List of doctoral projects available for the academic year 2023/2024

Instytut Immunologii i Terapii Doświadczalnej im. L. Hirszfelda Polskiej Akademii Nauk

INTiBS PAN WROCŁAW

Chemistry/Physics

Supervisor: Marek Daszkiewicz, D.Sc. (dr hab.) (m.daszkiewicz@intibs.pl)

Subject: ***Anisotropy of intermolecular interactions in crystals at extreme conditions.***

Discipline: Chemistry

Description: The aim of the doctoral thesis is to synthesize a series of organic and organic-inorganic compounds in the crystalline of biological importance. In the crystal structure, the molecules should interact with each other by various types of interactions including hydrogen bonds, stacking interactions, halogen-halogen etc. Changes of the systems of intermolecular interactions will be monitored using X-ray diffraction at different temperature (100-400 K) and high pressure conditions. Indicatrices of thermal expansion and compressibility will be determined. Mechanical properties of the crystals will be correlated with the crystal packing and network of intermolecular interactions..

Supervisor: Przemysław Dereń, prof. (p.deren@intibs.pl)

Subject: ***Synthesis of aluminosilicates and silicates doped with Pr3+ and/or other lanthanide ions and examination of the UV emission of these samples excited by visible light..***

Discipline: Chemistry

Description: The objective of the doctoral thesis will be to develop the synthesis of polycrystalline aluminosilicates and silicates doped with Pr3+ and/or other lanthanide ions and to study the UV emission induced by up-conversion, i.e. i.e. with light with a photon energy lower than the emission photon. Transitions between 5d and 4f electronic configurations as well as within the 4f configuration will be studied.
The UV emission thus obtained can be used for surface disinfection, sterilization or to support the treatment of cancerous tumors. For sterilization to be effective with this radiation, the emission must take place in the UV-C range, that is to say between 200 and 280 nm. The biggest challenge will be to achieve upconversion with low-density of excitation radiation. Success will depend on the morphology of the samples and the dopants used. The doctorate will therefore include both work in the chemical laboratory and spectroscopic research..

Additional information: The doctorate will be implemented as part of a project led by prof. Przemysław Dereń: "Phosphors for UVC LEDs: self-disinfecting surfaces", OPUS grant no. 2021/41 / B / ST5 / 03792) at the Optical Spectroscopy Department (INTiBS PAN) in Wrocław, The planned scholarship is PLN 5,000 gross per month..

Supervisor: Jan Janczak, prof. (j.janczak@intibs.pl)

Subject: ***Stereochemistry and properties of metallophthalocyanine derivatives.***

Discipline: Chemistry

Description: Metal (II) phthalocyanines (for example MgPc, ZnPc, MnPc, FePc, CoPc), although they have been known for several decades, are still of great interest due to their various applications. The properties of metallophthalocyanines of the transition metals, as representatives of the metallophthalocyanine family with the metal at +2 oxidation state, differ significantly from magnesium and zinc phthalocyanine (Mg, d^0, Zn, d^{10}) due to the electronic structure of the central ion (Mn^{2+} (Ar)$3d^5$; Fe^{2+}, (Ar)$3d^6$, Co^{2+}, (Ar)$3d^7$). Therefore, the aim of the work will be to obtain and characterize new complexes of metal phthalocyanines with additional axially coordinating N and O-donor ligands in the crystalline form as well as perform their structural analysis. In addition, the physicochemical characterization of the obtained metallophthalocyanine derivatives should be performed. Moreover, DFT calculations of the geometry of the obtained derivatives and TD-DFT calculations as well as correlation with the experimental UV-Vis spectra should be performed.

Supervisor: Leszek Kępiński, prof. (l.kepinski@intibs.pl)
Auxiliary Supervisor: Karolina Ledwa, dr.

