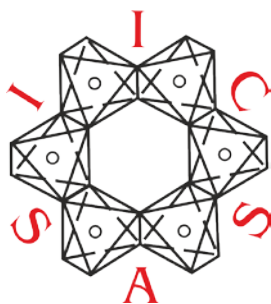Workshop on the occasion of 70th anniversary
of the Institute of Inorganic Chemistry SAS

DESIGN OF ADVANCED INORGANIC MATERIALS

Book of abstracts

3.–4. May 2023, Congress Centre SAS, Smolenice, Slovakia

Workshop on the occasion of the 70th anniversary
of the Institute of Inorganic Chemistry SAS

Design of advanced inorganic materials

Book of abstracts

3. – 4. May 2023, Congress Centre SAS, Smolenice, Slovakia

Institute of Inorganic Chemistry Slovak Academy of Sciences

CONTENT

NA ÚVOD

Vážení kolegovia,

Oslava výročia založenia ústavu je výnimočná príležitosť, aby sme si pripomenuli množstvo nezabudnuteľných chvíľ, ktoré sme spolu prežili, aby sa stretla súčasná mladá a mladšia generácia s bývalými kolegami, aby sme si zaspomínali na kolegov, ktorí už žiaľ nie sú medzi nami. Ich príbehy, a to čo na ústave prežili sa stali legendami, ktoré sa budú šíriť ďalej k ďalším generáciám.

Ústavu savpočas existencie podarilo dosiahnuť množstvo vedeckých úspechov a ocenení. Na svojej „Odysei" sme zažili rôzne dobrodružstvá, tie na ktoré spomíname s radosťou a pýchou, ale aj tie, ku ktorým sa nechceme v spomienkach vracať. Často sa hovorí, čo človeka nezabije, to ho posilní. A preto verím, že aj keď ďalšie roky prinesú mnohé prekážky, tak ich prekonáme s noblesou. Počas svojej dlhej histórie ústav nadviazal kontakty s množstvom rôznych organizácií, prvotné kontakty sa často pretavili do dlhoročných spoluprác a priateľstiev. Môžem tiež s potešením povedať, že ústav vychoval skvelých vedcov, ktorí si našli uplatnenie na významných pozíciách v zahraničí alebo u nás doma. Mnohí z nich udržujú kontakt s ústavom, aj keď odišli na iné pracovisko, alebo do dôchodku. Veľmi si vážim tento záujem a určite je pre nás prínosom.

Svet a veda sa neustále vyvíja a aj my musíme nabiehať na nové výskumné smery a nové myšlienky. To je to, čo nás udržuje v centre diania, v tých oblastiach výskumu, v ktorých pôsobíme, ale netreba zabúdať ani na širší kontext. Moja predstava o správne fungujúcej inštitúcii je založená na zodpovednosti, dôvere, pracovitosti a vzájomnej úcte. Pri tejto príležitosti mám aj výzvu pre mladšie generácie, a to intenzívne študovať a získať rozhľad v oblasti svojej expertízy, neustále rozvíjať medzinárodnú spoluprácu, aby ste sa stali novými piliermi budúcnosti ústavu. Ak toto dosiahneme/dosiahnete, tak sa o budúcnosť ústavu neobávam.

Na záver by som chcel vysloviť úprimné poďakovanie všetkým, ktorí sa podieľali a podieľajú na budovaní dobrého mena ústavu a želám Vám množstvo úspechov aj v ďalších rokoch.

Miroslav Boča

Improving singlet oxygen production in porphyrin-based photosensitizers immobilized on solid carriers via control of dye aggregation and adsorption-induced emission

P. Boháč[1,2] ✉, R. Sasai[3], T. Fujimura[3], J. Bujdák[1,4]

[1]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2]Centre for Advanced Material Application, Slovak Academy of Sciences, Bratislava, Slovakia
[3]Graduate School of Natural Science and Technology, Shimane University, Matsue, Japan
[4]Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia

KEYWORDS: Singlet oxygen, hybrid materials, molecular aggregation, adsorption induced emission

The ability of various dyes to sensitize highly reactive singlet oxygen is a useful tool with potential applications in synthetic photochemistry, environmental and medical fields, such as antibacterial materials. However, for many of these applications, it is necessary to immobilize the photosensitizers on solid carriers, which can pose a challenge due to molecular aggregation of the dye molecules, leading to reduced singlet oxygen production [1].

This study investigates the relationship between molecular aggregation of two metalo-porphyrin-based photosensitizers and singlet oxygen production efficiency in hybrid systems with synthetic saponite Sumecton SA. We controlled the molecular aggregation of porphyrins by varying the silicate/dye ratio ($n_{dye}/m_{silicate}$ - mmol/g) and/or by pre-modifying saponite with cetyltrimethylammonium cation. In addition, we observed the phenomenon of adsorption-induced emission caused by the planarization of metalloporphyrins on the smectite surface. This planarization suppressed the non-radiative deactivation of molecules [2].

Overall, these findings provide insights into optimizing singlet oxygen production in photosensitizer immobilization on solid carriers, which could have significant implications for the development of new applications in various fields.

References

[1] I. Pibiri, S. Buscemi, A. Palumbo Piccionello, A. Pace (2018) Photochemically Produced Singlet Oxygen: Applications and Perspectives. ChemPhotoChem. 2, 535-547.
[2] J. Bujdák, T.S. Baranyaiová, P. Boháč, P, R. Mészáros (2023) Adsorption of Dye Molecules and Its Potential for the Development of Photoactive Hybrid Materials Based on Layered Silicates. J. Phys. Chem. B. 127, 1063–1073.

✉ peter.bohac@savba.sk

CONSTRAINED THERMODYNAMIC INTEGRATION WITH HARMONIC REFERENCE

T. Bučko[1,2] ✉, J. Amsler[3], P.N. Plessow[3], F. Studt[3,4]

[1] Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia
[2] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislav, Slovakia
[3] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany
[4] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

KEYWORDS: Free energy, ab initio molecular dynamics, adsorption, reaction kinetics

Despite an enormous growth of CPU power commonly available for molecular simulations, calculations of free energy remain extremely challenging. This is particularly true for the adsorption problems, where the traditional path-based methods, such as umbrella sampling [1], metadynamics [2], or blue moon ensemble approach [3] can not be applied in practice as they require sampling of full transformation pathways that are notoriously difficult to parametrize. In this respect, the thermodynamic integration technique (TI) [4] with harmonic reference, a method commonly used in simulations of crystalline systems [5], appears to be promising. However, its application to adsorption problem is limited by several obstacles, which we address in this work. First, we reformulate the method in terms of translationally and rotationally invariant internal coordinates, enabling us to efficiently treat the systems with free and hindered rotational and translational degrees of freedom [6]. Second, we introduce a formalism based on holonomic constraints improving the efficiency of sampling of slow degrees of freedom that often cause convergence problems in conventional TI [7]. Finally, we generalize the method for the calculations of free energies of activation, allowing us to determine, e.g., anharmonic apparent activation energies for heterogenous catalytic reactions starting in the gas phase, which are extremely difficult to access by other simulation techniques [7]. The performance of our variant of the TI method is demonstrated in a number of real-world examples.

Acknowledgment:

References

[1] G. M. Torrie, J. P. Valleau (1977) Monte Carlo free energy estimates using non-Boltzmann sampling: Application to the sub-critical Lennard-Jones fluid, J. Comp. Phys. 23, 187
[2] A. Laio, M. Parinello (2002) Escaping free-energy minima, Proc. Natl. Acad. Sci. U. S. A. 99, 12562
[3] E. A. Carter, G. Ciccotti, J. T. Hynes, R. Kapral (1989) Constrained reaction coordinate dynamics for the simulation of rare events, Chem. Phys. Lett. 156, 472
[4] J. G. Kirkwood (1935) Statistical mechanics of fluid mixtures, J. Chem. Phys. 3, 300
[5] S.G. Moustafa, A.J. Schultz, D.A. Kofke (2015) Very fast averaging of thermal properties of crystals by molecular simulation, Phys. Rev. E 92, 043303
[6] J. Amsler, P.N. Plessow, F. Studt, T. Bučko (2021) Anharmonic correction to adsorption free energy from DFT-based MD using thermodynamic integration, J. Chem. Theory Comput. 17, 1155
[7] J. Amsler, P.N. Plessow, F. Studt, T. Bučko (2021) Anharmonic correction to free energy barriers from DFT-based molecular dynamics using constrained thermodynamic integration, J. Chem. Theory Comput. 10.1021/acs.jctc.3c00169

✉ tomas.bucko@uniba.sk

ON THE MECHANISM OF THE FORMATION OF PHYLLOSILICATE / POLYCATION / DYE LAYER-BY-LAYER ASSEMBLIES

J. Bujdák[1,2] ✉

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic
[2] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovak Republic

KEYWORDS: LBL films, cyanine dyes, J-aggregates, spectral properties, polyelectrolytes.

