Centre for functional and surface functionalized glass (FunGlass)
Dissertations topics for academic year 2017/2018 in PhD study program: *Inorganic technologies and non-metallic materials*

1. A MODEL FOR THE RELATIONSHIPS BETWEEN STRUCTURE AND THERMODYNAMICS IN PHOSPHATE GLASSES

Supervisor: prof. M. Liška/ Partner research institution: CSIC - Spanish National Research Council (Spain, supervised by prof. A. Durán)

Phosphate glasses are a class of special materials with a broad interest in optical applications and since they possess large emission cross sections and low non-linear refractive indices they are ideal for their use as solid state matrices for the emission of laser radiation. However, the use of glasses as laser hosts requires the production of generally large dimensions with a very high optical homogeneity and high quantum efficiencies, thus needing of very special processing conditions and a strict control of the glass composition. Additionally, the melting of phosphate glasses may also imply certain difficulties such as those regarding high volatility of their constituents, easiness of devitrification and rapid change of the viscosity with temperature due to their higher fragile character. The ability to choose the right composition as well as the adequate processing conditions for their preparation lies in the precise knowledge of the atomic structure and its influence on the glass properties.

This project proposal will be carried out within the area of Optical Materials and its main objective will be to set up the fundamentals for a model based on the relationships between the thermodynamics and the structure of the phosphate melts and glasses. The core of the proposal will employ the theoretical methodology previously developed by the group at TNUAD for phosphate glasses that uses the Shakhmatkin and Vedishcheva thermodynamic model [2]. This approach uses structural data obtained through Nuclear Magnetic Resonance and Raman spectroscopies by which it was possible to calculate the Gibbs free energy of formation of the oxides in the glass composition [3]. The final aim of the project will be to obtain a model that based on the relationships between the structure and thermodynamics of the phosphate melts can be able to predict the glass forming ability and the main properties of the glasses.

This PhD work will be divided into two periods: the first, of two years, at the laboratories of CSIC for the preparation and study of the structure of the glasses; and a second of one year for the evaluation of the thermodynamic model at TNUAD.

References:
[1] J.H. Campbell, J.S. Hayden, A. Marker, High power solid state lasers: a laser glass perspective, Int. J. App. Glass Sci. 2 (2011) 3-29.
[2] B. A. Shakhmatkin, N. M. Vedishcheva, M. M. Shultz, A. C. Wright, The thermodynamic properties of oxide glasses and glass-forming liquids and their chemical structure, J. Non-Cryst. Solids 177 (1994) 249-256.
[3] M. Liska, J. Machacek, M. Chromcikova, O. Gedeon, Thermodynamic model and structure of ZnO-MoO3-P2O5 glasses, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B 56(2) (2015) 63-66.

2. SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF PHOSPHORS BASED ON STOICHIOMETRIC ALUMINATES, SILICATES AND ALUMINA-SILICATES FOR APPLICATIONS IN PC-WLEDS

Supervisor: Dr. R. Klement/ Partner research institution: Friedrich Schiller University Jena (Germany, supervised by prof. L. Wondraczek)

The topic of a PhD. work is focused on the preparation of phosphors for applications in pc-WLEDs. Basic (un-doped) and doped (e.g. by Ce^{3+}, Eu^{2+}, Mn^{2+}/Mn^{4+}, or other RE and/or TM ions) systems as glasses (glass microspheres) and polycrystalline materials (as aluminates, silicates, luminosilicates) will be prepared and studied. The structure of un-doped glasses will be investigated by spectroscopic methods (MAS NMR, IR and Raman spectroscopy), then thermal properties (thermal analysis) and crystallization kinetics to characterise glass systems in details. Thereafter, RE and TM doped glasses and polycrystalline materials will be prepared and studied. The concentration of luminescence active ions will be optimised to achieve sufficient emission also in the red spectral region. The optical (UV-VIS-NIR) and photoluminescence properties will be studied in details: steady-state PL, decay curves (TCSPC), effect of temperature on PL properties. The special attention will be placed on: relation of emission properties (after excitation by blue/NUV light) vs. structure and morphology of materials, concentration of RE and TM ions, effect of alkaline earth ions on emission properties of material.