Subject: ***Nanostructured catalysts for thermochemical CO2 valorization.***

Discipline: Chemistry

Description: Global warming due to anthropogenic emissions of greenhouse gases is the greatest challenge of our generation. Carbon dioxide, which is by far the largest contributor to global warming, is currently considered a promising prospective for potential applications as a raw material for the production of fine chemicals, like hydrocarbons, alcohols, ethers, etc.
The main aim of the proposed thesis is to develop well-defined, highly active nanostructured heterogeneous catalysts dedicated to the hydrogenation of CO2 into more valuable chemicals. Synthesized catalysts will be composed of a high surface area support with well-defined 3D geometry (e.g., amorphous mesoporous support with uniform ordered pores, various types of 3D hierarchical flower-like supports, etc.), and nanosized active phase with uniform particle size distribution (cheap transition metals in mono- or bimetallic configurations). Obtained systems will be characterized using a wide range of experimental methods (electron microscopy, X-ray diffraction, NMR, FTIR, Raman spectroscopy, XPS, gas adsorption, etc.) to find how the catalyst structure, chemical architecture, and geometry influence their chemical properties. Then, the catalytic activity and selectivity of obtained catalysts will be checked in the appropriate CO2 hydrogenation process, depending on chosen active phase activity. An essential step to elucidate the catalysts' behavior at reaction conditions will be in situ investigations (e.g. in situ TEM, in situ DRIFTS), planned to be performed in collaboration with other institutions..

Supervisor: Leszek Kępiński, prof. (l.kepinski@intibs.pl)
Auxiliary Supervisor: Rafael de Lima Oliveira, dr.

Subject: ***Metal nanoparticles confined in doped porous carbonaceous materials and their application in catalysis.***

Discipline: Chemistry

Description: Hydrogenation and oxidation of organic compounds correspond to essential reactions in the chemical industry. Traditionally, these reactions are done by stoichiometric amounts (or excess) of toxic reagents such as sodium borohydride as a reduction agent or potassium permanganate as an oxidizing agent, resulting in processes with low selectivity and the generation of much waste. Thus, these traditional processes are environmentally and economically unsuitable. The use of supported catalysts emerged as an alternative for producing valuable chemicals more sustainably.
The project's primary goal is to develop a new class of doped porous carbonaceous materials synthesized using diverse techniques, such as the hard template method or the post-activation of carbons. Waste materials such as glycerol (a by-product of biodiesel synthesis) will be used as a carbon precursor.
Metal nanoparticles (NPS) will be deposited in the structure of the carbon materials aiming for a strong interaction between the metal NPS and the carbon materials creating a synergy between them. The materials will be characterized using various techniques such as microscopies (TEM and SEM), N2 physisorption, XRD, XPS, and XAS.
The prepared metal/carbon materials will be tested as catalysts for the oxidation reactions (such as selective oxidation of alcohols and alkenes), hydrogenation reactions (CO2 or biomass compounds), and hydrogen transfer reactions.

Supervisor: Małgorzata Małecka, D.Sc. (dr hab.) (m.malecka@intibs.pl)

Subject: ***Hierarchical Ce1-xMxO2-y systems (M - transition metal) as catalysts for oxidation reactions.***

Discipline: Chemistry

Description: The main research goal of the project is to design active oxidation catalyst with a hierarchical 3D structure based on modified CeO2. Hierarchical materials are very interesting from a catalytic point of view because of their 3D structure and interesting pore characteristics. In addition, the active supports, which are pure and doped cerium oxides, have excellent reversible reduction-oxidation capabilities of cerium ions and oxygen transport in the ceria lattice. The combination of these advantages with the red-ox properties of cerium oxide materials could lead to the development of highly active catalysts. The multitude of possibilities to interfere with the 3D structure and microstructure of such material gives hope for obtaining a "tailor-made" catalyst for a selected chemical reaction.
Work in the laboratory will be carried out on the basis of wet chemistry methods and hydro(solwo)thermal techniques. The samples prepared in this way will be characterized by the following techniques: TEM, SEM, EDX, XRD, IR, RAMAN, N2 adsorption-desorption, TG, catalytic oxidation tests. The candidate is expected to be involved in laboratory work and to expand his/her knowledge.

Supervisor: Łukasz Marciniak, prof. (l.marciniak @intibs.pl)

Subject ***Luminescence thermometry based on first-order structural phase transition.*** **(2 positions)**

