which aims to improve the quality of education and to strengthen the research performance, to foster innovation and knowledge transfer, ensuring that innovative ideas can be turned into new products and services;
- European Commission`s (EC) recommendations for the development strategy of Latvia, strategy for smart specialization, priority directions in science and regional development plans.

The information gained by the Research Programme is linked with investigations of the national and regional situation and future perspectives to define the roadmap to transform ISSP UL into a new competitive European level scientific center, where research, education and business work together and complement each other.

Guidelines for Science, Technology Development, and Innovation 2014-2020 (Cabinet of Ministers of the Republic of Latvia order No 685, 28 December 2013) state that for the transformation of the national economy to the knowledge- and innovation-based model it is necessary to form globally competitive Latvian science, technology and innovation industry that could support the needs for the development of the national economy and society[1]. It is clear that successful impact of research and innovations on economic development depends not only on the results of activities, but also on cooperation, infrastructure, environment and regeneration of human resources.

The goal of the ISSP UL Research Programme and strategic development plans is to maintain and increase the fundamental research level (that has been highly evaluated in the International research assessment exercise from “Technopolis group”[2]) but also to promote further development of research and industry connection by offering infrastructural and intellectual support.

The foundation of the ISSP UL Research Programme maintains the compliance not only with European directives but also with the Priority Directions in Science for 2014-2020 “Innovative and advanced materials, smart technologies (multi-functional materials and composite materials, nanotechnologies and photonics, computing, computer science, information and communications technologies, signal processing technologies)”, in accordance with Section 13, Paragraph two, Clause 3 and Section 34, Paragraph four of the Law On Scientific Activity. All corresponding research areas smoothly overlap since the scientific and research activities at the ISSP UL are multi- and interdisciplinary, as well as take into account all respective priorities of Key enabling technologies (KET - Advanced Materials, Photonics, Nanotechnology and Micro- and Nanoelectronics) and smart specialization strategy (RIS3).

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[1] https://www.em.gov.lv/files/nozares_politika/2014ino.pdf
[2] http://www.izm.gov.lv/images/zinatne/ZISI/Latvia-systems-review_2014.pdf

Based on knowledge, experience, cooperation and competences of ISSP UL, the Research Programme promotes various scientific and educational activities in material science. Open access laboratories equipped with modern infrastructure, competent researchers, and a scalable easy-to-access system (supported by laboratory information management system and quality management system) are the conditions, necessary to create and maintain long-lasting cooperation and mutual support between scientists, entrepreneurs and students.

The long-term mission of the Research Programme and Strategic development plan is to raise capacity of ISSP UL to better integrate in the European Research Area and to heighten involvement in joint research programs and projects with EU Member States, especially in the Baltic Sea region.

Priority research directions

1. Theoretical and experimental studies of materials structure and properties

1.1. Theoretical material science and modelling

The research activities of theoretical material science are focused on the role of defects and impurities in insulating materials, predominantly for energy applications – fuel cells, energy harvesting via piezoelectricity and fusion reactors. Special attention is paid to nano-materials and low-dimensional systems: surfaces/interfaces and modelling of processes under realistic external conditions (high temperatures, gas pressure).

For this purpose, we use a thermodynamic approach, based on the first principles calculations of the atomic, electronic, magnetic structure of advanced materials. Such studies need calculations of the vibrational spectra of solids with defects. Most of research studies are performed in a close collaboration with experimental groups.

The goal of studies is the 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.

The first principles hybrid functional calculations of the atomic and electronic structure of several iodine-related point defects in $CsPbI_3$, a material relevant for photovoltaic applications were completed. The results show that the presence of neutral interstitial I atoms or electron holes leads to the formation of di-halide dumbbells of I_2^- (analogous to the well-known situation in alkali halides). Their formation and one-electron energies in the band gap are determined. These parameters are important for estimation of photovoltaic properties.

In particular, traditional calculations of the optical absorption and luminescence are combined with modelling magnetic resonance and vibrational spectroscopic methods (EPR and Raman, IR and neutron scattering) in order to monitor the development of the radiation damage in several functional materials for nuclear applications - diamond (used in diagnostics and as high power microwave transmission window for plasma stabilization).

The study of interstitial ion migration is of key importance for the prediction of radiation damage in oxides. Several possible migration trajectories for neutral and charged interstitial oxygen ions are calculated in $MgAl_2O_4$ spinel using the first principles calculations of atomic and electronic structure. The lowest energy barriers are ≈1.0–1.1 eV and 0.8 eV, respectively. The effective atomic charges, charge redistribution, and lengths of bonds closest to O interstitials are analyzed in detail. Thus, the radiation stability of this oxide material is limited by interstitial oxygen possible migration.

Radiation resistant insulating materials are important components of the future fusion reactors, including elements of diagnostics, coating etc. Study of radiation damage in these materials is of special importance. Some of projects are related to the topic of MATERIALS in EUROfusion activities with focus on several promising materials and their characterization by means of vibrational spectroscopy (RAMAN, IR).

The annealing kinetics of the primary electronic F-type color centers (oxygen vacancies with trapped one or two electrons) is analyzed for three ionic materials (Al_2O_3, MgO, and MgF_2) exposed to intensive irradiation by electrons, neutrons, and heavy swift ions. Phenomenological theory of diffusion-controlled recombination of the

F-type centers with much more mobile interstitial ions (complementary hole centers) allows us to extract from experimental data the migration energy of interstitials and pre-exponential factor of diffusion. The obtained migration energies are compared with available first-principles calculations. It is demonstrated that with the increase of radiation fluence both the migration energy and pre-exponent are decreasing in all three materials, irrespective of the type of irradiation. Their correlation satisfies the Meyer-Neldel rule observed earlier in glasses, liquids, and disordered materials. The origin of this effect is discussed. This study demonstrates that in the quantitative analysis of the radiation damage of real materials the dependence of the defect migration parameters on the radiation fluence plays an important role and cannot be neglected.

The influence of shape and size of perovskite nanoparticles on the piezoelectricity based on ab-initio calculations is studied. 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. Theory of self-assembling process is developed, and it suggests how to control this process.

The results of *ab initio* (first-principles) computations of structural, elastic and piezoelectric properties of $Ba_{(1-x)}Sr_xTiO_3$ (BSTO) and $Ba_{(1-x)}Ca_xTiO_3$ (BCTO) perovskite solid solutions showed that both BSTO and BCTO have significantly enhanced piezoelectric properties, in a comparison with pure $BaTiO_3$. It is predicted that due to decrease of the elastic constants in BCTO, it has much higher converse piezoelectric constants than BSTO.