3. PREPARATION AND LUMINESCENCE STUDY OF LONG LASTING PHOSPHORS WITH MELILITE STRUCTURE

Supervisor: Dr. R. Klement/ Partner research institution: Friedrich Schiller University Jena (Germany, supervised by prof. L. Wondraczek)

The topic of a PhD. work is focused on the preparation of long lasting phosphors with light emission up to several hours after sample irradiation exposure to UV light. Doped (e.g. by Eu^{2+}, Mn^{2+}, Dy^{3+}, or other RE and/or TM ions) aluminosilicate systems will be prepared in the form of glass (glass microspheres) and polycrystalline materials of melilite structure (e.g. with ackermanite ($Ca_2MgSi_2O_7$) and gehlenite composition ($Ca_2Al_2SiO_7$)). The prepared materials will be characterised from the point of morphology (e.g. optical microscopy, SEM), phase composition (XRD), structure (MAS NMR, IR and Raman spectroscopy), thermal properties (thermal analysis) and spectral properties (UV-VIS-NIR, fluorescence spectroscopy, EPR spectroscopy). The effect of glass vs. crystalline matrix, type of alkaline earth ions in glass and polycrystalline, and RE/TM concentration on emission intensity and afterglow decay time will be studied in detail. The mechanism responsible for afterglow emission will be proposed for studied materials; the known afterglow mechanisms will be assessed critically.

4. MESOPOROUS AND HOLLOW GLASS MICROSPHERES FOR SELECTIVE TARGETING OF CANCER CELLS

Supervisor: prof. D. Galusek/ Partner research institution: Friedrich-Alexander University Erlangen-Nürnberg (Germany, supervised by prof. A. R. Boccaccini)

Incorporation of drugs, genes and other therapeutic agents in bioactive glass particles for targeted drug delivery is an attractive route for localized cancer treatment, since it decreases the systemic dose delivered to the patient and simultaneously conveys a very high and controllable localized drug dose at the diseased site. This delivery route also improves the delivery and dosage of unstable compounds or poorly absorbed or soluble drugs that would prove to be very innefective via other delivery methods, e.g. oral intake. The incorporation of said substances can be achieved through surface modification of the bioactive glass particles to include functional groups that will allow the anchorage of certain therapeutic molecules, in processes that may be governed through changes in the local pH, for example. Ordered mesoporous bioactive glasses also offer the possibility of adsorbing and releasing organic molecules relevant for cancer treatment, such as bisphosphonates, in a controlled manner. Also, bioactive glass particles may be used in combination with magnetic materials that can be activated locally using an external alternating magnetic field to generate heat, therefore causing a temperature increase in the surrounding tissue. In this manner, osseous cancerous lesions can be treated through local hyperthermia, reducing the side effects of more conventional treatment routes.

5. BIOGLASSES WITH TAILORED RELEASE OF THERAPEUTIC IONS

Supervisor: prof. D. Galusek/ Partner research institution: Friedrich-Alexander University Erlangen-Nürnberg (Germany, supervised by prof. A. R. Boccaccini)

The scope of the project will be synthesis a development of new types of bioactive glasses that have potential to serve as delivery systems for therapeutic inorganics ions (TII) such as copper, strontium, zinc, cobalt, silicon and boron. Mentioned metallic ions have emerged as perspective therapeutic agents and they are involved in progressively expanding field of therapeutic tissue engineering and regenerative medicine, mainly of hard tissues, but also emerging applications in contact with soft tissues. Bioactive glasses loaded with TII can be used for cell proliferation and differentiation, wound healing process, nerve regeneration, and cancer treatment. They have potential osteogenic, antibacterial, anti-inflammatory, pro-angiogenic and neuroprotective effects. Compared to organic biomolecules, to the benefits of TII belongs their lower cost, higher stability, their ability to interact with other ions to alter biological functions and the possibility to be processed under typical manufacturing conditions. Loading inorganic matrices (scaffolds), such as bioactive ceramics and glasses, with TII could offer a great opportunity to develop robust carrier systems with high bioactivity and new functionalities. Metallic ions may have toxic effect: to avoid systemic adverse toxicity it is requested to control release of ions to the target tissues. Designed matrices which ensure local release, controlled level of ions in the body and enable sustained, gradual release are therefore of high interest. Novel bioactive glasses will be produced by introducing controlled amounts of specific therapeutic ions during the production of the bioactive glass by melting, sol–gel or molten salt ion exchange methods. As effective carriers for TII can be used silicate, borate and phosphate base glasses.

6. CORROSION PROTECTION OF METAL USING INTEGRATED SELF-HEALING SYSTEMS

Supervisor: prof. D. Galusek/ Partner research institution: CSIC - Spanish National Research Council (Spain, supervised by prof. A. Durán)

The project proposes to investigate the preparation of integrated self-healing systems for light metal alloys based on anodic, organic, hybrid and inorganic layers. These systems will be able to provide active behavior suppressing corrosion processes near defects combining different repairing mechanisms which will be progressively activated, to provide a prolonged life time. Cr (VI) -based compounds represent the state of the art in corrosion protection of aluminum alloys in the aerospace field. The self-healing ability, present in the chromate conversion, is superior to any other protection system currently available, but European directives strongly limit the use of Cr (VI) for its health and environmental toxicity.