Discipline: Chemistry/Physics

Description: The PhD thesis will be carried out within the framework of the NCN Opus 2022/45/B/ST5/01629 project entitled "Luminescent thermometry based on first-order structural phase transition". As part of its implementation, inorganic luminescent materials doped with lanthanide ions and exhibiting a first-order structural phase transition will be designed. The possibility of exploiting changes in the spectroscopic properties of phosphors observed under temperature changes makes it possible to develop luminescent thermometers. With the remote temperature readout offered by such thermometers, it is possible to thermally image, for example, biological systems or mechanical components in a manner with reduced invasiveness. In order to increase the reliability and accuracy of temperature reading using luminescent thermometers, materials and solutions are being sought to achieve high relative sensitivity while maintaining high emission brightness. To meet these requirements, this project proposes a new and unique solution based on the use of lanthanide ion-doped phosphors in which a temperature-induced first-order structural phase transition is observed. This effect, associated with a change in point symmetry around the lanthanide ion, significantly affects the configuration of its energy levels and thus its spectroscopic properties. Therefore, in the temperature range around the phase transition temperature, the observed spectacular changes in the shape of the emission spectrum make it possible to develop a ratiometric luminescence thermometer with high sensitivity. The project plans to develop luminescent thermometers operating in different temperature ranges by optimizing the composition of the host material, dopant ion concentration and nanoparticle size. The ongoing research will provide important information on the influence of the first-order structural phase transition on the spectroscopic properties of nanoscale lanthanide ion-doped luminophores. The potential of the obtained results is expected to go far beyond luminescence thermometry.
The doctoral student's tasks will include the synthesis of the described materials, their structural and morphological characterization, and the study of spectroscopic properties over a wide temperature range in order to determine the thermometric parameters of the developed thermometers. In addition, the doctoral student will be responsible for the analysis of the obtained results, preparation of scientific publications and presentation of research results at scientific conferences in the form of posters and oral presentations.

Additional information: The Ph.D. thesis will be carried out within the framework of the NCN Opus 2022/45/B/ST5/01629 project entitled "Luminescent thermometry based on first-order structural phase transition**.** The planned scholarship is PLN 5,000 gross per month.

Supervisor: Włodzimierz Miśta, D.Sc. (dr hab.) (w.mista@intibs.pl)

Subject: ***Synthesis, characterization and catalytic activity of metal-organic framework HKUST-1 with encapsulated selected noble metals.***

Discipline: Chemistry

Description: This thesis focuses on the development of a hydro/solvothermal method and or microwave-assisted synthesis for the rapid synthesis of good quality copper benzene-1,3,5-tricarboxylate (Cu-BTC referred also to as HKUST-1) with high yield under mild preparation conditions. Different synthesis conditions and activation methods were studied to understand their influence on the properties of HKUST-1. An additional attempt will be made to in situ synthesis/immobilization of HKUST-1 in macro-/mesoporous silica/nickel monoliths for continuous flow catalysis with low-pressure drop.
As synthesized MOF will be activated by encapsulation of selected noble metals (Au, Pt, Pd…). Interactions between metal nanoparticles (NPs) and metal-organic frameworks (MOFs) in their composite forms have proven to exhibit beneficial properties, such as enhanced catalytic performance through synergistic effects. As prepared hybrid MOF materials will be characterized by: XRD , SEM–EDS, HRTEM, thermal analysis (TG), N2 (77K) physisorption analysis, CO2 and H2 volumetric adsorption, termo-programmed reaction (TPR-H2, TPD-MS, TPO), Raman, IR spectroscopy and by catalytic activity (CO oxidation, PROX).

Supervisor: Włodzimierz Miśta, D.Sc. (dr hab.) (w.mista@intibs.pl)

Subject: ***Synthesis, characterization and catalytic activity of selected perovskites ($LaMO_3$; M= Mn,Co, Fe…) doped with noble metals.***

Discipline: Chemistry

Description: This thesis focuses on the preparation and characterization of perovskite materials (LaMO3; M=Mn, Co, Fe…). The following preparation methods will be used: sol-gel citrate methods, solvothermal methods / microwave-assisted, nano casting technique using mesoporous SBA-15 silica materials as a template. The perovskite structures ABO3 can incorporate ions of various sizes and charges showing great flexibility of composition. Moreover, substitutions of ions into the A- and/or B-sites forming A1-xA'xB1-yB'yO3 or deviation from ideal stoichiometry resulted in altering the electronic properties and also catalytic activity of the perovskites. Therefore the effect of substituting additional different metal cations (Ce+4, Ca+2, …) in A and/or B sites of perovskite cells on catalytic activity will be investigated. Therefore the incorporation of selected noble metals into perovskite lattice will be studied. Exposing the catalyst to oxidizing and reducing atmosphere resulted in the recovery of the high dispersion of noble metals and the excellent stability of the perovskite structure.
As prepared perovskite samples will be characterized by: XRD, SEM–EDS, HRTEM, thermal analysis (TG), N2 (77K) physisorption analysis, thermo-programmed reaction (TPR-H2, O2-TPD-MS, TPO), Raman and FTIR spectroscopy and catalytic activity for CO, VOC, and soot oxidation.