Scintillator and dosimetry materials, currently used for particle physics, neutron research and medical imaging, are studied in order to improve their performance. The promising is $ZnGa_2O_4$ spinel ceramics doped with Mn^{2+} ions was prepared by a solid-state reaction at 1200 °C in air. Manganese concentration was equal to 0.05 mol.% of MnO with respect to ZnO. Ceramics produced in this way show an efficient green emission at about 505 nm under UV or X-ray excitations, which is caused by Mn^{2+} ions. This green emission is observed also as a relatively long afterglow after switching-off the X-ray excitation. Time profiles of the beginning of glow and afterglow are studied together with thermally stimulated (TSL) and optically stimulated (OSL) luminescence. Experimental results demonstrate a presence of few types of shallow and deep traps responsible for the observed afterglow and TSL/OSL emission of the material. The possibility of pulsed optical stimulation is demonstrated, and the time-resolved OSL characteristics of $ZnGa_2O_4$: Mn^{2+} are obtained for the first time. The presented results suggest the $ZnGa_2O_4$: Mn^{2+} spinel as a promising material for further fundamental research and the possibility of its application as a green long-lasting phosphor or storage phosphor for TSL/OSL radiation dosimetry.

Some of new activities are focused on understanding of chemical and physical material properties in the photocatalytic process and design of the effective photocatalysts for water splitting based on perovskite crystallites and nanoparticles. This needs a combination of the band gap engineering and selection of proper catalysts.

Publications

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3 The names of authors from ISSP LU here and further below are marked with **bold** letters

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9. A. Luchechko, Ya. Zhydachevskyy, S. Ubizskii, O. Kravets, **A.I. Popov, U. Rogulis, E. Elsts**, E. Bulur, A. Suchocki – Afterglow, TL and OSL properties of Mn^{2+}-doped $ZnGa_2O_4$ phosphor – *Sci. Rep.*, 9, (2019), 9544 (pp. 1-8).
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11. R.A. Evarestov, A. Senocrate, **E.A. Kotomin**, J. Maier – First-principles calculations of iodine-related point defects in $CsPbI_3$ – Phys. Chem. Chem. Phys., 21,(2019), pp. 7841-7846.

1.2. X-ray absorption spectroscopy

Knowledge of the structure is crucial for understanding and optimizing the properties of materials and ultimately affects their practical applications. X-ray absorption spectroscopy (XAS) is an excellent local atomic and electronic structure probe applicable to crystalline, nanocrystalline and disordered solids as well as to liquids and gases in a wide range of *in-situ* and *in-operando* conditions [1]. With the increased availability of synchrotron radiation sources (16 such facilities are available today in the EU Member States and over 50 worldwide) and the tremendous improvement in their parameters, the popularity of the XAS technique has increased, and the quality of the experimental X-ray absorption spectra has improved dramatically. Moreover, nowadays cutting-edge femtosecond X-ray radiation sources as free-electron lasers (FELs) become the driving force of groundbreaking time-resolved X-ray absorption experiments [2].

ISSP UL participates in European Synchrotron and FEL user organization (ESUO) as well as in International X-ray Absorption Society (IXAS). More than 40 projects has been realized in the last 10 years at PETRA-III/DORIS (Hamburg), SOLEIL (Paris), ELETTRA (Trieste), ALBA (Barcelona) and ESRF (Grenoble) synchrotrons, which led to more than 80 peer-reviewed publications.

The development of the experimental techniques has occurred alongside with and stimulated the progress in XAS theory [3]. As a result, more accurate and reliable structural information can be currently obtained from X-ray absorption spectra using advanced data analysis approaches, which have been explored at ISSP UL during the last 10 years [4, 5]. The methods based on the regularization technique and atomistic simulations as molecular dynamics and reverse Monte Carlo modelling allow ISSP UL researchers to reveal the full potential of XAS providing a natural way to incorporate static and thermal disorder into the structural models, thus opening new possibilities for the investigation of the structure-property relationships. These achievements have led to a number of success stories, some of which are worth noting. The relationship between the local lattice dynamics and thermal expansion of perovskite-type materials are investigated and explained in ReO_3, ScF_3 and Cu_3N [6-8]. The origin of metallization at high pressure (up to 40 GPa) has been studied and explained in several functional materials ($SnWO_4$, Cu_3N) [9, 10]. Rare phenomenon as pressure-induced inverse photoconductivity in n-type WO_3 nanocuboids functionalized with p-type CuO nanoparticles are demonstrated and explained in [11]. A series of studies are dedicated to $CuMoO_4$-based thermochromic compounds to elucidate the structural origin of their optical properties [12]. The chemistry and physics of bulk and thin-film hafnia-zirconia polymorphs are studied in relation to their ferroelectric properties being of great scientific and technological interest [13]. Finally, a novel analysis method based on an artificial neural network (ANN) approach are used to shed light on the ferritic-to-austenitic phase transition in bulk iron at about 1190 K [14].

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1.3. Spectroscopy

Because of their extraordinary sensitivity, optical spectroscopic techniques are well suited for addressing a broad range of questions that usually arise in solid-state physics. Basic spectroscopic properties such as absorbance, fluorescence and its temporal characteristics are used for general characterization of a material. Additionally, in the case of optical devices, like windows, optical fibers, or scintillators, these properties represent the major application-related characteristics. Raman spectroscopy and Fourier-transform infrared (FTIR) absorption yield vibrational spectra of materials, which are employed for the elucidation of their molecular structure. Another advanced technique – ellipsometry, being non-destructive by its nature, allows the accurate characterization of a range of properties of thin films and coatings, including the layer thickness (from a few angstroms to tens of microns), optical constants, chemical composition, crystallinity, anisotropy and uniformity of a single layer or complex multilayer structures.

Magnetic resonance spectroscopy tools, like Electron Paramagnetic Resonance (EPR) and Optically Detected Magnetic Resonance (ODMR) – are indispensable techniques for identification of point defects and photochemical reactions in solid-state materials and characterization of their local structure.

Finally, electron spectroscopy, like X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA), is a technique for analyzing the surface chemistry of a material. XPS can measure the elemental composition, empirical formula, chemical state and electronic state of the elements within a material and is of special importance for characterization of thin films and coatings.

