XXVIII. ročník odborného semináře doktorandů

ANORGANICKÉ NEKOVOVÉ MATERIÁLY

procesy • technologie • vlastnosti

8. – 9. února 2023

Ústav skla a keramiky

VŠCHT

Úvod

Programem semináře jsou odborné přednášky doktorandů různých akademických pracovišť působících v oblasti chemie a technologie anorganických nekovových materiálů.

Organizátor semináře

Ústav skla a keramiky, VŠCHT Praha

Webové stránky

https://sil.vscht.cz/o-ustavu/ANM

Kontakt

Ing. Petra Šimonová, *simonovb@vscht.cz*

Poděkování

Ústav skla a keramiky děkuje všem zaměstnancům VŠCHT Praha a doktorandům, kteří se na přípravě semináře podíleli. Dále děkujeme firmě Glass Service, Silikátové společnosti a nadačnímu fondu prof. Rudolfa Bárty za poskytnuté ceny pro soutěžící.

GLASS SERVICE

Silikátová společnost České republiky z.s.

Program semináře 2023

Středa 8. února 2023

Úvodní slovo (9:30-9:40)

1. Blok – keramická soutěžní sekce (11 příspěvků) (9:40-15:10)

předsedající: *doc. Ing. Ondřej Jankovský, Ph.D.*

Ing. Vojtěch Nečina (9:40-10:00)
Preparation of transparent alumina by templated grain growth

Ing. Tomáš Netolický (10:00-10:20)
Near-infrared emission and upconversion in nanocrystalline Er^{3+}/Ho^{3+}-doped $Yb_3Ga_5O_{12}$ garnet

Ing. Lucie Kotrbová (10:20-10:40)
Models for the effective thermal conductivity of carbon-containing nanofluids compared with literature data

Ing. Daniel Valášek (10:40-11:00)
High entropy ceramic – metal composites prepared by Spark Plasma Sintering

Přestávka (11:00-11:20)

Ing. Petra Šimonová (11:20-11:40)
Elastic properties measurement of isotropic ceramics using the ultrasonic technique and theoretical prediction of the porosity dependence of the sound velocity

Ing. Fedor Levchenko (11:40-12:00)
Understanding the relationship between Ga/Sc/Al in co-doped Ce:$Gd_3(Ga,Sc,Al)_5O_{12}$

Ing. Jan Havlíček (12:00-12:20)
Preparation of $GdAlO_3$:Ce crystals by micro-pulling down method

Pauza na oběd (12:20-13:20)

Ing. Lucie Pejchalová (13:20-13:40)
Selective in vivo cell infiltration into durable calcium phosphate scaffolds

Ing. Tomáš Thoř (13:40-14:00)
Transparent ceramics of $LiAl_5O_8$ prepared by spark plasma sintering

Maliha Siddiqui M.Sc (14:00-14:20)
Cold sintered $BaTiO_3$ - tailoring of phase transformation by post annealing

Ing. Václav Doležal (14:20-14:40)
Dielectric properties of calcium and europium copper titanate ceramics prepared by a sol-gel method

Přestávka (14:40-15:00)

Vyhlášení výsledků keramické soutěžní sekce (15:00-15:10)

Čtvrtek 9. února 2023

2. Blok – sklářská soutěžní sekce (5 příspěvků) (9:30-11:40)

předsedající: *doc. Ing. Jaroslav Kloužek, CSc.*

Ing. Karolína Opavová (9:30-9:50)
The effect of TRIS-HCl buffer on *in vitro* testing of bioactive glasses

Ing. Jiří Jemelka (9:50-10:10)
Deposition of a solution-processed thin films of As-S-Se system, prepared from modified $As_{50}Se_{50}$ chalcogenide glass solution

Ing. Tomáš Pipota (10:10-10:30)
Dissolution kinetics of phosphate glasses

Ing. Mohamed Abdelkader (10:30-10:50)
Directed Energy Deposition 3D Glass Printing for Realizing Customized Optical Sensors