This project proposes to replace chromate conversion coatings by developing systems that combine different self-healing mechanisms in the same system, joining different layers that constitute a corrosion resistant architecture.

The project considers the development of anodic oxide layers for light alloys based on the incorporation of encapsulated corrosion inhibitors into the oxide layer and thus leading to self-healing ability. Then, a sol-gel coating will be deposited onto anodic films as an alternative sealing method to enhance the corrosion performance of these coatings. The infiltration of the anodic films using different sol-gel sols will be also considered.

In the sol-gel part, the development of novel inorganic films combining organic and/or inorganic inhibitors as salts (cerium or rare earth) will be considered. These inhibitors are activated by environmental

parameters promoting the self-healing mechanisms effect; e.g. Glass-like CexOy coatings incorporating CexOy NPs. On the other hand, hybrid organic-inorganic coatings will be developed incorporating inhibitors with different release kinetics and activation mechanisms. In all cases, improve the density and adhesion to metals and paints and self-healing ability will be the principal goals.

The project involves the optimization of compositions and synthesis conditions together with the characterization of the integrated systems. The following general tasks will be carried out:

- To develop anodic oxide layers incorporating corrosion inhibitor.
- To develop effective inorganic, hybrid and organic coatings with self-healing ability for light Al and Mg alloys;
- To develop integrated self-healing coating systems, showing superior self-healing performance (activity, stability, long life protection).
- Characterization of integrated self-healing systems (thickness, scanning electron microscope (SEM), adhesion properties, self-healing functionality of coatings, electrochemical and corrosion resistance tests…)

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3. C. Rosero-Navarro, S. A. Pellice, A. Durán, M. Aparicio. Corr. Sci. 50 (2008) 1283–1291.
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7. GEOPOLYMER-LIKE POROUS MATERIALS FROM ENGINEERED MIXTURES OF INORGANIC WASTE

Supervisor: prof. D. Galusek/ Partner research institution University of Padova (Italy, supervised by prof. E. Bernardo)

The alkali-activation is actually receiving a growing interest in the fields of ceramics. Usual alkali-activated materials, generally known as “geopolymers”, are produced through the reaction of an alumino-silicate raw material with an alkaline compound, which is typically a concentrated aqueous solution of alkali hydroxide or silicate. ‘Inorganic oligomers’ (molecules with few Si4+ and Al3+ ions mutually bonded by bridging oxygens, with OH terminations) formed by dissolution of the raw materials undergo condensation reactions, with water release and formation of a gel, at low temperature (typically below 100 °C). Actual geopolymers yield a ‘zeolite-like’ gel, consisting of a continuous, three-dimensional alumino-silicate network, generally possessing high chemical stability, so that, if inorganic wastes are included in the raw materials, pollutants may remain effectively trapped. The aim of the present investigation is the manufacturing of similar materials, from low temperature hardening, replacing most of mineral raw materials with inorganic waste, including recycled glassses. In case of condensation reaction not yielding a properly ‘zeolite-like’ gel, the chemical stability could be enhanced by application of a thermal treatment (at moderate temperatures), promoting viscous flow of the glass fraction. In addition, the gelification will be exploited for the shaping, e.g. for the obtainment of foams (applied in thermal and acoustic insulation) by mechanical stirring of suspensions undergoing progressive hardening.

8. ADDITIVE MANUFACTURING OF POLYMER-DERIVED GLASS-CERAMICS

Supervisor: prof. D. Galusek/ Partner research institution University of Padova (Italy, supervised by prof. E. Bernardo)

Silicone polymers are known as a fundamental class of preceramic polymers, yielding a remarkable amount of ceramic residue upon firing in air or inert atmosphere. Upon firing in air, silicones transform into amorphous silica, that may react with several oxides, dispersed in the starting polymer as reactive fillers (in form of oxide, hydroxides, carbonates etc.). The reaction may be exploited for the manufacturing of many types of silicate ceramics, especially in the form of highly porous bodies. In selected cases, a liquid phase formed by the melting of borate or phosphate fillers may catalyse the ionic interdiffusion and the synthesis of silicates; upon cooling, the liquid phase transforms into a glass phase, with the obtainment of new kind of glass-ceramics. The aim of the present investigation is the manufacturing of highly porous glass-ceramics by application to silicone-based mixtures of additive manufacturing technologies, such as direct ink writing of silicone-based inks. In particular, reticulated 3D scaffolds, composed of bioactive glass-ceramic, will be a fundamental (but not the only) target, for applications in tissue engineering. Fine glass particles will be studied as well, as alternative reactive fillers.