Over the last years, the list of equipment available at ISSP UL has considerably increased. It includes general-purpose items like optical absorption spectrophotometer (Agilent Cary 7000) and a modular high-end fluorescence and phosphorescence spectrometer for measuring spectra from the ultraviolet to the infrared spectral range. Determination of quantum yield as well as temporal characteristics of the fluorescence spanning from picoseconds to seconds will be available by Edinburgh Instruments FLS1000 (in the temperature range between 300 K and 4 K).

More specific and advanced state-of-the-art techniques like triple Raman spectrometer equipped with 3 lasers and a microscope (Spectroscopy@Imaging GmbH), Infrared Absorption FTIR Spectrometer (Bruker VERTEX 80v), Ellipsometer (Woolam RC2), Hamamatsu streak-camera (C10910-01) for decay kinetics measurements in a picosecond time domain with wavelength-tuneable excitation from deep UV up to IR range are present.

Modern Electron Paramagnetic Resonance system (Bruker Elexsys-II E500) with Q- and X-band, ENDOR extension and liquid helium flow cryostats for low temperature measurements has been in operation since 2019.

XPS equipment (Escalab Xi+ from Thermo Fisher Scientific) is recently installed. It features two detector systems: one is optimized for spectroscopy, and one is for parallel imaging; and with various options like ultraviolet photoelectron spectroscopy (UPS), reflected electron energy loss spectroscopy (REELS) and monoatomic and cluster Ar+ gun for rapid, high-resolution depth profiling and UPS.

The availability of these reliable and robust basic spectroscopic tools and services creates an excellent environment for many technology areas, which require simple or advanced spectroscopic analysis. High-level advanced optical spectroscopy tools help researchers to perform internationally acknowledged work, and in this way provide contact, cooperation and idea-generation opportunities with more advanced institutions in EU and worldwide. The presence of the equipment combined with the knowledge and experience of the scientific staff on both the basic and advanced levels in university-related research centre helps student training in science and engineering fields. Additionally, the availability of such tools allows for closer collaboration with local small and medium-sized enterprises (GroGlass, Light Guide Optics International, Ceram Optec, SIDRABE).

Publications

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1.4 Morphology and structure

The Laboratory of Materials Morphology and Structure Investigations has been established in 2017 and focuses on the study of materials structure, morphology and composition using modern experimental and theoretical methods.

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

I. Electron microscopy is a relatively new direction at ISSP UL; however, active work was performed to obtain expertise in this field. The effort has led to multiple research publications [1–4] already and the number of publications, where these methods are actively used, increases with every year.

II. The XRD is one of the most used characterization methods at the Institute. As with most characterization methods, the analysis of the results is as important as the acquisition itself, therefore the laboratory has secured an access to the newest databases and has experience in correct application of them. Advanced XRD result analysis is also available: Rietveld refinements of the XRD data are often used to analyze X-ray diffraction data by comparing experimentally obtained spectra with theoretical models. By using the Rietveld method, it is possible to determine the phase distribution, sizes and shapes of crystallites and bond lengths of the material, as well as structural defects. These possibilities are exploited within a number of scientific papers, e.g., [5–7].

III. Personnel working in the laboratory also has decades of experience in nanoindentation, thus attracting researchers from all over Baltics resulting in joint research in high ranking scientific journals [8–11] (e.g. *Energy and Environmental Science* IF32**)**.

IV. AFM studies nowadays are used for studies of specific sample surfaces. The researchers of ISSP UL are successfully applying this technique [12–14]. With the expansion of the laboratory, purchase of new hardware for AFM is being considered to upgrade the available instruments.

Scientific output in form of publications is accompanied by the fulfillment of multiple industry contracts in the framework of ISSP UL services provided for third parties. The recent progress and international cooperation demonstrate the current scientific capacity and experience of the researchers involved to perform state-of the art characterization of material morphology and structure.

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2. Nanotechnology, thin films, nanocomposites and ceramics

2.1. Nanomaterials and nanostructures

The R&D activities cover novel nanomaterials and nanostructures, crystals, glasses, nanoceramics, polymer nanocomposites, and hybrid structures.

The application areas are:

- dosimeters and sensors using thermoluminescence (TL) and optical stimulated luminescence (OSL) in nitrides and oxides;
- scintillators for high-energy physics and medical applications; sensors for diagnostics and persistent short wave infrared phosphors for bioimaging;
- low temperature persistent phosphors sensors; transparent nanocomposite oxyfluoride materials for optical applications;
- nanostructured upconversion luminescent environmental sensors;
- refrigerators based on high-value electrocaloric effect in ferroelectric perovskites; electromechanical actuators based on ferroelectric NBT composition ceramics.

Nanostructured materials such as nanoparticles, nanostructured ceramics and glasses with certain predictable and tailored characteristics are under investigation. The possibility to engineer, control and modify the material properties at the nanoscale is of fundamental and applied importance for the EU and Latvian economies, going towards a more knowledge-intensive manufacturing.

Currently work on synthesis and characterization of nanoparticles, nanocrystals, nanowires, nanotubes and other nanomaterials is highly intensive [1]. Variety of nanomaterials are produced by colloidal chemistry methods, which have proved to be flexible and powerful routines for synthesis of different nanostructures (metal nanowires and nanoparticles, metal oxides, fluorides, sulfides, selenides, etc.) allowing to control their morphology, shape and size. Sol-gel chemistry is combined with colloidal chemical methods to synthesize various hybrid materials. Related chemical methods are hydrothermal and microwave assisted synthesis methods. All these methods can be easily scaled up for mass production.

ISSP UL has the infrastructure and the instruments to characterize and optimize the synthesized nanomaterials using many experimental and theoretical methods. There are scanning and transmission electron microscopy, optical spectroscopy in different range of wavelengths, X-ray diffraction and analysis methods, electron paramagnetic resonance spectroscopy and other. Moreover, full spectrum of theoretical modeling and calculations are available to simulate and interpret the obtained experimental results.

Main application areas of nanomaterials produced at ISSP UL are white light sources and light up-convertors, hydrogen and solar cell energetics, catalyzers, gases and other sensors, NEMS nanocomponents, photodetectors, transparent conductive electrodes, nanocomponents for photonics and plasmonics, for biological and biomedical applications, etc. Few other examples of nanomaterials applications: metal nanowires (Ag, Cu, etc.) being real candidates for printable electronics and transparent conductive coatings, luminescent coatings [2–4].