The formation of layer-by-layer (LBL) assemblies is a straightforward process suitable for producing thin films with well-defined structures and compositions based on mono-layers of molecules and nanoparticles hold by electrostatic forces [1]. The films investigated in this work were based on phyllosilicates, cationic organic dyes, and polydiallyldimethylammonium (PDDA). The individual steps of the assemblies' formation were investigated by absorption and fluorescence spectroscopy in a visible range sensitively reflecting the state and interaction of present organic dyes. Simple, one component films were investigated first; each having a cationic dye, either laser dye oxazine 1 (Ox1) or pseudoisocyanine (PIC) forming J aggregates. More complex films consisting of alternating layers, each having one of the two dyes, were prepared and each step of the deposition was characterized by the spectral methods. Detailed analysis based on chemometric methods (Principal Component Analysis, Multivariate Curve Resolution - Alternating Least Squares) have confirmed the very complex nature of the mechanism. During the assembly process, an outer surface of the formed layer is most affected by the formation of an additional layer. A partial dye desorption and structural rearrangements of adsorbed dye species occurred with the addition of PDDA layer. Other main changes were related to photophysical phenomena in complex films such as fluorescence quenching and intermolecular resonance energy transfer from PIC J-aggregates to Ox1 molecules. The obtained results may promote further studies to develop photofunctional materials based on ternary and more complex systems of a similar type.

References

[1] J. Bujdák, Journal of Physical Chemistry C 2014, 118, (13), 7152-7162.

✉ juraj.bujdak@savba.sk

EFFECT OF SINTERING ADDITIVES ON FUNCTIONAL PROPERTIES OF SILICON CARBIDE GRAPHENE COMPOSITES

O. Hanzel[1] ✉, Z. Lenčéš[1], Y-W. Kim[2], M. Hičák[1], P. Šajgalík[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic
[2] Functional Ceramics Laboratory, Department of Materials Science and Engineering, University of Seoul, Seoul, Republic of Korea

KEYWORDS: silicon carbide, graphene, thermal conductivity, electrical conductivity

Almost fully dense (RD ≥ 98%) silicon carbide - graphene composites with two different type of sintering additives (Y_2O_3–Sc_2O_3 or Y_2O_3–Al_2O_3) and with amount of graphene (graphene nanoplatelets and graphene oxide) in the range from 1 to 5 wt. % were sintered in rapid hot press (RHP). Functional properties as a function of amount of graphene, its orientation in SiC matrix and also effect of sintering additives, sintering conditions and effect of annealing were investigated.

Remarkable improvement of electrical conductivity was achieved by annealing the SiC composites with Y_2O_3–Sc_2O_3 additives in N_2 atmosphere and the highest value of 92 S/cm was obtained for the sample with 5 wt.% GNPs. The highest thermal conductivities were obtained at room temperature in parallel direction to GNPs for annealed SiC-Y_2O_3–Sc_2O_3 material with 1% GO (λ = 238 W/m.K) and 5% GNPs (λ= 233 W/m.K).

The obtained results show that homogeneous distribution of GNPs in SiC matrix, appropriate choice of sintering additives, preferential orientation of graphene, rapid hot-pressing and annealing of samples at 1800°C for 6 h in N_2 atmosphere allows to obtain SiC ceramics with very high electrical and thermal conductivity.
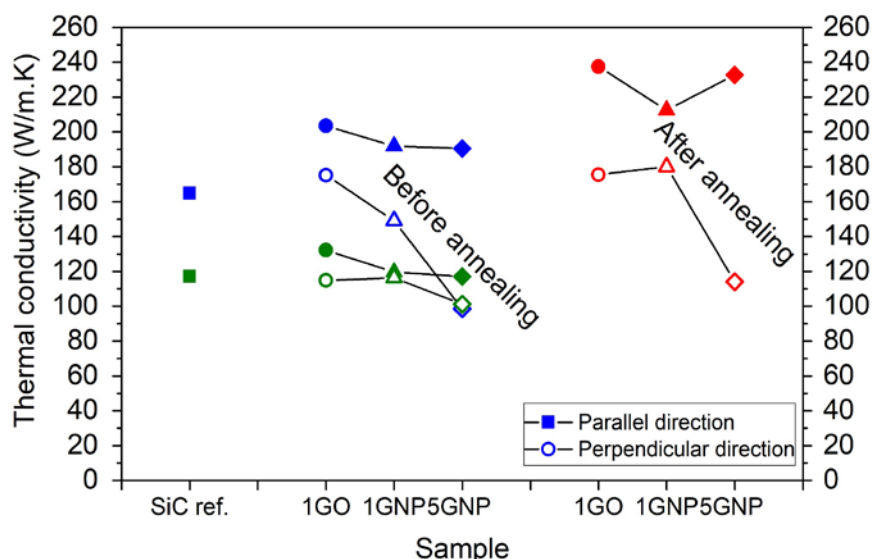

Fig. 1: Thermal conductivity of SiC-Y_2O_3-Al_2O_3 composites (green) and SiC-Y_2O_3-Sc_2O_3 composites before annealing (blue) and after annealing (red) with different amount of graphene

✉ ondrej.hanzel@savba.sk

POLYPROPYLOXAZOLINE CLAY INTERCALATES

Ľ. Jankovič[1] ✉

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: Oxazoline, montmorillonite, intercalation, diffraction

The aim of the present study is to study the effect of poly-2-propyl-2-oxazoline (PPrOx) intercalation on the structural properties of the Na-exchanged montmorillonite (Na-Mt). The nanocomposite was prepared by the intercalation of PPrOx into the montmorillonite Na-Mt. The X-ray diffraction analysis revealed a significant increase in the inter-planar distance from 12.5 to 21.3 Å.

In recent years, poly-2-propyl-2-oxazoline (PPrOx) has received great attention due to its biocompatibility, nontoxicity, and for excellent physical and chemical properties [1]. PPrOx is an amorphous polymer exhibiting a good solubility in water and organic solvents with excellent thermal stability, facile melt fabrication, and high miscibility with various common thermoplastics. The performance and chemical stability of this polymer are superior when compared to those of commonly used polymers, i.e., poly(ethylene-glycol). PPrOx is used in various applications such as biological, biomedicine, and biomedical applications, i.e., drug, protein, microparticles, microspheres or microbeads, layer-by-layer capsules or films, micelles.

The montmorillonite (Mt) is the most smectite clay commonly used due to its high permeability, high surface area, swelling behavior, adsorption, and high cation exchange capacity (CEC) [2]. Mt is used in various applications such as hydrogeology, civil engineering, petroleum engineering, environmental sciences and biological applications and catalysis. This clay is 2:1 type of alumino-silicate with a crystalline structure presenting an alumina octahedral sandwiched between two tetrahedral layers of silica. Because of the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer, the negative surface charge on the clay is compensated by exchangeable cations Na^+, Ca^{2+}, K^+.

PPrOx/montmorillonite samples were successfully prepared by the intercalation of poly-2-propyl-2-oxazoline into the homoionic-exchanged montmorillonite with sodium [3]. The elementary analysis confirmed the presence of C and N elements in the nanocomposite. The XRD showed that the inter-planar distance increases from 11.7 to 21.2 Å. These nanocomposites could find potential use in biomedical applications

References

[1] F. Pooch, V. Teltevskij, E. Karjalainen, H. Tenhu, F. M. Winnik. Poly(2-propyl-2-oxazoline)s in Aqueous Methanol: To Dissolve or not to Dissolve. Macromolecules 2019, 52, 17, 6361–6368.

[2] M. F. Brigatti, E. Galan, B. K. Theng. Structures and mineralogy of clay Minerals. F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Handbook of Clay Science, Developments in Clay Science, Vol. 1, Elsevier (2006), pp. 19-86.

[3] J. Madejová, M. Barlog, M. Slaný, S. Bashir, E. Scholtzová, D. Tunega, L. Jankovič. Advanced materials based on montmorillonite modified with poly(ethylenimine) and poly(2-methyl-2-oxazoline): Experimental and DFT study. Colloids and Surfaces A: Physicochemical and Engineering Aspects 659, 130784 (2023)

✉ lubos.jankovic@savba.sk

Fluoride-free electrochemical surface treatment of 3D printed Ti-6Al-4V biomedical substrates

A. Kityk[1,2] ✉, M. Hnatko[1,2], E. Hadzimová[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Centre of Excellence for Advanced Materials Application, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: Electrochemical treatment, ethaline, Ti alloy, bio-inspiration

Titanium and its alloys have long held the leading position among various materials for manufacturing biomedical devices (mainly commercial dental implants and joint prostheses) [1]. However, Ti alloys without special pretreatment cannot completely meet the high requirements of clinical applications due to the bio-inert nature. In this connection, a several surface modification methods have been proposed in literature [2]. The electrochemical surface treatment deserves a special attention due to its advantages over other methods. Usually, the process of electrochemical surface treatment of Ti alloys is carried out in electrolytes, which contain fluorides [3].

In this work was proposed novel eco-friendly fluoride-free method of electrochemical surface treatment of 3D printed Ti-6Al-4V biomedical substrates. It was demonstrated that electrochemical galvanostatic treatment of Ti-6Al-4V alloy samples in choline chloride-based deep eutectic solvent Ethaline can be used for the flexible design of the surface properties. The change in current density of electrochemical treatment in Ethaline (form 2 mA cm^{-2} up to 50 mA cm^{-2}) affects the color of the formed oxide layer (golden, bronze, silver gray and shadow gray colors); its chemical composition (from almost pure TiO_2 oxide layer to the TiO_2, Ti_2O_3, TiO, Al_2O_3, V_2O_5, V_2O_3 and VO_2 containing oxide layers); roughness (RMS = 300–1695 nm) and some other surface properties. By varying the current density of Ti-6Al-4V electrochemical processing, it is possible to obtain both micro (at low current densities) and nano-inhomogeneous surfaces (at high current densities), which are characterized by markedly better corrosion resistance (corrosion rates decreased by more than 35 times), sufficient wettability (Wa = 116–133 mN m^{-1}), good cells adhesion properties (viabilities of MRC-5 cells ≥75%, doubling times are comparable and better than in control nutrient medium for growing) and improved bacterial resistance (markedly reduced bacteria amount for the polished Ti-6Al-4V alloy surfaces, i = 20–50 mA cm^{-2}). Thus, electrochemical surface treatment of Ti-6Al-4V alloy in Ethaline deep eutectic solvent can be considered as promising, efficient and eco-friendly alternative to the common technologies of titanium processing.