Ing. Nikola Klusoňová (10:50-11:10)
Preparation of $CuCr_2O_4$ nanofibers using crystallization in molten glass

Přestávka (11:10-11:30)

Vyhlášení výsledků sklářské soutěžní sekce (11:30-11:40)

3. Blok – nesoutěžní sekce (7 příspěvků) (11:40-15:00)

předsedající: *prof. RNDr. Ondrej Gedeon, Ph.D., DSc.*

Ing. Jakub Suský (11:40-12:00)
Skla systému TeO_2-ZnO-La_2O_3 dopovaná Er^{3+}

Ing. Katarína Heglasová (12:00-12:20)
Characterization and thermal analysis of oxide glasses

Ing. Klára Pulcová (12:20-12:40)
Vlastnosti hydraulického pojiva připraveného z metakaolinu, anhydritu II a vápna

Pauza na oběd (12:40-13:40)

Ing. Eva Bedrnová (13:40-14:00)
Adsorpce fosfátů a amonných iontů na odpadní stavební kaly

Ing. Jakub Michalík (14:00-14:20)
Nové sklokeramické materiály v systéme Al_2O_3-RE_2O_3 so zaujímavými optickými vlastnosťami

Ing. Radka Bakajsová (14:20-14:40)
Porovnanie statického a dynamického korózneho testovania žiaruvzdorných materiálov

Ing. Timur Babii (14:40-15:00)
Preparation of Nickel-containing mixed oxide catalysts and their performance in the total oxidation of volatile organic compounds

Ukončení semináře (15:00)

Ceramics Student Speech Contest

8th February 2023, UCT Prague, Section of ANM 2023

The presentation duration will be 15 minutes, followed by 5 minutes disscusion from the judging committee and the audience.

The jury will be composed of three members:

- doc. Ing. Ondřej Jankovský, Ph.D.
- doc. Ing. František Šoukal Ph.D.
- prof. Dr. Dipl.-Min. Willi Pabst

The list of participants:

- Ing. Vojtěch Nečina
- Ing. Tomáš Netolický
- Ing. Lucie Kotrbová
- Ing. Daniel Valášek
- Ing. Petra Šimonová
- Ing. Fedor Levchenko
- Ing. Jan Havlíček
- Ing. Lucie Pejchalová
- Ing. Tomáš Thoř
- Maliha Siddiqui M.Sc
- Ing. Václav Doležal

Glass Student Speech Contest

9th February 2023, UCT Prague, Section of ANM 2023

The presentation duration will be 15 minutes, followed by 5 minutes disscusion from the judging committee and the audience.

The jury will be composed of three members:

- doc. Ing. Jaroslav Kloužek, CSc.
- prof. Ing. Aleš Helebrant, CSc.
- Ing. Jan Macháček, Ph.D.

The list of participants:

- Ing. Karolína Opavová
- Ing. Jiří Jemelka
- Ing. Tomáš Pipota
- Ing. Mohamed Abdelkader
- Ing. Nikola Klusoňová

ABSTRAKTY
Soutěžní sekce
(Keramická)

Preparation of transparent alumina by templated grain growth

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Fabrication of transparent alumina (Al_2O_3) is challenging task due to its birefringence which usually makes such materials only translucent. Usually, the goal is to keep the grain size of alumina as small as possible (<500 nm), so relevant wavelength of light is no longer able to distinguish between individual grains and the system becomes transparent. However, there are other options; for example, orientation of alumina particles in very strong magnetic fields (>10 T) prior to sintering during slip-casting. Another option (utilized in this study) is promotion of orientation during grain growth by introduction of templates which are oriented in the same direction into a fine-grained matrix. In present work, the orientation was achieved by lithography-based method and sintering was performed by spark plasma sintering (SPS). Transparent samples (see Fig. 1) were successfully prepared achieving maximum in-line transmittance of 54.6 % at 550 nm and thickness of 0.8 mm.