The nanosized materials are known in various forms, however most often the more appropriate for application are nanoparticles embedded in some matrix. The composite material (shortened term – composite) is a combination of two or more materials and in the simplest case the composite reveals a combination of the individual properties of the materials incorporated, however new functionality can appear also. The study of oxyfluoride glass nanocomposites containing Eu^{3+} allowed determination of RE^{3+} ion distribution in nanocomposite [5]. It is shown that transparent glass ceramics containing $NaErF_4$ nanocrystals are advanced up-conversion materials for infrared radiation visualization [6].

With Plasma Electrolytic Oxidation (PEO), one can easily obtain thick (tens of microns), mechanically resilient and chemically stable oxide nanostructured coatings on aluminum, titanium, magnesium and other valve metal alloys. The study of luminescent PEO coatings is a relatively new subfield of the already well-established coating preparation method adding new possibilities for functional applications. Since the first publication focused on luminescence of PEO coatings that was submitted by ISSP UL [7], many other research groups have devoted significant effort in expanding the list of possible practical applications of the phenomena. As of today, some possible marketable applications are already evaluated and proposed by researchers from ISSP UL: production of ionizing radiation detection coatings, gas sensors [8, 9] and even oxide coatings, which are *both* fluorescent and protective. It is important to mention that all additional properties are achieved without losing the outstanding mechanical and chemical resilience of hard and dense oxide formed on the metal surface. Moreover, they are acquired in industrially friendly process – cheap to perform and easily automated. Therefore, some of the technology developed in ISSP UL is especially interesting for automotive and industrial applications. Although the luminescence of PEO is under investigation for a couple of years now, many applications are still not studied and require careful investigation of feasibility, which will be performed in the upcoming work.

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2.2. Thin films and coating technologies

The existing hard competition in coating manufacturing requests from producers to improve functionality and quality of thin films as well as coatings. This is the reason for the further development of a cooperation between ISSP UL and producers, what is especially efficient with local industrial companies (SIDRABE, GROGLASS, ALFA). The role of ISSP UL is to work out new and improve existing applications, followed by transferring of the corresponding deposition technologies to manufacturing. Functionalizing of large area glass surface for smart, energy saving windows is one example of area of cooperation.

New plasma technologies of High Power Impulse Magnetron Sputtering (HIPIMS) [1-3] and plasma processes bear an enormous potential for manufacturing coatings with properties exceeding by far those of the state-of-the-art. Improvement will be available in the fields of Photovoltaics, Green Buildings (Smart windows), Automotive, Aerospace, Mechanical Engineering, Tribology, Decoration, Displays, Tools, etc. Thus, lifetime, reliability, fuel consumption, performance and cost in the named applications can be optimized significantly.

The aim is to establish ISSP UL as a recognized Center of Excellence for thin film nanotechnologies in EU, and as the most important thin film technology Center in Baltic countries.

The SAF25/50 multifunctional thin film deposition cluster installed at ISSP UL cleanrooms in 2015 and upgraded in 2018 is intended for research and innovation work. The plant is a multifunctional, expandable, modular and flexible system. The plant comprises an input/output chamber with ion gun, a central substrate transfer chamber with radial telescopic transport arm and up to 7 deposition chambers. The substrate is positioned horizontally on a holder. Deposition zones are configured for substrate rotation or displacement during upward deposition.

Vacuum plasma deposition technologies (PVD-Plasma Vapor Deposition, MOCVD Metal-Organic Chemical Vapor Deposition) recently developed at the ISSP UL are widely used for thin films and coatings production. Magnetron sputtering has become the process of choice in many applications. Especially HIPIMS processes developed at the Institute, using highly ionized pulse plasmas, play an important role for modification of material properties. The ZnO is compound with unique physical properties [4]. It is shown that during HIPIMS process the ZnO:Al films can be produced at high oxygen partial pressure [5].

PLD (Pulsed Laser Deposition) is a valuable tool for production of thin films and 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 of deposition allow varying of properties of films in a wide range. ISSP UL has experience in making high-quality thin films of perovskite structures by PLD, studying structure, surface topology (by AFM), dielectric and electromechanical properties. The Institute has experience in the characterization of PLD thin films by developing of ReRAM’s [6-8].

Transition metal oxide-based thin films and coating technologies (PVD, HIPIMS, CVD, MOCVD, PLD) are at the core next-generation microelectronic, nanoelectronic, microelectromechanical devices expected to revolutionize fields of major social relevance as digital information and communication technologies, microactuation/microsensing and energy conversion. This class of materials is characterized by unique properties, often being relevant to different fields of applications, found in compounds that are similar to each other in terms of chemistry and crystal structure. The prospective applications include:

- electrochromic and thermochromic thin film devices and technologies (Smart windows);

- photocatalytic coatings (WO_3-TiO_2, IrO_2-NiO);
- highly oxygen-permeable nano-structured oxygen transport membranes.
- low-cost transparent conducting oxides thin films and technologies;

Transition metal oxide thin films (WO_3, MoO_3, NiO, IrO_2 etc.) are used as optical coatings in electrochromic devices (such as "smart windows") where they change their transmittance upon insertion or extraction of electrical charge. The market of these devices is still limited to niche applications (mainly in automotive technology) due to the high manufacturing costs. Redox-based resistive switching in these compounds (as NiO, Ta_2O_5, TiO_2, doped $SrTiO_3$), is under the attention of the industry for the next-generation of nonvolatile memories (resistive RAM) and for the implementation of a new electronic circuit element, in the memristor.

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3. Functional materials for photonics and electronics

3.1. Organic materials for photonics

The organic materials investigations carried out in ISSP UL are focused on both fundamental and applied studies of organic materials. The aim is to enhance knowledge of the physical properties of organic materials and to develop methods for studying organic materials. This includes not only developing basic knowledge but also demonstrating the practical applications of functional organic materials in both photonics and electronics. Such an approach gives a possibility to make a full cycle from the basic design of molecule to functional application.