References

[1] A. Kityk, V. Protsenko, F. Danilov, L. Bobrova, M. Hnatko, V. Pavlik, J. Šoltýs, M. Labudová, M. Rusková, D. Pangallo. Design of Ti-6Al-4V alloy surface properties by galvanostatic electrochemical treatment in a deep eutectic solvent Ethaline. Surf. Coat. Technol., 429 (2022) 127936.
[2] X. Liu, P.K. Chu, C. Ding. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Mater. Sci. Eng. R, 47 (2004), pp. 49-121.
[3] D. Regonini, C.R. Bowen, A. Jaroenworaluck, R. Stevens. A review of growth mechanism, structure and crystallinity of anodized TiO_2 nanotubes. Mater Sci Eng R Rep, 74 (12) (2013), pp. 377-406.

✉ cemaanki@savba.sk

RELATIVISTIC THEORY OF EPR: FUNDAMENTAL ASPECTS OF THE G-TENSOR?

S. Komorovsky[1] ✉

[1] Institute of Inorgaic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: Dirac–Coulomb–Breit Hamiltonian, Dirac–Kohn–Sham, EPR g-tensor, relativity

The relativistic approaches based on the Dirac–Coulomb–Breit Hamiltonian and restricted kinetically and magnetically balanced basis sets are considered the gold standard in the scientific field of quantum chemistry. In the ReSpect program (respectprogram.org) we have implemented over the years methods for prediction of various spectroscopic parameters: (p)NMR, EPR, EAS, ECD, and others. For this purpose we emply the noncollinear Dirac-Kohn-Sham theory based on the Dirac–Coulomb Hamiltonian. We develop the relativistic methods for both closed- and open-shell species, i.e. for systems with both non-degenerate and degenerate ground state. We utilize the time-reversal symmetry which provides us with all the necessary tools to make the implemented methods numerically robust and computationally feasible.

In the book chapter [1] and in the publication [2], the basic aspects of the EPR theory are revisited and their validity is discussed within the relativistic domain described by the Dirac–Coulomb–Breit Hamiltonian. Among other the following questions are answered:

Is the g-tensor a tensor? Is the g-tensor an observable quantity? Can the g-tensor be diagonalized? What is the connection of the principal axis system of the g- and D-tensors? What is the validity of the standard textbook EPR effective Hamiltonian? What is the fundamental difference between the Kramers and non-Kramers partners? Can the sign of the g-tensor eigenvalues be measured?

Most of the theories necessary to answer these questions can be found in refs by Chibotaru [3], Griffith [4], Abragam and Bleaney[5], and Bolvin and Autschbach[6]. A review of the relativistic pNMR and EPR theory as well as filling of some gaps present in other works [3-6] is presented in a book chapter [1] and ref [2].

Acknowledgment:

References

[1] S. Komorovsky (2023) Relativistic Effects and The Chemistry of Heavy Elements: Relativistic Theory of EPR and (p)NMR, edited by K. Ruud (Elsevier).
[2] S. Komorovsky (2023) The existence and unambiguity of the principal axis system of the EPR tensors, in preparation.
[3] L. F. Chibotaru (2013) Ab initio methodology for pseudospin hamiltonians of anisotropic magnetic complexes, in: Advances in Chemical Physics, John Wiley & Sons, Inc., 397–519.
[4] J. S. Griffith (1963), Phys. Rev. 132, 316–319.
[5] A. Abragam, B. Bleaney (1970) Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, Oxford.
[6] H. Bolvin, J. Autschbach (2016) Relativistic methods for calculating electron paramagnetic resonance (EPR) parameters, Springer Berlin Heidelberg.

✉ stanislav.komorovsky@savba.sk

THE PHASE EQUILIBRIA OF N_3AlF_6–NdF_3 AND $(Na_3AlF_6$–$NdF_3)_{eut}$–Nd_2O_3 SYSTEMS

D. Krishnan[1] ✉, M. Korenko[1], F. Šimko[1], and B. Kubíková[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovaki

KEYWORDS: Molten salts, electrical conductivity, rare earth metals

Electrowinning (molten salt electrolysis) is the dominating industrial method for rare earth metal extraction from their oxides in the salt extraction process [1]. Molten salts provide a unique working environment. They offer an ionic, nonaqueous habitat wherein various metal oxides may be dissolved. This also applies to neodymium. It is industrially produced by high temperature electrolysis of Nd_2O_3 dissolved in molten LiF–NdF_3 electrolyte with oxide concentration in the molten fluoride electrolyte to be around 2 wt. % (0.96 mol %) and the operational temperature between 1050–1100 °C [2,3]. The very low solubility of the neodymium oxide in the molten electrolyte is obvious disadvantage of the current industrial electrolysis. It has a direct impact on the low current efficiency of the process.

Therefore, the phase equilibria of Na_3AlF_6–NdF_3 and $(Na_3AlF_6$–$NdF_3)_{eut}$–Nd_2O_3 systems have been analyzed by means of thermal analysis and for the first time, to our knowledge, presented. Both investigated mixtures seem to form a simple eutectic system. It can be concluded that the solubility of Nd_2O_3 in the molten eutectic system of Na_3AlF_6–NdF_3 is relatively high compared to the solubility of Nd_2O_3 in the current molten industrial electrolyte (2 wt. %) for the electrowinning of neodymium (LiF–NdF_3).

References
[1] Abbasalizadeh A et al (2013) Highlights of the salt extraction process. JOM 65(11), 2013, 1552–1558.
[2] K. Grjotheim, H. Kvande, L. Qingfeng, Q. Zhuxian, Metal Production by Molten Salt Electrolysis: Especially Aluminium and Magnesium, China University of Mining and Technology Press, Xuzhou, 1998.
[3] N. Krishnamurty and Ch.K. Gupta, Extractive Metallurgy of Rare Earth, 2nd. Ed., CRC Press, Boca Raton, 2016.

✉ dhiya.krishnan@savba.sk

Saponite modified with a fluorescent polymer and photosensitizer – resonance energy transfer

V. Kureková[1] ✉, P. Boháč[1], S. Belušáková[1], J. Bujdák[1, 2]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia

KEYWORDS: FRET, fluorescein, Phloxine B, saponite

Hybrid systems composed of clay minerals and organic dyes represent materials with unique optical, photophysical and photochemical properties. Photosensitizer get a lot of attention due to various potential applications, such as active components of photo-disinfectants. The aim of this work was to prepare films that exhibit efficient absorption of visible light and excitation energy transfer from fluorescein luminophore groups (FITC) to phloxine B (PhB) molecules. The studied hybrid materials consisted of synthetic saponite (Sap) particles, dextran polymer with positively charged alkylammonium and FITC groups, and photosensitizer - PhB. Solid films of these materials were prepared by vacuum filtration from colloidal precursors. The film composition has been designed in such a way that the amount of fluorescently active components was constant and only the ratio between chromophores and the amount of Sap was changed. The basic characterizations of materials were performed by XRD analysis and infrared spectroscopy in the middle and near infrared region. In addition to the basic characterization of materials, the emphasis was on evaluating the spectral properties of the films and their colloidal precursors by UV/VIS and fluorescence spectroscopy. Studied hybrids were relatively complex systems manifested by a change in the photophysical properties of the individual components depending on the concentration of other components, and also by the interactions between the components, which in addition to the chemical interactions also included several photophysical phenomena. By assembling the complex systems, significant shifts of spectral bands were observed. The changes led at least to the different spectral properties of the fluorophores; however, in extreme cases, the consequence was a complete loss of the colour of a substance. The interpretations of major events were based on the interactions between negatively charged Sap particles and positively charged alkylammonium groups in dextran polymers, competing with the present anionic FITC groups and PhB anions, respectively. In the materials of high saponite/polymer ratios, the positive charge of the polymer was effectively saturated. This was exceptionally manifested by the loss of colloidal stability. For the stable colloids and prepared films, the changes of spectral properties were explained by the equilibria between anionic forms of the chromophores. The films exhibited an efficient light absorption in a relatively wide range of the VIS spectrum, leading to the increased excitation of the photosensitizer - Phloxine B, through resonance energy transfer. Such systems could be used as photosensitizing materials with efficient harvesting of polychromatic light.