Fig. 1: Transparent alumina prepared by templated grain growth in SPS.

Near-infrared emission and upconversion in nanocrystalline Er^{3+}/Ho^{3+}-doped $Yb_3Ga_5O_{12}$ garnet

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Nanocrystalline oxide of composition $Yb_3Ga_5O_{12}$ belongs to the family of materials with garnet-related structure. It is a promising material with potential applications in the fields of optics and photonics when doped by Er^{3+} or Ho^{3+} ions. High content of Yb^{3+} ions in the $Yb_{15-x}Er_xGa_{25}O_{60}$ and $Yb_{15-x}Ho_xGa_{25}O_{60}$ hosts results in strong absorption band observed from ≈850 to ≈1050 nm due to the Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Excitation using ≈980 nm laser leads to efficient energy transfer from the Yb^{3+} ions to the neighbouring Er^{3+}/Ho^{3+} ions. Subsequent radiative transition of Er^{3+}/Ho^{3+} ions from the upper- and lower-lying excited energy levels provide emission bands observed in visible and near-infrared region, respectively. Nanocrystals of composition $Yb_{15-x}Er_xGa_{25}O_{60}$ and $Yb_{15-x}Ho_xGa_{25}O_{60}$ (with x = 0, 0.01, 0.1, 0.5, 1 and 2 at. %) were prepared by sol-gel combustion technique using citric acid as chelation agent. Structure and morphology of the annealed powders were studied by X-ray diffraction, ATR-FTIR spectroscopy and by scanning electron microscopy. Optical reflectance of the powders and absorption bands of present lanthanides were investigated by diffuse reflectance spectroscopy. Photoluminescence spectroscopy was used for measurement of the steady-state and time-dependent Er^3+ and Ho^{3+} emission spectra. Near-infrared (Stokes) and upconversion (anti-Stokes) luminescence mechanisms are proposed using energy level diagrams of the Yb^{3+}, Er^{3+} and Ho^{3+} ions.

Acknowledgement: The author thanks for financial support from the grant of the Ministry of Education, Youth and Sports of Czech Republic (grant LM2018103), the European Regional Development Fund-Project "Modernization and upgrade of the CEMNAT" (No.CZ.02.1.01/0.0/0.0/16_013/0001829), the project NANOMAT CZ.02.1.01/0.0/0.0/17_048/0007376 and the project of Faculty of Chemical Technology, University of Pardubice „Excellent teams" 2020.

Models for the effective thermal conductivity of carbon-containing nanofluids compared with literature data

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Nanofluids are suspensions of nanoparticles of any shape (isometric, prolate or oblate) in base fluids. Since solid particles usually have a significantly higher thermal conductivity than liquids (e.g. water), the effective thermal conductivity of nanofluids is much higher than that of the base fluids, even if the volume fraction of nanoparticles is relatively low. Therefore, nanofluids are promising candidates for application as efficient heat transfer media. The highest increase of thermal conductivity is expected for nanofluids containing carbon in the form of carbon nanotubes (CNTs) or graphene nanoplatelets (GNPs), because the in-plane conductivity of the graphene sheet is the highest thermal conductivity value known.

This contribution explains the modeling approach that should be used to predict the thermal conductivity of carbon-containing nanofluids. This approach is based on Fricke's model, which is a Maxwell-type effective medium approximation that extends the classical Maxwell model for spheres to the case of spheroids (prolate or oblate). The modeling approach presented in this contribution, which combines Fricke's model with a specific type of averaging using the so-called Molyneux bounds, is in conflict with a very popular model called the Hamilton-Crosser model, but the latter can be shown to be incorrect. The model predictions calculated in this contribution are compared with literature data for CNT and GNP nanofluids. Nothwithstanding the various difficulties in comparing literature data for real systems with the highly idealized predictions, the overall agreement is very reasonable, which means that the repeated claims concerning the "non-classical" behavior of nanofluids are largely unjustified. The results achieved in this work are a solid basis for modeling the thermal conductivity of carbon-containing nanocomposites.