The scientific activities are divided into two large and complementary parts. The first part is related to fundamental physical processes in organic materials, as well as to the study of the fundamental properties of new organic materials to predict the potential applications of these compounds. The work basically starts with an idea of the molecular structure and quantum chemical calculations. This usually involves working with chemists from other Universities to formulate the most promising compounds. The properties of the solution with the organic molecules are further investigated to determine the properties of the compounds itself and then thin films are studied. The researchers involved have expertise in the determination of both the optical and electrical properties of organic materials. Optical properties like absorption, emission and nonlinear effects are investigated [1-3]. Determination of photoluminescence spectra and quantum yield, fluorescence kinetics, second and third-order nonlinear optical coefficients is essential to define possible organic compound applications in photonic devices. Some of the applications are related to both optical and electrical properties. The organic light-emitting diode are one of the examples. Therefore, a great attention is paid to the investigation of energy structure and electrical properties of organic semiconductors. Energy levels of the compounds are studied by photoelectron emission spectroscopy (PES) and spectral dependence of intrinsic photoconductivity. PES gives information about molecule ionization energy (IE) and the second method gives a good estimation of the energy bandgap between IE and electron affinity (EA) energy [4]. Local trap states in the bandgap are investigated by temperature modulated space charge limited current method. Charge carrier mobility is obtained by Charge Carrier Extraction by Linearly Increasing Voltage (CELIV) techniques [5]. Getting complete information about a chemical compound one can determine its potential use in photonic or opto-electronic devices. In such a case, structures that are more complex are made to show the application of the organic compound in practical devices. So far, the research activities involved the development of solar cells, organic light-emitting diodes [6-8], Mach–Zehnder interferometer, organic solid-state lasers and gas sensors [2]. Despite such a wide range of directions, it should be noted that the design of these "devices" involves similar methods. The most commonly used are thin film deposition, thin film vacuum evaporation, and optical lithography.

A sufficiently large base of experimental methods to determine the optical and electrical properties of most organic thin film compounds is now available at ISSP UL. Several methods, such as the charge carrier flow rate method, the temperature-stimulated current method, and time-dependent process measurement methods should be developed and adapted to an accessible level of use.

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3.2. Materials for light convertors, sensors, dosimeters and waveguides

A large variety of materials is known as “cold” emitters of light, among them the most intensively investigated ones are organic as well as inorganic solids having various chemical compositions and forms. Investigations clarify some basic questions concerning electronic and ionic processes in these solids. This knowledge was successfully used, and a large number of applications for “cold” light emitters were developed (LED, OLED, economic luminescent light sources, luminescent safety signs, scintillators for ionizing radiation detectors etc.). Despite previous achievements, the current need for efficient light emitting materials is unsaturated. Search for these materials is based on detailed understanding of the electronic–ionic processes. Therefore, investigations into these areas are of great interest and are conducted worldwide. ISSP UL has developed and characterized a wide range of light emitting materials. These materials include nanosized oxides and nitrides [1,2], organic glass-like and polymer materials [3,4] and some other compositions for up-conversion [5,6] as well as for permanent afterglow [7,8].

With the proliferation of nano- and information sciences in virtually every field of technology and everyday life, sensors and actuators become increasingly important as a bridge between the real world and information processing. Given the rapidly increasing information processing power, the performance of the sensors is often the "rate determining step". Finding new materials, operation principles and designs of sensors and improvement of the existing ones is important in order to meet the environment, energy and health care challenges.

Several Labs at ISSP UL perform work relevant to the sensor and actuator field. In the past, significant work in thermoluminescent dosimetry materials for ionizing and UV radiation [9,10] has been accomplished and an experimental technique for thermostimulated luminescence has been developed. Fluoride-based nanocrystalline up-conversion luminescence materials, suitable for luminescent sensing and imaging in biological systems are developed and studied [11,12].

Optical sensing often requires fiber optic waveguides to deliver or extract light to or from the area of interest. This puts application-specific requirements on waveguides used, which are very different from those for standard communication fibers. Characteristics like wide spectral transparency, stability against hostile environment – ultraviolet, high energy radiation, lasers, high temperatures are often required. These fibers are based on SiO_2 and related glassy materials. The Institute has performed a number of internationally well-recognized studies of these materials, e.g., [13,14], aimed at increasing their optical transparency and stability under UV or ionizing radiation [15].

ISSP UL has existing R&D collaboration and possible technology transfer in these fields to Latvia-based industry like Light Guide Optics International, CeramOptec, Baltic Scientific Instruments.

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3.3. Applications for visual perception and image processing

The processes taking place in living organisms are not understood in detail up to now. These biological processes are complicated; and the knowledge of their chemical as well as physical foundations is of high importance, in particular, for human health protection. The researchers ISSP UL contribute to the understanding of the human visual perception by developing the methods, materials and devices for human vision study.

New diffractive optics elements and methods of coded diffraction patterns to be used for phase retrieval from intensity measurements, have been developed and verified. The method has been tested both in simulations and practical experiments. The micro-optical elements needed for the phase retrieval have been designed in the clean room at the ISSP using photolithographic methods. At the same time, transparent microstructures have been created to simulate the vitreous floaters.

Electrically controlled focusing and scattering of light are investigated using appliances based on polymer dispersed liquid crystals and liquid lenses, both causing contrast alteration of an optical image in a real eye and/or model eye and digital photodetector. Thus, the eye lens cataract-induced visual performance loss and/or scattering errors can be detected by commercial wavefront analyzers.

Phase retrieval is essential for recovering the structure of an object under study. The phase problem, i.e., the loss of information about phase is faced in various fields of science and especially in optics. An emerging area of phase retrieval in optics is based on mathematical optimization methods using coded diffractive imaging (CDI). At the ISSP UL studies of phase retrieval based on unique modulation of the object under study are carried out [1-3]. The results obtained are of interest for vision science and astronomy.

The chromatic properties of displays and nonlinear peculiarities of visual perception on flat screens are studied. Tuneable liquid lenses are combined with virtual reality adapter [4]. This device is going to be tested now in vision training exercises. The researchers of ISSP UL carefully follow the recent developments of high pixel-density displays and their spectral emission in order to evaluate and control the metabolism of melatonin by prolonged eye exposition.

Hyperspectral color imaging [5] is still in the researcher focus. Laboratory of Visual Perception currently monitors ambient illumination in Latvia, both by convenient methods and by hyperspectral analysis and together with 55 countries participates in creation of joint data basis of these observations [6]. A patent application was prepared based on hyperspectral color imaging study [7] of color vision deficiency tests.