✉ valeria.bizovska@savba.sk

LONG-RANGE ^{13}C–^{31}P J-COUPLING IN GROUP 10 ELEMENT BMT COMPLEXES

F. Lemken[1] ✉, V.M. Miranda[2], O.L. Malkina[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Universidade de São Paulo, São Paulo, Brazil

KEYWORDS: Theoretical Chemistry, ^{13}C-NMR, J-Coupling,

C-P *J*-coupling is an essential factor in the interpretation of ^{13}C-NMR spectra of phosphorus containing organic molecules. Phosphorus being highly spin polarisable allows for intensive coupling even with partners removed by several formal bonds (long-range coupling). This makes the interpretation of ^{13}C-NMR spectra considerably more complicated. Further, long-range couplings occur along various propagation paths. They are not limited to covalent bonds ("through-bond"), but can also include "through-space" coupling in which electrons transfer magnetisation in absence of any formal bond (e.g. via lone-pairs). Studying models of coupling pathways [1] has helped several studies of long-range *J*-coupling in the past (e.g. ref. [2]).

Three complexes of group 10 metals (cf. fig. 1) containing PPh$_3$ and BMT ligands were synthesised, and their ^{13}C-NMR spectra were measured. Three long-range C-P-couplings were observed for the Ni & Pt system, but four for the Pd system. It is counterintuitive to observe one coupling only in one system. Furthermore, ^4J(C3-P) > ^3J(C2-P) was observed for all systems despite the clear expectation that the coupling intensity for vicinal carbon atoms would decrease for atoms further away from the common coupling partner.

To explain both counter intuitive observations a theoretical analysis was performed. We started by visualising coupling pathways to identify the most essential structural elements for the transfer of
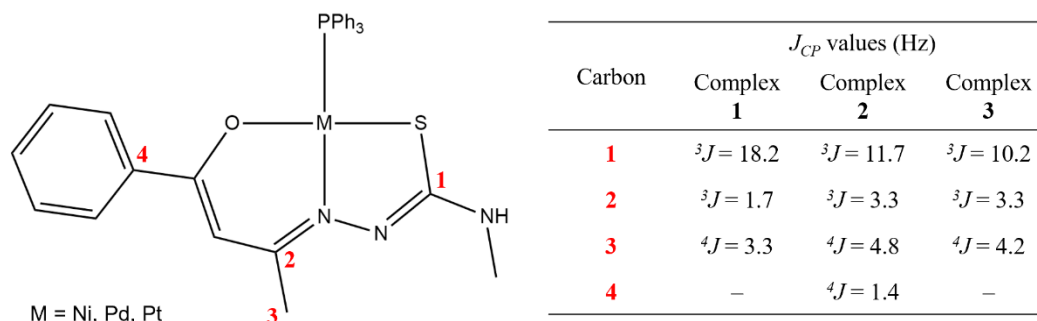

Carbon	J_{CP} values (Hz)		
	Complex 1	Complex 2	Complex 3
1	^3J = 18.2	^3J = 11.7	^3J = 10.2
2	^3J = 1.7	^3J = 3.3	^3J = 3.3
3	^4J = 3.3	^4J = 4.8	^4J = 4.2
4	–	^4J = 1.4	–

Figure 1: 5-hydroxy-N,3-dimethyl-5-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide triphenyl phosphine complexes and J-coupling constants / Hz between P atom and designated C atoms.

magnetisation in the molecules. We investigated the effect of solvation implicitly and explicitly as well as the effect of internal dynamics at those structural elements using highly accurate relativistic DFT methods [3].

References
[1] O. L. Malkina and V. G. Malkin (2003) Angew. Chem. Int. Ed. *42*, 4335–4338.
[2] M. Dračínský, M. Buchta, M. Buděšínský, J. Vacek-Chocholoušová, I. Stará and I. Starý, O. L. Malkina (2018) Chem. Sci. *9*, 7437-7446.

✉ florian.lemken@savba.sk

POLYMER PRECURSOR DERIVED SILICON OXYCARBIDE CERAMIC ANODES FOR Na-ION BATTERIES

A. Güneren, E. Hadzimová, P. Petrisková, Z. Lenčéš✉

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: Na-ion batteries, anode, silicon oxycarbide, binder

Sodium-ion batteries (SIBs) gained a high attention in the last years for energy storage applications because of the limited lithium resources and the intention to use widely abundant and sustainable materials paving the way toward greener, more sustainable, and lower-cost energy storage. Contrary to lithium-ion batteries (LIBs), graphite is not sufficient anode material for Na-ion intercalation due to its low interlayer space distance. The development of new anode materials which have better sodiation capability is one of the key points to produce NIBs on commercial scale. Among others the chemically and structurally stable silicon oxycarbide-based ceramic materials are good candidates as supports for anodes. In this work SiOC-based porous anode was prepared from cross-linked (1200°C/1 h) and pyrolysed Polyramic polysiloxane. The final powder was characterized by means of phase composition, elemental analysis and particle size.

The pyrolysed SiOC powder and conductive carbon C65 were milled in a tungsten carbide planetary ball mill to obtain homogenous powder mixture. Water based slurry was prepared and cast onto copper foil. The anode composition was adjusted as 80:10:10 for active material : conductive carbon: binder. The cells were assembled using Na metal as counter electrode. $NaPF_6$ and/or NaFSI in EC/DMC (50:50) solution was used as electrolyte. Galvanostatic charging/discharging was carried out in the voltage range of 0.005 - 2.5 V at room temperature between 0.25 A/g and 2 A/g current density. Both electrodes reached a specific discharge capacity 160-170 mAh/g after 60 cycles. Cyclic voltammetry was performed to observe the redox peaks in the voltage range of 0 - 2.5 V at room temperature with the scan rate of 0.05 mV/s. Moreover, also the SiOC/tin ceramic-metal nanocomposite as anode matrix and modified alginate-based binders were tested.

✉ uachlenc@savba.sk

NEAR IR STUDY OF THE ARRANGEMENT OF THE ALKYLAMMONIUM CATIONS IN MONTMORILLONITE INTERLAYERS

J. Madejová✉, M. Slaný, Ľ. Jankovič

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

*

KEYWORDS: Organoclay, conformation, head-group structure

The properties of organoclays, employed in a variety of industrial and environmental applications, depend largely on the structure and arrangement of organic cations (surfactants), within clay mineral interlayers. Useful information on the conformation of surfactants, most often alkylammonium cations, provides also near-infrared (NIR) spectroscopy. The present work evaluates the effect of the chain length and head-group structure on the ordering of surfactants in montmorillonite interlayers by NIR spectroscopy. The samples were prepared from Na-montmorillonite Jelšový Potok (JP, Slovakia) and trimethylalkylammonium (C_N–$N(CH_3)_3$) and alkylammonium (C_N–NH_3) cations with increasing number of carbons (N = 6, 8, 10, 12, 14, 16, and 18) in alkyl chain. The NIR spectra of organo-montmorillonites showed the complex band in the 6100-5600 cm^{-1} region related to the first overtone (2vCH) of the CH_3 and CH_2 groups. The position of the $2v_{as}CH_2$ component, observed in the 5820-5780 cm^{-1} interval, reflected an abundance of disordered *gauche* and ordered *trans* conformers. With increasing alkyl chain length the band was shifted to lower wavenumbers indicating decreasing amount of disordered in favour of ordered conformers. The mutual comparison of the spectra of the samples with the same alkyl chain length but different head-groups showed that the position of the $2v_{as}CH_2$ band was always higher for C_N–NH_3–JP than for C_N–$N(CH_3)_3$–JP sample. Due to the different mode of head-group binding, namely N-H···O-Si hydrogen bonds for –NH_3 versus more flexible bonding of –$N(CH_3)_3$ to basal oxygens, the C_N–NH_3 surfactants adopted less ordered conformation than their C_N–$N(CH_3)_3$ counterparts.

✉ jana.madejova@savba.sk

DISTINGUISHING "THROUGH-SPACE" FROM "THROUGH-BONDS" CONTRIBUTION IN INDIRECT NUCLEAR SPIN−SPIN COUPLING

O.L. Malkina[1] ✉, Y. Jean-Cyrille Hierso[2], V.G. Malkin[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Institut de Chimie Moléculaire de l'Université de Bourgogne Dijon Cedex, France

KEYWORDS: NMR, DFT, spin-spin coupling

Indirect NMR spin-spin couplings contain invaluable information about the structure of molecules, especially when other techniques, such as X-ray analysis, are not available. However, this information cannot be extracted without understanding the relationship between the structure of the molecule and the spin-spin interactions themselves in the system under study. The phenomenon of indirect spin-spin couplings is notably conceptually poorly understood in complex experimental situations in which both nonbonded ("through-space") but also more classical bonding ("through-bond") interaction pathways are potentially involved. In this work, we proposed computational procedures that allow the visualization of individual transmission pathways and the estimation of their relative weight.[1] These methods are applicable to large systems with complex interaction of nuclear magnetic moments. In addition, the overall picture of transmission pathways in a complex system can be further refined by analyzing the contributions of individual molecular orbitals or their pairs, which are related to any fragment of the molecular structure. The proposed methods are also applicable to the analysis of hyperfine coupling pathways in EPR spectroscopy. For example, they could help answering the question how the spin polarization generated by the paramagnetic center(s) reaches a particular magnetically active nucleus.

References

[1] O.L. Malkina, J-C. Hierso, V.G. Malkin (2022), "Distinguishing "Through-Space" from "Through-Bonds" Contribution in Indirect Nuclear Spin–Spin Coupling: General Approaches Applied to Complex JPP and JPSe Scalar Couplings", J. Am. Chem. Soc. 2022, 144, 10768–10784.