Acknowledgment: This work was supported from the grant of Specific university research – grant No A1 FCHT_2022_002 and No A1 FCHT_2023_005.

High entropy ceramic – metal composites prepared by Spark Plasma Sintering

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High Entropy Alloys (HEA) were discovered in 2004, closely followed in 2005 by the discovery of High Entropy Ceramics (HEC). High entropy materials are defined as multicomponent materials containing at least five various elements with at least 5-35 at% and entropy of mixing higher than 1.5R. HEC differ from HEA by the addition of an additional non-metallic element (for example, O, C, B, N, Si) with a role of an anion. Both of these material groups are multi-component and are stabilized thanks to the changes of balance between the Gibbs energy and entropy of mixing. These advanced materials bring better mechanical and functional properties than traditional ceramics and alloys. For example, in the case of high entropy carbides, this means better hardness or oxidation resistance, making them promising candidates for cutting tool applications.

Preparation of HEC requires lengthy ball milling processes of elemental powders in order to reach a homogenous mixture of powders before sintering. Furthermore, the reactive sintering of non-oxide high entropy ceramics needs high temperatures and pressures. In the presented work the vanadium, niobium, molybdenum, tantalum and tungsten carbide formation was tested. A HEA in the form of powder was mixed together with carbon and subsequently sintered by Spark Plasma Sintering (SPS) process at a temperature of 2000 °C under an applied pressure of 50 MPa. The result is a composite consisting of sintered HEA and carbides. Scanning Electron Microscopy (SEM) was used to observe the microstructure of the composite, and X-Ray diffraction measurement was carried out as well. Preliminary values of Vickers hardness for the sintered composite were also gathered. The formation of carbides in equiatomic metal mixture is discussed.

Elastic properties measurement of isotropic ceramics using the ultrasonic technique and theoretical prediction of the porosity dependence of the sound velocity

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Sound velocities (of transverse and longitudinal waves) in solids are directly related to their elastic properties. Therefore, elastic properties can be measured by ultrasound wave propagation techniques. However, predictions for sound velocities on porosity have not been adequately investigated in the past, so that most models proposed in the previous literature for the description of the porosity dependence of sound velocities were of semi-empirical or purely empirical character.

In this contribution we present theoretical models for the porosity dependence of transverse and longitudinal sound velocities in isotropic porous ceramics [1]. Six theoretical models have been derived both for the porosity dependence of the transverse sound velocity based on well-known models for the porosity dependence of Young's modulus, viz. Maxwell's model, the self-consistent model, the differential model / power-law relation, an exponential relation, a percolation relation and a benchmark relation obtained by fitting numerical calculations on computer-generated model microstructures. Moreover, using reasonable approximations for the porosity dependence of the Poisson ratio, it is shown that also the longitudinal sound velocity can be predicted. All models predict a decrease of sound velocities with increasing porosity. In a recent paper they have been compared with literature data [1]. Here these predictions are compared with experimentally measured data obtained on ceramics prepared in our laboratory. Sound velocities and elastic properties determined via the ultrasonic technique and the impulse excitation technique are also compared. The results obtained by both methods are mutually consistent and thus the data can be considered as very reliable. The data were obtained on different type of ceramics bodies with porosities from almost 0 % up to more than 50 %. The samples were prepared from commercial powders by two different techniques (uniaxial pressing and subsequent conventional sintering in the air; spark plasma sintering in vacuum). A total of 5 different types of ceramics were investigated, viz. pure alumina ceramics, zirconia ceramics doped with 3 mol. % and 8 mol. % of Y_2O_3, composites of alumina and 3 mol.% zirconia (in weight ratio 2 : 8) and two different types of mullite ceramics with different chemical composition.