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3.4. Prototyping of photonic and electronic devices

The progress of materials investigation and material properties tailoring, as well as the new technologies development nowadays is very fast. Quite often, basic research findings are proposed as promising for applications. However, the necessary further process, including applied research and prototyping of the appropriate device is not performed at all or is delayed. Thus, the development of new advanced devices and innovation is slowed down in many cases. To overcome this barrier, the domain of Prototyping of electronic and photonic devices was established at ISSP LU in 2019. The tasks of this domain are to elaborate the prospective technologies and device prototypes, based on the findings of ISSP LU researchers; and to supplement these findings with knowledge of external researchers, if necessary.

The activities at present are focused on human health – personalized and precision medicine, in particular:

- 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. One of the main obstacles in research of microbiome and cancer biomarkers (such as extracellular vesicles) is the lack of suitable test methods and models. By combining the expertise in easy-to-use microfluidic device design and fabrication capabilities of the institute, there is a good chance for creating a novel and impactful biological study test-bed.

In the near future, electrochemical and optical sensors should be incorporated in microfluidic chips. Right now, development of fluorescence activated cell sorting is considered for microbiome research. The importance of these activities is confirmed by a large number of scientific papers, e.g.:

Organ-on-chip in numbers:

- 96 articles in Nature & related journals in last 5 years (Nature IF: ~43) + 7 publications in Science (Science IF:~41) + 95 publications in Cell & related journals (Cell impact factor: ~36);
- 1200 publications in general in the last 5 years, top 20 among them have ~5600 citations. Relatively new field - 16% of publications are in top tier journals, so it is trendy/popular and impactful;
- Harvard and associated/co-authored papers account for 161 records ± 10% of OOC publications.

The present status and problems are:

- Proof of principle shown for various organs/systems;
- Multiple organ integration achieved;
- All done on prototyping-only materials and device fabrication methods;
- No real “baseline” performance defined – hard to compare studies now, since all devices and designs are different;
- Lacks a “killer application” – likely due to the fact that it is hard to compare various studies;
- Need: better materials and manufacturing methods allow for sensitive studies/targets, where naturally porous materials absorb these;
- All devices are still quite crude – they are not user-friendly;

- To be expert in OOC: one needs to know microfabrication, polymer science and surface chemistry, biology, cell culturing and instrument development/design. Lot of expertise required, clearly, devices are not yet user friendly, which limits the applications

- Need: more user-friendly, plug& play devices – this will truly enable the research in OOC, and unleash the potential of the field

Considering that OOC development is done both, in academic and industrial setting, it is complex to evaluate exact TLR levels for the field as such. There are multiple examples of multi-organ chip systems published thus ensuring TLR of at least 4-6. However, there is still lacking a sophisticated system that would reduce the device complexity experienced by the end-users, meaning that the system is unlikely to be higher than TLR 6. Quite a lot of early user feedback as presented in the *Organ-on-a-Chip: Current Gaps and Future Directions conference* has been focused on the severe complexity and continuous effort required to run these systems.

Key international actors / competitors / partners.

- The Wyss Institute for Biologically Inspired Engineering is a cross-disciplinary research institute at Harvard University, which focuses on developing new bioinspired materials and devices for applications in healthcare, manufacturing, robotics, energy, and sustainable architecture. Budget $75-80 million. 300-400 employees;

- University of Twente BIOS: Lab-on-a-chip group, 40-50 employees.

Networking.

- Latvian Biomedical Research and Study center. Four project proposals submitted in 2019 in field of cancer research;

- A/S HansaMatrix. Project submitted together with Latvian Biomedical Center (BMC). Potential partner in other project proposals with device fabrication in biomedical field capabilities such as CNC and injection molding.

4. Materials for energy harvesting and storage, clean energy transformation

4.1 Materials for batteries, hydrogen energetics, photovoltaics and fuel cells

European Long Term Climate Strategy identifies that hydrogen and electricity are two main cornerstones providing a strong decarbonizing EU economy, and that green hydrogen and battery technologies are key to enable sustainable electrification, both for the energy and transport sectors. Europe's answer to the emission reduction challenge in the transport sector is a shift to low-emission mobility. By 2050, greenhouse gas emissions from transport will need to be at least 60% lower than in 1990 and be firmly on the path towards zero. Hydrogen is an essential element in the energy transition and can account for 24% of final energy demand and 5.4m jobs by 2050.

The electrification of the economy and the large-scale integration of intermittent renewable energy sources requires large scale energy storage, enabling seasonal storage and the efficient transport of clean energy across regions at low cost. Hydrogen is the only large-scale technology capable of addressing all these challenges. Important Projects of Common European Interests (IPCEI), the most important tools to upscale the European Strategic Value Chain (SVC) on hydrogen technologies and systems, seen as a key sector in the EU. Notably for its expected contribution to achieving the EU climate objectives (more than €60 billion over the next 5-10 years), once completed, will save 35 million tons of CO_2 emissions per year.

Europe needs sustained and coordinated efforts to support investments in research and innovation in advanced materials and chemistries for batteries to enhance their performance, and to pursue leadership in the next generation of battery technologies. Current state-of-the-art batteries are largely based on lithium-ion chemistry, but the demand for higher energy density and performance requires short- to medium-term improvements, together with more radical changes towards a new generation of post-Li-ion batteries based on new advanced materials. The other emerging battery types are Na-ion, Mg-ion, Ca-ion, Al-ion, metal-sulphur, anion shuttle, metal-air, semi-solid flow and redox-flow batteries. Out of these, Na-ion battery technology is the most mature, especially when considering the increasing needs for stationary energy storage [1]. With sodium being 6th most abundant element in Earth's crust, the raw material costs are expected to be significantly lower. Moreover, the high rate capability, stability and recyclability of SIBs are considered to be very attractive [2]. However, cycle life, energy density and rate capability still need to be improved [3]. 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 considered to be the more efficient approach [4].

The main industrial hydrogen production processes are electrolysis, photolysis, thermolysis. Additionally, the process of obtaining biohydrogen obtained from biomass fermentation is under development [5]. Cheap, productive and stable catalysts that replace platinum in hydrogen technologies are needed for hydrogen production (water electrolysis in the membrane process), storage (hydrogen bonding in solids or on the surface) and for use in energy production (microbial and proton exchange membrane fuel cells (MBFC and PEMFC respectively) [5]. Potential substitute for Pt and noble metals in electrocatalytic electrodes could be N-doped graphene [6]. Various methods are also possible in which nitrogen doping can be carried out, for example, the use of controlled atmospheric chemical vapor deposition, arc discharge, solvo-thermic processes, and the doping of already synthesized graphite oxides with nitrogen in thermal, plasma, electrochemical and other processes. Most of these processes are to be carried out under severe conditions (high temperatures, pressures) or using expensive equipment, or in long and incremental processes using health and environmentally harmful reagents, which increases the cost of the end product (catalyst).