✉ olga.malkin@savba.sk

TRANSMISSION OF SPIN-POLARIZATION BY π-ORBITALS

V.G. Malkin[1] ✉, F. Lemken[1], J.R. Asher[1], J-C. Hierso[2], M. Bühl[3], O.L. Malkina[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Institut de Chimie Moléculaire de l'Université de Bourgogne Dijon Cedex, France
[3] EaStChem School of Chemistry, University of St Andrews, St Andrews, UK

KEYWORDS: NMR, EPR, DFT, spin-polarisation

A new approach to assessing the effect of the transmission of spin-polarization by π-orbitals (π-TSP) is presented [1]. In order to switch off the π-TSP effect, we artificially average the α- and β-densities of the valence π-orbitals when calculating the exchange–correlation contribution to the Fock matrix in the unrestricted Kohn–Sham framework. The π-TSP effect is then evaluated as the difference between the results obtained with switched-on and switched-off options. This approach is applied to estimate the π-TSP effect on the Fermi-contact contribution to spin–spin couplings and EPR hyperfine structure coupling constants. The sign alternation of the spin-polarization transmitted by π-orbitals is explained in a theoretical framework based on perturbation theory. However, the delocalized nature of the π-system can interfere with the sign alternation in certain cases, two of which – the cyclobutadiene dication and the cyclooctatetraene dication – are examined, and an explanation for which is provided.

References

[1] O.L. Malkina, F. Lemken, J.R. Asher, J-C. Hierso, M. Bühl, V. Malkin (2022) Transmission of spin-polarization by pi-orbitals: an approach to assessing its effect on NMR spin-spin coupling and EPR hyperfine structure. Phys. Chem. Chem. Phys., 24, no. 32, p. 24039-24049.

✉ vladimir.malkin@savba.sk

DOUBLE-STACK ENCAPSULATION OF SMALL MOLECULES

M. Matejdes[1] ✉, J. Bujdák[1], V. Dudko[2], J. Breu[2]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Department of Chemistry and Bavarian Polymer Institute, University of Bayreuth, Bayreuth, Germany

*

KEYWORDS: Ion-exchange, kinetics, double-stacks, synthetic fluorohectorite

The interlayer space of clay minerals provides an environment capable to protect photo-functional species against undesired reactions degrading the overall photo-functional performance. Protective capability is mainly desired in manufacturing processes where devices such as optoelectronic sensors, organic light-emitting diodes, and light-emitting electrochemical cells are produced. Further post-processing is greatly limited due to formed agglomerates with non-uniform sizes and shapes as a result of coagulation and precipitation, which usually occurs during the functionalization of delaminated clay minerals with cationic species. Therefore, it is desirable to produce monolayered functional species encapsulated between two layers of clay mineral with a high aspect ratio. To prevent the formation of domains with different photo-physical properties, the preparation of the so-called double-stacks has to be done with synthetic clay minerals possessing a homogenously distributed layer charge [1]. The production of double-stacks proceeds via crystalline swelling and partial ion-exchange of the functional species into a synthetic layered silicate yielding an ordered heterostructure with two types of strictly alternating interlayers containing a monolayer of cationic species and a monolayer of solvated sodium cations [2]. Later, osmotic swelling triggers the repulsive formation of double-stacks in dispersed form. The kinetics of the ion-exchange reaction is mainly controlled by the partition function describing the affinity of the cationic species towards the bulk solvent and the interlayer space. The kinetics of cationic molecules containing long alkyl chains can be very effectively controlled with binary solvents, while the kinetics of small cationic molecules is very fast even in binary solvents with low water content. This ion-exchange usually ends with phase-segregated crystallites unsuitable for creating double-stacks. Here we would like to present the preparation of double-stacks even with small cationic molecules via a novel sodium-ammonium approach.

References
[1] V. Dudko et al. (2022) Delamination by Repulsive Osmotic Swelling of Synthetic Na-Hectorite with Variable Charge in Binary Dimethyl Sulfoxide–Water Mixtures. Langmuir, 38, 10781-10790.
[2] M. Stoter et al. (2014) Ordered Heterostructures of Two Strictly Alternating Types of Nanoreactors. Chemistry of Materials, 26, 5412-5419.

✉ marian.matejdes@savba.sk

XPS STUDY OF SOME ALKALINE METAL HEPTAFLUOROZIRCONATES/HAFNATES

O. Matselko[1] ✉, Z. Vaskova[1], M. Mičušík[2], M. Boča[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: zirconium, hafnium, fluorides, XPS

Fluorides, homocation K_3HfF_7 and mixed cation Na_2KZrF_7, Na_2KHfF_7, $Na_2K(Zr,Hf)F_7$ (refined composition $Na_2KZr_{0.48(1)}Hf_{0.52(1)}F_7$) have been synthesized by reactions in aqueous solutions and structurally characterized by means of powder X-ray diffraction. In order to prove the coordination of the transition metals and absence of bridging F atoms in the structures XPS study was performed. Obtained spectra (Fig. 1) support the coordination of the transition metals exclusively by F atoms. Values of bonding energies of F $1s$ electrons correspond to the values for terminally bonded F atoms as was reported in [1]. Bonding energies of F $1s$ electrons in the bridging bonding (Zr-F-Zr) are at higher values starting from 685.5 eV and rising up to 687.1 eV, *e.g.* for $Na_5Zr_2F_{13}$. On other side, the presence of F atoms in ionic form can be excluded as the values of bonding energies of F $1s$ electrons of such ions are expected to be lower, below 684 eV [2]. Values of the bonding

Figure 2. High resolution XPS survey spectra of the studied samples.

energies of Zr $3d$ electrons perfectly match with other seven coordinated zirconium atoms, *i.e.* span to the range of 184.3 eV (for Na_3ZrF_7) - 184.8 eV (for $[NH_4]_3ZrF_7$). In addition, impurities of oxygen can be excluded as well, as in such case the bonding energies of Zr $3d$ electrons are lower at *ca.* 182 eV (Zr-O bond) [3]. Such signals have not been observed for the analyzed samples.
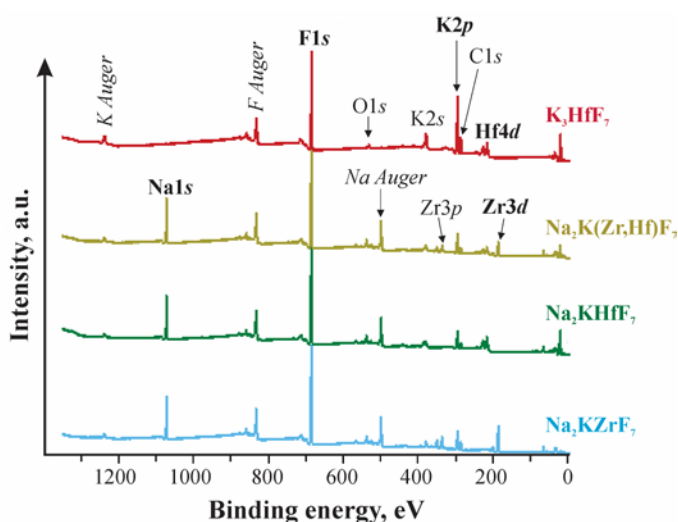
References

[1] A. Rakhmatullin, M. Boča, J. Mlynarikova, E. Hadzimova, Z. Vaskova, I.B. Polovov, M. Mičušik (2018) Solid state NMR and XPS of ternary fluorido-zirconates of various coordination modes. J. Fluorine Chem. 208, 24-35.
[2] M. Boča, A. Rakhmatullin, J. Mlynáriková, E. Hadzimová, Z. Vasková, M. Mičušík (2015) Differences in XPS and solid state NMR spectral data and thermo-chemical properties of iso-structural compounds in the series $KTaF_6$, K_2TaF_7 and K_3TaF_8 and $KNbF_6$, K_2NbF_7 and K_3NbF_8. Dalton Trans. 44 (39), 17106-17117.
[3] R. Jerome, P. Teyssie, J.J. Pireaux, J.J. Verbist (1986) Surface analysis of polymers end-capped with metal carboxylates using x-ray photoelectron spectroscopy. Applied Surface Science 27 (1), 93-105.

✉ oksana.matselko@savba.sk

Viscous flow sintering of glasses with YAG and YAG+24% Al$_2$O$_3$

M. Michálková[1] ✉, J. Kraxner[2], M. Parchovianský[2], R. Klement[2], V. Pouchlý[3,4], K. Maca[3,4], D. Galusek[1,2]

[1] Joint Glass Centre of the IIC SAS, TnUAD, FChPT STU, FunGlass, Trenčín, Slovakia
[2] FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia
[3] CEITEC BUT, Brno University of Technology, Brno, Czech Republic
[4] Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic

KEYWORDS: Viscous flow sintering, YAG,

Yttrium aluminium garnet – YAG (Y$_3$Al$_5$O$_{12}$) represents a group of materials (single crystals, glass-ceramics, phosphor powders, and ceramics) that are good candidates for optical and lighting applications (high-power lasers, color displays, and optical sensors). However, YAG ceramic is usually prepared at high temperatures and long annealing times (e.g. vacuum sintering at 1840°C for 8h) [1]. Viscous flow sintering is the option how to densify glass in the composition of YAG at a significantly lower temperature [2]. For this purpose, flame synthesis was employed to prepare glass microspheres in pure YAG composition and in the composition of YAG enriched by 24 wt.% of alumina. The second step was the densification of glass microspheres by SPS (spark plasma sintering). The densification by viscous flow took place between 840 and 912 ∘C, with the maximum densification rate at 887 ∘C. Figure 1 presents digital photographs of SPS sintered glass with YAG 24 wt. % Al$_2$O$_3$ composition. More discussion can be found in [3].