Supervisor: Rafał Wiglusz, prof. (r.wiglusz@intibs.pl) **Subject:** ***Design, preparation and investigation of new block copolymer hydrogels intended for tissue engineering.*** **Discipline:** Chemistry **Description:** The main aim of the PhD thesis is to design and develop an intelligent biocomposite based on the intelligent three-dimensional (3D) printed block copolymer hydrogels (e.g. poly(ethylene glycol) (PEG or PEO), poly(propylene oxide) (PPO) and aliphatic polyesters, such as poly(glycolide) (PGA), as well as polysaccharides – e.g. cellulose derivatives) and their biocomposites as a specific scaffold for nanophosphates doped with metal ions (e.g. lithium (I) ions) dispersed inside it. The obtained biocomposites will be used in further stages of the project to evaluate regenerative and proliferative properties for nerve cells such as olfactory cells. In addition, the work will undertake the task of reconstructing the damaged neuronal pathway. The work will focus on obtaining nanophosphates doped with various ions, e.g., lithium(I), dispersed in a block copolymer hydrogel carrier and evaluating its effect on olfactory cells to stimulate limited nerve regenerative properties and neuronal growth, and consequently restore the sense of smell..
Supervisor: Przemysław Dereń, prof. (p.deren@intibs.pl) **Subject:** ***Synthesis by levitation of amorphous binary compounds, e.g. Al_2O_3 and ternary compounds, such as $LaAlO_3$, doped with rare earth and transition metal ions followed by the preparation of nanoceramics and the study of the spectroscopic properties of the obtained samples.*** **Discipline:** Physics/Chemistry **Description:** Obtaining glasses is limited to materials in which there is a network of ions forming the structure of the glass, typically silicate or borate glasses. However, classical methods cannot be used to obtain glasses of oxides such as Al_2O_3 or ternary compounds like $LaAlO_3$, as any contact with the container or surface will cause crystallization. To obtain amorphous samples of these materials, a special melting technique without any contact with containers or surfaces is required. The levitation method is suitable for this purpose. In this method, the material is levitated in an inert gas flow, and the temperature is raised to approximately 2000°C using CO_2 laser radiation. Stopping the laser rapidly cools the material at a rate of around 600°C/min, resulting in a frozen amorphous form. Our plan is to obtain these materials doped with lanthanide ions. The newly obtained optical materials will be examined for their potential use as active elements in lasers and temperature sensors. In the subsequent research phase, heating these materials will induce the formation of Al_2O_3 or $LaAlO_3$ nanocrystals within the material, and their spectroscopic properties will also be examined.

Supervisor: Andrzej Jeżowski, prof. (a.jezowski@intibs.pl)
Auxiliary Supervisor: Daria Szewczyk, dr

Subject: ***Low-temperature properties of structurally complex solids.***

Discipline: Physics

Description: The diffusion-mediated heat transfer, which in particular manifests itself in the temperature dependencies of thermal properties in crystalline and disordered materials, and composites is the center of a recently announced unified theory of thermal transport in crystals and glasses.
The main postulates are two channels of thermal conduction: gas-kinetic and diffuse. It is believed, that the new, diffuse channel is universal, independent of the crystal structure or amorphous nature of the material, What is most important it can be observed in many types of materials, like disordered molecular crystals, composites, highly anisotropic crystals and low dimensional systems.
The purpose of the study will be to obtain empirical evidence of the hypothesis presented. The study will use the uniaxial stationary heat flow method to determine thermal conductivity and the thermal relaxation method to determine the heat capacity of materials exhibiting low thermal conductivity as promising candidates for the dominant quantum tunneling mechanism of heat transfer.
Within the framework of the proposed research topic, the objects of study will be structurally complex solids, especially composites, using measurement equipment directly available at INTiBS PAN. The research topic will be carried out in cooperation with Politecnica de Catalonia,Barcelona, Spain and the Institute for Low Temperature Physics and Engineering NASU, Kharkov , Ukraine.

Supervisor: Dariusz Kaczorowski, prof. (d.kaczorowski@intibs.pl)
Auxiliary Supervisor: Grzegorz Chajewski, dr

Subject: ***Unconventional superconductivity and long-range magnetic ordering in Ce-Pd-In and Ce-Pt-In dense Kondo systems.***

Discipline: Physics

Description: Since the spectacular discovery of the phenomenon in 1979, advanced experimental and theoretical studies on heavy-fermion superconductivity have continued to be at the very forefront of modern condensed matter physics. This is due to the special character of the superconducting state, which cannot be described in terms of the conventional theory of superconductivity, as well as due to a variety of unusual physical behavior observed in the normal state. The microscopic nature of all these anomalous phenomena originates from strong electronic correlations in metallic systems bearing localized magnetic moments. In recent years, significant progress has been made in understanding the fundamental mechanisms responsible for the simultaneous presence of magnetism and superconductivity (by a number of decades considered as entirely antagonistic). In consequence, the scenarios of competition, coexistence or sometimes even interplay of the two cooperative phenomena have been recognized. Nevertheless, a consistent universal theory of the heavy-fermion superconductivity that might account for all its intriguing aspects is still lacking. Furthermore, new experimental discoveries in the field often result in identification of novel scientific challenges.