Energy harvesting with lowest environmental impact is one of key elements for cleaner future. Photocatalytic as well as electrocatalytic CO_2 reformation processes 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 [7].

The activities of ISSP LU are carried out in the three main directions:

1) *Development of cathode and anode materials for lithium/sodium ion batteries with high performance,* improving nanotechnologies and selecting carbon additives with high surface area; development of new electrolytes based on ionic liquids to reduce the electrical resistance of interfaces between the electrolyte and the anode/cathode electrodes as well as to increase the voltage window for battery application.
As proven by our publication track record [8-19], we have processes and equipment in place for all steps necessary for preparing and characterizing battery materials.

Cathode materials studied at ISSP UL include for the most part $LiFePO_4$ in the form of powder material and thin films, $LiFePO_4$ composite with graphene, reduced graphene oxide and other carbon additives [8-19]. Large capacity and high rate capability $LiFePO_4$/C/graphene cathodes and $LiFePO_4$ thin films, which can possibly be upscaled to develop large area thin films, have been prepared at the Institute. Surface modification of the cathode active material by applying coating and the development of new electrolytes based on ionic liquids helps to reduce the risk of oxidative decomposition at the interface of cathode/electrolyte [20].

Anode materials: graphene, reduced graphene oxide, high surface area carbon, MeO (Me=Fe, Ti) composites with carbon containing additives have been studied at ISSP UL [18,19]. The high charge capacity of graphene composites indicates that they are promising anode materials for future rechargeable batteries.

Current efforts in post-lithium ion batteries is focused on developing $NaMO_2$ and $Na_2MP_2O_7$-type materials for Na-ion batteries (M – Fe, Mn) and understanding their phase-change mechanism. We also plan to develop imidazolium-based polymer ionic liquid electrolyte for Na-ion batteries and have recently submitted a grant proposal on this topic.

2) *Advanced material synthesis and investigations for energy harvesting and storage:*

- photo-catalytic electrode materials for water splitting and wastewater treatment;
- electro-catalytic electrode material for exhaust CO_2 reformation into valuable fuel;
- H_2 storage in nanostructured materials and compressing CH_4 and H_2 blends for applications in transport and heating systems to reduce harmful emissions affecting health and climate changes;
- research of intercalation materials (red-ox mediators) for water electrolysis; synthesis and research of polymer membrane composites for fuel-cell (FC) based applications;
- advanced materials and technologies for linear generator to harvest energy from ocean waves and ram pumps.

Different thin film technologies (electrochemical deposition, spray pyrolysis, electrophoretic deposition, anodic oxidation, magnetron sputtering) are used in ISSP UL to obtain electrodes for hydrogen production in electrolysis and photo-electrochemical splitting methods.

Important tasks are

- to analyze hydrogen production technologies and their suitability resources, conditions:
- the role of hydrogen in current and future energy transport and storage;
- technologies for the production of synthetic methane from renewable energy sources and exhaust CO_2;
- biohydrogen and its production prospects in Latvia and in the world;
- to explore the global experience of hydrogen transport and storage in existing natural gas networks and its feasibility in Latvia [20].

3) *Waste material reuse* - graphene from graphite crucibles - for industrial and green energy applications, development of innovative exfoliation technique to obtain nanostructured graphene sheet stacks and modify them with nitrogen and/or metals, - new catalyst materials are being searched to replace noble metals in hydrogen technologies and for gas sensing in environmental monitoring. Utilization of organic wastes from biofuel industry (glycerol) and food industry (milk whey) for hydrogen production provides inexpensive energy generation with simultaneous waste treatment – research in tight cooperation with biologists to develop efficient hydrogen separation and electrode materials.

In ISSP LU, one of the main challenges is to develop a methodology for the self-extracted nanostructured carbon materials (multi-layer stacks of graphene from waste graphite, and alkaline activated nanoporous carbon from charcoal, kraft-lignin, cellulosic wastewater sludge materials) for nitrogen-doping. The work is in progress to develop a methodology for obtaining electrodes and composites from NC and intercalate materials, to test them for use in gas sensors, electrolysers, batteries, supercapacitors, microbial fuel cells. The results are obtained, analyzed, reports prepared for conferences, publications written etc. For example, reduced few-layer graphene (rFLG) is incorporated into NC matrix in the form of free-standing and supported films. The supported films show a more planar orientation of rFLG sheets than in the case of freestanding films. The composite film shows p-type conductance from both Hall and gas sensing measurements. We have shown that utilization of composite material for sensor material can provide response reaction from both parts of the composite – NC solvent vapors and gases interacting with rFLG NH_3, NO_2 and NO. Composite film is able to detect nitric oxide at concentrations as low as 77 ppm but the film's electrical resistance is partly non-reversible in relatively short periods – this is in contrast to solvents, water and ammonia.

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4.2. Advanced constructive and functional materials for fusion

An ambitious yet realistic roadmap to fusion electricity by 2050 was adopted by EFDA at the end of 2012 in line with the European Commission proposal for the EURATOM programme in Horizon 2020. This roadmap aims at achieving all the necessary know-how to start the construction of a Demonstration Fusion Power Plant (DEMO) by 2030, in order to reach the goal of fusion electricity in the grid by 2050. This programme has the goal of implementing the activities described in the Roadmap during Horizon 2020 through a joint programme of the members of the EUROfusion Consortium. In line with the European Fusion Roadmap, work focused on preparing for ITER operation and the development of a DEMO was launched under the co-ordination of the ITER Physics and the Power Plant Physics & Technology Departments of the EUROfusion Programme Management Unit.