Fig. 1 Bulk glass in the composition of YAG + 24 wt. % Al$_2$O$_3$ sample sintered in viscous flow.

References

[1] T. Zhou *et al.*, Toward vacuum sintering of YAG transparent ceramic using divalent dopant as sintering aids: Investigation of microstructural evolution and optical property, *Ceram. Int.*, vol. 43, 3140–3146, 2017, doi: 10.1016/j.ceramint.2016.11.131.
[2] A. Rosenflanz, M. Frey, B. Endres, T. Anderson, E. Richards, and C. Schardt, Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides, *Nature*, vol. 430, 761–764, 2004, doi: 10.1038/nature02729.
[3] M. Michálková *et al.*, Viscous flow spark plasma sintering of glass microspheres with YAG composition and high tendency to crystallization, *J. Eur. Ceram. Soc.*, vol. 41, 1537–1542, 2021, doi: 10.1016/j.jeurceramsoc.2020.10.015.

✉ monika.michalkova@savba.sk

THE DENSITIES AND VOLUME PROPERTIES OF THE MELTS OF THE SYSTEMS $MF − K_2ZrF6$ (MF = LiF; NaF AND KF)

J. Mlynáriková[1] ✉, Z. Netriová[1], I. Macková[1], V. Silliková[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: molten salts, density, volume properties

Density is one of the most important thermodynamic properties of liquids. From the density data volume properties can be calculated and volumetric studies are of considerable value in investigation of the structure of liquids. Based on the experimentally measured data of density (determined by the Archimedean method) of the melts systems (MF − K_2ZrF_6 (MF = LiF, NaF and KF) molar volumes, partial molar volumes and the excess molar volumes were calculated. The partial molar volumes of K_2ZrF_6 were obtained by using two different approaches - simple polynomial regression analysis and multicomponent polynomial regression in the form of the Redlich-Kister equation. Based on excess partial molar volumes of compounds (so called parameter of compressibility) we have discussed the volume contraction/expansion. Volume contraction was identified in all three binary systems based on negative values of excess molar volumes.

✉ jarmila.mlynarikova@savba.sk

DOPAMINE GRAFTED ON KAOLINITE

D. Moreno-Rodríguez[1] ✉, E. Scholtzová[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

*

KEYWORDS: dopamine, kaolinite, grafting, density functional theory

The modification of the kaolinite (Kao) surface can tune the properties, enhancing the compatibility and affinity with other molecules, e.g., hydrophobic organic compounds. One way is by grafting molecules with specific functional groups, particularly on the alumina surface (Al–OH). The grafted molecules present a more stable immobilization on the surface, high thermal stability, and resistance to hydrolysis and leaching [1].

Thus, the purpose of this work is to investigate the grafting of the dopamine molecule on the kaolinite Al–OH surface.

The Density Functional Theory method in the solid state was used with the PBE functional [2] and the Tkatchenko-Scheffler scheme [3] for dispersion corrections to study the dopamine-Kao models: adsorbed on the Al–OH surface and grafted monodentate and bidentate in different arrangements.

The results have shown that the location of the alumina-catechol bonds on the Kao surface influenced the different arrangements of the dopamine molecule, e.g., mostly perpendicular to the Kao surface and affecting the amine group disposition which was sometimes out of the plain formed by the dopamine molecule.

References

[1] Yuan, P., Thill, A., Bergaya, F. (2016). Nanosized tubular clay minerals. Halloysite and imogolite, 1st edition, Ed. Elsevier, Amsterdam.

[2] Perdew, J. P., Burke, K., & Wang, Y. (1996). Generalized gradient approximation for the exchange-correlation hole of a many-electron system. Physical Review B, 54(23), 16533–16539. doi:10.1103/physrevb.54.16533

[3] Tkatchenko, A., & Scheffler, M. (2009). Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. Physical Review Letters, 102(7). doi:10.1103/physrevlett.102.073005

✉ daniel.moreno@savba.sk

FLAW-INSENSITIVE TRANSPARENT CERAMICS FOR FLEXIBLE ELECTRONICS

A. Najafzadehkhoee[1] ✉, A. Talimian[2], K. Maca[3,4], R. Bermejo[5], D. Galusek[1,2]

[1] Joint Glass Centre of the IIC SAS, TnUAD and FChPT STU, Trenčín, Slovakia
[2] Centre for Functional and Surface Functionalised Glass, Alexander Dubček University of Trenčín, Trenčín, Slovakia
[3] CEITEC - Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic
[4] Institute of Materials Science and Engineering, Brno University of Technology, Brno, Czech Republic
[5.] Montanuniversität Leoben, Department of Materials Science, Leoben, Austria

KEYWORDS: Laminated ceramics, mechanical properties, tape casting, spark plasma sintering

Despite the high demand for damage-resistance transparent materials in flexible electronics, ceramics have scarcely been used due to their brittle nature [1]. In this study, damage-tolerant flexible laminar ceramics were obtained by engineering the residual stresses generated during sintering due to densification and thermal expansion mismatch in layered ceramics. Multi-layered bodies were fabricated by thermo-compressing of thin layers produced from 8YSZ, 10YSZ, Al_2O_3 and $MgAl_2O_4$, with a thickness between 30 and 60 μm shaped by aqueous tape casting. The laminar bodies were then consolidated using spark plasma sintering [2]. The produced laminar ceramics were characterised in terms of elastic properties, hardness, bending strength, and distribution of residual stress. Tailoring the residual stress distribution, the resistance to the propagation of cracks was engineered and flaw-insensitive transparent ceramics were produced.

Acknowledgement:

References

[1] K. Takagi, Electronic devices with textured zirconia-based components, US20220256720A1, 2022. https://patents.google.com/patent/US20220256720A1/en?oq=2022%2f0256720 (accessed March 29, 2023).

[2] A. Talimian, A. Najafzadehkhoee, D. Galusek, V. Pouchly, K. Maca, Improving Mechanical Properties of Laminated Transparent Ceramics by Engineering Residual Stress Profiles, Perugia, 2022. http://2022.cimtec-congress.org/abstracts_symposium-ca.

✉ ali.najafzadeh@tnuni.sk

Immobilization of metal nanoparticles on organo-modified layered silicates

H. Pálková[1] ✉, M. Zimowska[2], Ľ. Jankovič[1], H. Bujdáková[3]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Kraków, Poland
[3] Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, Bratislava, Slovakia

Keywords: cationic polymer, silver nanoparticles, antibacterial activity

Preparation of suitable supports based on organomodified clay minerals for immobilization and stabilization of metallic nanoparticles is active research area, because of their potential in the field of catalysis or medical applications. Organic cationic species were applied for tuning of growth in size and restricting of possible aggregation of metal nanoparticles. Good dispersion of nanoparticles of defined size, shape, and composition within clay matrix influences functionality of composite material. The objective of this work was to investigate properties of composite materials based on organomodified clay minerals with immobilised Ag nanoparticles towards their application as disinfection materials.

Two clay minerals were selected for this work: synthetic trioctahedral hectorite Laponite RD (Lap) and natural montmorillonite Kunipia (Kun). Polymeric polydiallyldimethylammonium cation (PDDA) was used as dispersant of silver nanoparticles. Two samples for each clay mineral were acquired by reduction of Ag^+ to Ag^0 at different stages of synthesis (Kun1, Lap1, Kun2, Lap2). Carbon content determined for both clay mineral samples was 3 to 3.7%. SEM micrographs registered with backscattered-electron detector (SEM-BSE) confirmed heterogeneous distribution and particle sizes of Ag^0, with part of silver buried within matrix.

Antibacterial activity of studied materials was assayed using microorganisms *Staphylococcus aureus.* Preliminary results showed absolute inhibition of biofilm formation for samples prepared via same approach (Kun2 and Lap2) upon their dilution 2.5 times. With further dilution of samples (10x) Kun2 inhibited microorganism growth for 2.5 log (very good), while for Lap2 and Lap1 antibacterial activity was lower 1 log, Kun1 did not showed any activity against microorganism growth. The results confirmed influence of samples preparation on final properties of prepared samples and subsequently on their antibacterial performance.

✉ helena.palkova@savba.sk

UNDERSTANDING THE IMPACT OF ADDITIVES AND CRUCIBLE MATERIALS ON CORROSION RATES IN MOLTEN FLUORIDE SALTS USING ACCELERATED TESTING

V. Pavlík[1] ✉, P. Weiner[1], J. Priščák[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic

KEYWORDS: High-temperature accelerated corrosion, molten fluoride salt, Ni-based superalloys, additions/impurities.