The ternary Ce-Pd-In and Ce-Pt-In systems comprise several phases crystallizing with diverse crystal structures, including a few prototype ones. Some of them have been found to exhibit the coexistence of superconductivity and magnetic ordering. Amidst those materials, especially interesting are dense Kondo compounds with multiple Ce atoms sites in their crystallographic unit cells.

In this doctoral work, we intend to investigate comprehensively a few representatives of this unique family of Ce-based heavy-fermion superconductors. The research will be carried out on high-quality single-crystalline specimens in wide ranges of temperature, magnetic field and hydrostatic pressure, employing a variety of modern bulk and local-probe research techniques. We expect that successful accomplishment of this PhD project will significantly contribute to the general understanding of the emergence of magnetism and superconductivity in strongly correlated electron systems, and the results will be published in the most prestigious scientific journals and presented at major scientific conferences.

Supervisor: Adam Pikul, D.Sc.(dr hab.) (a.pikul@intibs.pl)

Subject: ***Thermal expansion and magnetostriction of uranium intermetallic compounds as potential advanced next-generation nuclear fuel.***

Discipline: Physics/Chemistry

Description: Construction of nuclear reactors based on advanced nuclear fuels is one of the conditions for effective decarbonization of the world energy industry. The most commonly used fuel in modern nuclear power plants is semi-conducting uranium dioxide, which (although relatively cheap and easy to produce) is not free from defects and limitations in its use. Problems include swelling and cracking of fuel rods and their low thermal conductivity which is a consequence not only of the burning of uranium dioxide but also of its physical and chemical properties. Therefore, a new generation of nuclear fuels referred to as ATF (accident tolerant fuel) is being searched for i.a. among uranium intermetallic compounds. The proposed PhD thesis will support this search at the level of basic research. Its aim will be to synthesize and study physical properties of selected uranium intermetallic compounds and to attempt to relate these properties to magnetism of the 5f electrons of uranium. The research will consist of growing monocrystals of several carefully selected compounds and their physical characterization mainly through thermal expansion and magnetostriction measurements. Part of the experiments will be carried out in France and the USA (as part of an ongoing collaboration of the supervisor), and the results obtained will be published in specialized journals and presented at international scientific conferences.

Additional information: The condition of admission to work with radioactive isotopes is positive qualification by a doctor of occupational medicine (medical examinations will be conducted at the expense of INTiBS PAN).

Supervisor: Rafał Wiglusz, prof. (r.wiglusz@intibs.pl)
Auxiliary Supervisor: Adam Watras, dr.

Subject: ***Novel fluoride and oxyfluoride materials for use in bioimaging and thermal sensing.***

Discipline: Physics

Description: The main goal of the thesis is to design, prepare and study physicochemical properties of fluoride (LnF3) and oxyfluoride materials (LnOF, Ln4O3F6), where Ln = La-Lu, doped and co-doped with rare-earth ions for use in bioimaging and thermal sensing. Since both the bioimaging and thermal sensing is based on specific energy transfers inside or between different optically active ions, this thesis will be devoted to study the energy transfer mechanisms in the LnF3, LnOF and Ln4O3F6 matrices. The energy transfer including up-conversion phenomenon and the down-conversion processes will be studied. All samples will be prepared using a wet-chemistry methods such as modified Pechini's method, co-precipitation and microwave assisted hydrothermal method, which allow to tailor the final size of nanoparticles and minimize the particle agglomeration effects. For evaluation of crystal structure and morphology the X-ray powder diffraction and electron microscopy both SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) techniques will be used. Detailed structural properties will be obtained by FT-IR (Fourier-Transform Infra-Red) and Raman spectroscopy. The spectroscopic characterization will involves such measurements like absorption spectra in UV-VIS-NIR region, emission and excitation spectra in UV-VIS-NIR region, kinetics of luminescence measured with different excitation and at wide range of temperatures. Selected samples will be prepared for use in bio-imaging and temperature sensing...