The area of expertise of the Institute of ISSP UL includes research of materials for walls as well as other constructions of fusion reactor and diagnostics of these materials. Regarding the development of materials mentioned, the ISSP UL contributes to consolidating the materials database and material processing trials to improve the performance of key structural material candidates for in-vessel use, including Oxide Dispersion-Strengthened (ODS) steels. The ODS steels studies have provided unique information on the formation and atomic structure of oxide nanoparticles in steels. Synchrotron radiation X-ray absorption studies (XAS) of samples at every stage of the STARS ODS production process are performed. Detailed information on the evolution of the oxide nanoparticles during the completely manufacturing process are obtained [1]. The emphasis is put on the characterisation of samples produced by Hot Isostatic Pressing (HIP) at low temperature and subsequently hot-rolled (modified STARS route). Obtained results made it possible to evaluate the evolution of the structure of ODS steel throughout the manufacturing process and also complemented and validated the results obtained by other methods of analysis [2].

The ISSP UL contributes to the theoretical modelling of the radiation and thermal stability of materials. Theoretical analysis of the experimental data for the annealing kinetics for radiation defects in YAG is performed. Strong correlation between the effective diffusion energy and pre-exponential factor, which depends strongly on the radiation dose, is demonstrated. This important effect is very likely universal and is taken into account in the kinetics prediction for defect accumulation during the irradiation. Based on this study, experimental data are interpreted, and defect stability and radiation damage accumulation kinetics in oxide materials at high radiation fluencies during intensive irradiation by ions, protons, and neutrons are predicted [3, 4].

Theoretical studies aimed for a deeper understanding of radiation-induced damages of the fusion materials used in the intensive neutron and gamma radiation environment are supported by the experimental data of Raman, EPR and infrared spectroscopy, as well as photo- and cathodoluminescence studies on both irradiated and non-irradiated materials. The results show that colloid centres formation can be well explained by the atomistic model of radiation damage. The mechanism of the annealing of the electron centres is shown [5]. The energies corresponding to each stage of the annealing process are obtained. The dependence of the defect annealing on the fluence and type of irradiation is revealed.

Diagnostics play a very important role in the modern tokamak where optimum performance is essential. To achieve this, the device must be equipped with reliable and robust sensors and instrumentation that allow the operation envelope to be fully explored. Development of these diagnostics to maintain this reliability is necessary. The ISSP UL contributes to the development of diagnostic by participating in the implementation of a laser-induced breakdown spectroscopy (LIBS)-based fuel retention monitoring system and the demonstration of its performance in a realistic tokamak environment. LIBS has been developed as a viable monitoring tool, and ongoing studies give the possibility to obtain quantitative and qualitative composition and depth profiling of the impurities that occur in the plasma-facing materials during plasma discharge. Comparative study of the ablation using pico- and nanosecond lasers in low background pressure are performed [6].

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4.3. Advanced perovskites for energy harvesting and storage

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) containing compounds represent a large group of lead-free ferroelectrics. They mainly attract interest as a replacement of lead-containing ferroelectrics, now widely used in various applications, first of all in those, which exploit electromechanical properties [1]. This group of materials can also be modified to have a large, temperature-independent dielectric permittivity in a wide temperature range, necessary for high power capacitors and high values of induced polarization, perspective for application in energy harvesting [2]. Now some NBT-based compositions are very competitive in application of large power ultrasound devices [3]. Considering non-resonance applications presently there is no strong evidence that NBT-based materials could achieve large values of piezoelectric coefficients. At the same time, they are perspectives considering the field induced strains [4]. The existing research is mainly focused on morphotropic phase boundary, what does not look quite well justified.

The interest into electrocaloric effect (ECE) is mainly caused by the very attractive perspective to create a new generation of cooling devices. The main drawback of this effect until recent times was the low values of available temperature change (ΔT), created by ECE. Large values of ΔT, obtained by indirect method, do not look reliable due to possible effects of nonhomogeneous polarization in real material. There are some publications reporting large values of ΔT (up to 6K), obtained by direct method [5, 6] at ultra-high fields in bulk materials and thick films. Unfortunately, such reports are scarce and are not well-confirmed.

Lead-free materials of perovskite structure will be studied, first of all, NBT. This compound together with $BaTiO_3$ and $(K,Na)NbO_3$ represents large group of materials most intensively studied considering the replacement of widely-used lead containing piezoelectrics. NBT is also an essential model material for the study of the role of disorder in A-sublattice of ABO_3 perovskite ferroelectrics on relaxor properties related to non-regular distribution of Na^{1+} and Bi^{3+} ions in A-sublattice of ABO_3 perovskites. Field induced phase transition from metastable nonferro- to ferroelectric states is characteristic feature of NBT-based compositions. These materials possess high breakdown fields. NBT-based materials will be studied, considering the role of dopants and nonstoichiometry on microstructure and ferroelectric properties. Composition range of NBT-based solid solutions will be extended outside MPB. $Ba(Zr,Ti)O_3$ solid solutions are chosen as materials for further research taking into account the promising results obtained from direct measurements of ECE [5].

Studies of NBT and NBT-containing solid solutions, including novel compositions are in progress at ISSP UL. Structure and complex physical properties are studied for a new family of ternary solid solutions NBT-$SrTiO_3$-$PbTiO_3$ exhibiting a wide range of stability of relaxor properties and a pronounced electrocaloric effect [7]. Direct measurements of ECE, which are realized in medium field range (20-30 kV/cm) reveal a very limited range of materials, which have sufficiently large ΔT at room temperature [8]. Problems related with application of indirect evaluation of ECE are analyzed in [9].

Electromechanical properties were studied in solid solutions NBT-$BaTiO_3$-$NaNbO_3$ outside MPB, where increasing of concentration of $NaNbO_3$ allowed shifting of depolarization temperature below room temperature and utilized full deformation at field induced phase transition [10].

Luminescence is studied in Er and Eu doped NBT. Behavior of luminescence at low temperatures revealed a large variety of local environments, created by a Bi/Na disorder. Comparison of luminescence of poled and depoled samples at room temperature and above confirms the possibility of modulation by electric field of luminescence intensity in NBT-based materials [11, 12].

The role of nonstoichiometry, dopants and sintering parameters on microstructure is studied in NBT-based ceramics. The methods to reduce anomalous grain growth are developed [13].

Modern equipment for the measurement of ferroelectric properties is acquired and developed. For advanced synthesis of ferroelectric ceramic samples planetary mill, high temperature furnace with controlled atmosphere, hot pressing equipment and equipment for sawing and grinding of bulk ceramic specimens are implemented. Advanced equipment (x-ray diffractometers, SEM, equipment for EDS) for characterization of phase content and distribution of chemical elements in composition are also available.

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