Author's previous research on high-temperature molten fluoride salts is discussed, specifically focusing on the impact of selected additives, such as CrF_3, $CrF_3.3H_2O$, Cr_2O_3, Na_2O, KF, and KHF_2, on corrosion reactions. Due to discrepancies in the literature, the authors conducted accelerated corrosion tests to confirm previous findings [1, 2, 3]. The tests evaluated the corrosion efficiency of the FLiNaK eutectic mixture on the Incoloy 800H/HT model alloy with various salts, including those containing bound chromium, oxygen, hydrogen, or water, and using two different crucible materials: sintered alumina and glassy carbon. The results show that moisture can increase the corrosion rate by over 6 times by creating hydrogen fluoride. Hydrogen, in the form of HF and H_2O, can also independently increase corrosion. The surfaces of all samples displayed extensive corrosion attack, and SEM-EDX cross-sections revealed dealloying of elements, primarily chromium and iron. Gravimetric analysis showed that the weight changes depended heavily on the mixture used, particularly the concentration of the added salts. The corrosion rate increased when using glassy carbon crucibles due to galvanic corrosion. Overall, the corrosion rate can be increased by using acidic or hydrated salts, selecting a specific crucible, and adjusting the concentration and type of additives used.

References

[1] V. Pavlík, M. Boča, A. Kityk (2022) Accelerated corrosion testing in molten fluoride salts: Effect of additives and the crucible material, Corros. Sci., 195, 110011.

[2] V. Pavlík, M. Kontrík, M. Boča (2015) Corrosion behavior of Incoloy 800H/HT in the fluoride molten salt FLiNaK + MFx (MFx = CrF3, FeF2, FeF3 and NiF2), New J. Chem., 39, 9841-9847.

[3] N.S. Patel, V. Pavlík, B. Kubíková, M. Nosko, V. Danielik, M. Boča (2019) Corrosion behaviour of Ni-based superalloys in molten FLiNaK salts, Corros. Eng. Sci. Technol., 54, 46-53.

✉ viliam.pavlik@savba.sk

ELUCIDATING THE PHOTOPHYSICAL PROPERTIES OF CYANINE DYE AGGREGATES ON CLAY MINERAL SURFACES USING COMPUTATIONAL CHEMISTRY

V. Planetová[1] ✉, Š. Budzák[2], P. Boháč[1,3], J. Bujdák[1,4], R. Klement[5]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Department of Chemistry, Matej Bel University, Banská Bystrica, Slovakia
[3] Centre of Excellence for Advanced Materials Application, Slovak Academy of Sciences, Bratislava, Slovakia
[4] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia
[5] FunGlass-Centre for Functional and Surface Functionalized Glass, Trenčín, Slovakia

KEYWORDS: Aggregation, TD-DFT, cyanine dyes, spectral properties

The aggregation of cyanine dyes and their fixation on clay mineral surfaces can result in significant changes in photophysical properties, such as shifts in spectral bands' maxima, quenching, or enhancement of emission. [1]

In this study, we aimed to investigate the optical properties of these systems using computational chemistry methods. Specifically, we focused on the structure and photophysical properties of molecular aggregates of two cationic cyanine dyes, pseudoisocyanine (PIC) and oxocyanine (Ox-Cy), and their effects on absorption, emission, and vibrationally resolved spectra. We simulated the geometries and spectra of monomers and two types of dimers (of J- and H-type) using TD-DFT (M062X, CAM-B3LYP, MN15, wB97XD) and ab initio (SCS-MP2) methods and compared our results with experimental spectral data.

We also investigated the phenomenon of fluorescence of the PIC dye monomer form in colloidal dispersion with smectite and used various theoretical chemistry methods to analyze the vibronic structure of the spectra and explain the strong luminescence of the PIC monomer. Our findings suggest that the adsorption of dye molecules on smectite particles causes a change in the dihedral angle between pyridine subunits of the PIC molecule, hindering the nonradiative deactivation channel and promoting emission. [2]

Based on our ongoing research, we anticipate that a similar phenomenon may occur for other types of dyes.

References
[1] Bujdák, J., 2018. J. Photochem. Photobiol. C Photochem. Rev. 35, 108–133.
[2] Boháč, P., et al. 2022. The Journal of Physical Chemistry C. 126 (40), 17255-17265.

✉ viktoria.planetova@savba.sk

HYDROLYSIS OF A CYANINE DYE IN WATER-ETHANOL MIXTURES

M. Pribus[1] ✉, P. Boháč[1,2], J. Bujdák[1,3]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] Centre of Excellence for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Bratislava, Slovakia
[3] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia

KEYWORDS: 3,3'-diethylthiatricarbocyanine iodide, hydrolysis, UV-Vis spectroscopy, chemical kinetics

Cyanine dyes are synthetic heteroaromatic compounds belonging to the polymethine group of dyes [1]. Their main application is in biological imaging to label proteins, antibodies, peptides, nucleic acid probes, *etc.* [2]. Cyanine dyes are unstable in an aqueous environment and undergo hydrolysis. In our research, the decomposition of 3,3'-diethylthiatricarbocyanine iodide (DTTC) was studied. It was carried out with the presence of a small amount of ethanol (5 vol.%) to dissolve the dye completely. The DTTC concentrations were from $5.0 \cdot 10^{-7}$ to $1.0 \cdot 10^{-5}$ mol·dm^{-3} in the experiments for reaction order determination. For the experiments aimed at the temperature effect, the concentration of DTTC was always kept at $6.0 \cdot 10^{-6}$ mol·dm^{-3}. The reactant solutions were kept in a thermostat to get the required temperature and mixed just before the start of the measurement. UV-vis absorption spectra were recorded over time and the spectral matrices were decomposed to identify the spectral and concentration profiles of the components.

The order of the reaction was determined by plotting the logarithm of the reaction rate versus the logarithm of the DTTC concentration measured at different reaction times. This dependence is linear, and the slope was used for the calculation of the order of the reaction. The Eyring equation expresses the dependence of the reaction rate constant on temperature. A linear plot of the logarithm of a rate constant vs. the inverse value of thermodynamic temperature was used for the determination of the Gibbs free energy, enthalpy, and entropy of activation.

The mechanism and parameters of the reaction will be compared with DTTC decomposition in more complex systems such as colloids with polyelectrolytes and layered nanoparticles.

References
[1] Kvach, M. V.; Ustinov, A. V.; Stepanova, I. A.; Malakhov, A. D.; Skorobogatyi, M. V.; Shmanai, V. V.; Korshun, V. A. (2008). A Convenient Synthesis of Cyanine Dyes: Reagents for the Labeling of Biomolecules. Eur. J. Org. Chem. 2008, 2107 – 2117
[2] Armitage, B. A. (2005) Cyanine Dye – DNA Interactions: Intercalation, Groove Binding, and Aggregation. Top. Curr. Chem. 253, 55 – 76

✉ marek.pribus@savba.sk

THERMAL BEHAVIOR OF Er^{3+} DOPED YTTERBIUM -ALUMINATE GLASSES

A. Prnova[1] ✉, J. Valuchova[1], L. Sediva[2], D. Galusek[1,3]

[1] Joint Glass Centre of the IIC SAS, TnUAD and FChPT STU, Trenčín, Slovakia
[2] Alexander Dubček University of Trenčín, Faculty of Industrial Technologies, Púchov, Slovakia
[3] FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Trenčín, Slovakia

KEYWORDS: Differential scanning calorimetry, X-ray powder diffraction, ytterbium-aluminate glasses

Yb_2O_3-Al_2O_3 glasses with ytterbium-aluminate garnet (YbAG, $Yb_3Al_5O_{12}$) composition, doped by different content (0.5-10 mol.%) of Er^{3+} ions were prepared by a combination of sol-gel Pechini method and flame synthesis in the form of glass microspheres. For a successful conversion of the microspheres into bulk glasses by hot pressing or sintering of 3-D printed structures at temperatures above 1300°C, it is necessary to examine their thermal behavior in the specified temperature range. For this purpose, differential scanning calorimetry (DSC) measurements were carried out in nitrogen atmosphere, in the temperature range 25-1300°C, and at the heating rates of 2, 4, 6, 8 and 10°C.min^{-1}, followed by X-ray powder diffraction analysis (XRD) and scanning electron microscopy (SEM) for detailed examination. The results revealed a high tendency of the prepared systems to crystallization at the temperature of ∼ 914°C and a very narrow temperature interval 914-918°C for the crystallization of phase pure YbAG. Depending on the heating rate the glass transition temperature values ranged from 750 to 850°C, facilitating the sintering of these systems by viscous flow. In the systems doped with higher contents (2-10 mol.%) of Er^{3+} ions a 3-D crystal growth was predicted by the JMAK model. The prediction was verified and confirmed by isothermal experiments and subsequent analysis of the crystallized systems by X-ray and SEM.

✉ anna.prnova@tnuni.sk

GRAPHENE OXIDE AS AN EFFECTIVE SORBENT MATERIAL OF BENZETHONIUM CATION

E. Scholtzová[1] ✉, T. Szabó[2]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
[2] University of Szeged, Dept of Physical Chemistry and Materials Science, Szeged, Hungary

KEYWORDS: benzethonium, graphene oxide, kaolinite, adsorption, DFT-TS

Synthetic quaternary ammonium salt, benzethonium chloride (BtCl), with antiseptic and anti-infective properties, is used, for example, as a topical antimicrobial agent in first-aid antiseptics. However, the widespread use of BtCl caused its presence in wastewater. Thus effective sorbent material for the immobilization of BtCl is appreciated. This work studies the effectivity of graphene oxide (GO) as a sorbent material also on the atomic level to obtain additional information about the way of anchoring the BtCl pollutant onto the GO surface. The density functional theory method (DFT) with the Tkatchenko-Scheffler (TS) scheme for dispersion corrections was used. The model of graphene oxide was proposed according to our experimental findings. We also aim to relate the results of theoretical modelling with the interpretation of the experimentally determined adsorbed amounts of BtCl from aqueous solutions (Figure 1).
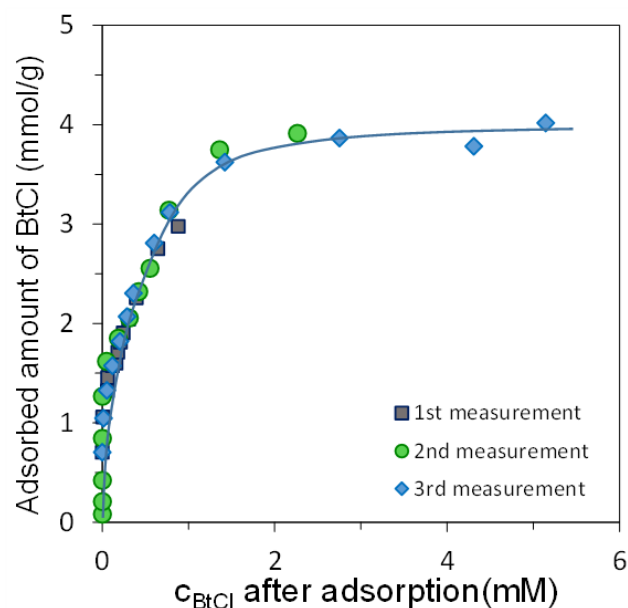
Figure 1. Adsorption isotherm of Benzethonium Chloride on GO at pH = 6 from 10 mM NaCl solution. Three parallel measurements were performed under identical conditions. The solid curve is a guide to the eyes.

✉ eva.scholtzova@savba.sk

ADSORPTION OF NITRATE AND NITRITE POLLUTANTS FROM WATER SOURCES AND SOILS BY ORGANICALLY-MODIFIED SMECTITES

P. Škorňa[1] ✉, E. Scholtzová[1], L. Jankovič[1]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: Nitrate and nitrite pollutants, DFT-D3, adsorption, smectites

Water pollution, with nitrate (NO_3^-) and nitrite (NO_2^-) oxyanions, is an increasing problem threatening both human health and ecosystems [1]. Nitrogen is needed for the production of chlorophyll in plants [2], and nitrogen compounds are widely used in agricultural fertilisers to increase crop yields. Nitrogen fertilisers are the major source of water-soluble nitrate and nitrite compounds in the soil that can be carried away via surface runoff into groundwater, rivers and drinking water [1,3,4]. Other important sources of nitrate contamination in freshwater systems are human, animal and industrial waste [4].

Furthermore, nitrogen is an essential element for the human body to synthesise proteins and nucleic acids. 75% of the ingested nitrate is excreted in the urine, and the remainder is reabsorbed from blood and ends up in salivary glands in the oral cavity, where it is reduced to nitrite and absorbed systemically [5]. In the stomach and other gastric organs, nitrite can be transformed into nitric oxide that acts as a cell signalling modulator. Nitrite can also form nitroso compounds, including N-nitrosamines, that can be carcinogenic in the stomach and intestine [6].

This research aims to provide detailed information about the structure of investigated systems, their structural stability and hydrogen bond interactions to anchor the nitrate and nitrite oxyanions on the surface of the organically-modified beidellite and montmorillonite layers. Furthermore, the calculated vibrational modes using *ab initio* molecular dynamics were analysed in detail and compared with measured FTIR spectra. The calculated projected vibrational density of states was used to identify the individual vibrational modes and overlapped bands in the measured FTIR spectra.

References
[1] J. Mateo-Sagasta, et al. (2018) More people, more food, worse water? A Global Review of Water Pollution from Agriculture, FAO, Rome (Italy)
[2] J.R. Evans, V.C. Clarke (2019) The nitrogen cost of photosynthesis. J. Exp. Bot. 70, p. 7-15
[3] F. Beeckman, et al. (2018) Nitrification in agricultural soils: impact, actors and mitigation Curr. Opin. Biotechnol. 50, p. 166-173
[4] S. Shukla, A. Saxena (2020) Sources and leaching of nitrate contamination in groundwater Curr. Sci. 118, p. 883-891
[5] J.O. Lundberg, et al. (2018) Metabolic effects of dietary nitrate in health and disease Cell Metabol. 28, p. 9-22
[6] M. Carlstrom, et al. (2020) Microbiota, diet and the generation of reactive nitrogen compounds Free Radic. Biol. Med. 161, p. 321-325

✉ peter.skorna@savba.sk

STRUCTURAL CHARACTERIZATION OF POLY(2-OXAZOLINE) MODIFIED MONTMORILLONITE

M. Slaný ✉, M. Matejdes, Ľ. Jankovič, J. Madejová

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

KEYWORDS: montmorillonite, poly(2-ethyl-2-oxazoline), FTIR, intercalation

Clay minerals, especially from the smectite group, are ideal candidates for organic modification [1]. Materials modified in this way represent new materials with improved utilization. In this work, powder samples consisting of montmorillonite (Jelšový Potok, Slovakia) and a unique and novel polymer poly(2-ethyl-2-oxazoline) (PEtOx) were prepared at different loadings (100, 200, 300, 400 and 500 mg/g). Their structural characterization was carried out by using XRD, mid-infrared (MIR) spectroscopy and SEM analysis. Based on XRD, the d001 value for raw montmorillonite (Mt) was determined to be 1.22 nm, confirming the presence of partially hydrated sodium cation. After the intercalation of PEtOx using a loading level of 100 mg/g, a weak diffraction emerged at 4.5°2θ (1.93 nm), indicating the incorporation of the PEtOx into the interlayer space of montmorillonite. During the intercalation of PEtOx using the highest loading level 500 mg/g, the d-spacing increased further up to 2.11 nm, corresponding to the pseudo-trimolecular arrangement. The MIR spectrum of Na-Mt shows the absorption assigned to the characteristic groups of the montmorillonite layer [2]. After modification of Mt with polymer, absorption bands belonging to poly2-ethyl-2-oxazoline appeared in the MIR spectrum. Vibrations of typical CH_3 and CH_2 of PEtOx are located at 2983, 2944, 2886 and 2855 cm^{-1} and a dominant band of the C=O group is located at 1640 cm^{-1}. The FTIR spectra clearly show that the intensity of these vibrational bands increases with increasing loading of PEtOx. From SEM images it is clearly visible that after PEtOx modification in different concentrations, the montmorillonite particles start to rearrange into a large planar structure. Environmentally friendly PEtOx derivatives of montmorillonite have future prospects as nanofillers in non-traditional polymer matrices and in environmental applications as adsorbents of inorganic and organic pollutants.

References
[1] Madejová, J., Barlog, M., Slaný, M., Bashir, S., Scholtzová, E., Tunega, D., Jankovič, Ľ. (2023). Advanced materials based on montmorillonite modified with poly(ethylenimine) and poly(2-methyl-2-oxazoline): Experimental and DFT study. Colloid Surf. A-Physicochem. Eng. Asp. Article number: 130784
[2] Slaný, M., Jankovič, Ľ, Madejová, J. (2019). Structural characterization of organo-montmorillonites prepared from a series of primary alkylamines salts: Mid-IR and near-IR study. Appl. Clay Sci. 176. pp. 11-20

✉ michal.slany@savba.sk

THERMAL PROPERTIES OF GLASSES IN THE SYSTEM Al_2O_3-Y_2O_3-ZrO_2

J. Valuchova[1] ✉, A. Prnova[1], P. Svancarek[1], D. Galusek[1,2]

[1] Joint Glass Centre of the IIC SAS, TnUAD and FChPT STU, Trenčín, Slovakia
[2] FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Trenčín, Slovakia

KEYWORDS: Differential scanning calorimetry, X-ray powder diffraction, HT X-ray powder diffraction

Al_2O_3-Y_2O_3-ZrO_2 glass microspheres with eutectic composition (76.8 mol.% Al_2O_3, 23.2 mol.% Y_2O_3), with different contents of Al_2O_3 or Y_2O_3 (5-10 mol.%) replaced by ZrO_2 were prepared by a combination of the sol-gel Pechini method and flame synthesis. The impact of different additions of ZrO_2 on thermal properties of yttrium-aluminate glasses was studied by DSC. The results showed different thermal behavior of the systems with different ZrO_2 content and the presence of several exothermic effects in the temperature interval 939-1142 °C in DSC curves. X-ray powder diffraction of the samples after heat treatment confirmed the presence of the crystalline phases YAG, α-Al_2O_3, θ-Al_2O_3, m-ZrO_2 and t-ZrO_2. For better understanding of the process of crystallization and its influence on the resulting microstructure of polycrystalline materials, isothermal crystallization experiments at selected temperatures with the holding time of 30 min were performed. A detailed examination of XRD records of the crystallized samples showed mainly a fast crystallization of YAG phase in the sample with the highest theoretical content of YAG, and t-ZrO_2 in the sample with the highest content of Al_2O_3. The results will be utilized in the preparation of glass-ceramic materials by pressure-assisted viscous flow sintering of microspheres.

Acknowledgment

✉ jana.valuchova@tnuni.sk

AUTHORS INDEX