References:

[1] Šimonová, P.; Pabst, W., The porosity dependence of sound velocities in ceramic materials, Journal of the European Ceramic Society 2023, 43 (4), 1597-1604.

Acknowledgement: This work was supported from the grant of specific university research – grant No A2_FCHT_2022_004.

Understanding the relationship between Ga/Sc/Al in co-doped Ce:$Gd_3(Ga,Sc,Al)_5O_{12}$

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Garnets witch stochiometric formula $Gd_3(Ga,Al)_5O_{12}$:Ce are common scintillators, but the physical maximum of their properties (such as scintillation yield, decay time and resolution) wasn't already reached and there are still possibilities to tune these properties. The most common way for tuning the properties is substitution on maxtrix. In this work we investigated how Ga and Sc co-doping on Al position in garnet structure influence the luminescence parameters of materials. All samples were prepared via co-precipitation method, following pressing into tablets, which were then annealed (1200°C for 2 h) to obtain the final samples. On these samples foto- and radioluminescence specters, decay times and afterglow were measured and strong correlation between the Ga and Sc substitution was show.

Preparation of $GdAlO_3$:Ce crystals by micro-pulling down method

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Scintillation materials are used in detection systems where they convert the energy of high-energy particles to UV/VIS light. One of the commercially used scintillators is the $YAlO_3:Ce^{3+}$ perovskite single crystal (YAP:Ce). YAP:Ce has suitable properties for applications in electron microscopy, gamma spectroscopy, X-ray and gamma counting and X-ray imaging screens. Based on the commercial success of YAP:Ce, other aluminate materials with the perovskite structure were studied with the aim to find a material with better scintillation properties. One of the studied materials is cerium-doped gadolinium aluminium perovskite $GdAlO_3$:Ce (GAP:Ce). It exhibits a higher density and effective atomic number compared to YAP:Ce. However, the light yield in this material is lower than expected and its scintillation kinetics contains slow components. These unwanted properties come from the energy transfer between gadolinium and cerium ions. In our previous work, we studied influence of cerium concentration and lanthanum co-dopation on scintillation properties of $GdAlO_3$:Ce [1]. This previous study was performed on ceramic pellets. Although it provided useful information, it is necessary to prepare single-crystal samples to confirm the effects of the material composition on scintillation properties.

This work pursues a preparation of $GdAlO_3$:Ce crystals by the micro-pulling down method (μPD). Growth of high-melting oxide crystals is generally expensive and demanding process. The μPD enables fast and inexpensive way to produce crystals for material research. The effect of cerium and lanthanum content was studied using radioluminescence spectroscopy and scintillation kinetics measurement. An improvement of scintillation properties (light yield and decay kinetics) was achieved.

References:

1. Havlíček J., Jakeš V., Rubešová K., Kučerková R., Beitlerová A., Nikl M., *Heavily cerium-doped (Gd,La)AlO_3 ceramic scintillators: Material optimization study.* Ceramics International, 2022. **48**(23): p. 34720-34727.

Selective in vivo cell infiltration into durable calcium phosphate scaffolds

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Bioceramic materials such as β-tricalcium phosphate or hydroxyapatite are usually used in regenerative medicine for their biocompatibility and bioactivity. However, calcium phosphate-based scaffolds must still exhibit other essential properties, including tailored porosity and sufficient mechanical stability. Freeze-casting of bioceramic materials allows the preparation of highly porous structures with ample mechanical stability. Our study aimed to characterize the mechanical stability and biological properties of calcium phosphate (CaP) scaffolds with tailored porosity and microstructure.

Calcium phosphate-based suspension was freeze-cast using liquid nitrogen (cooling medium). The oriented lamellar microstructure was obtained in the scaffolds as a result of controlled ice growth in one direction. Scaffolds were tested for flexural strength by the three-point bending test, after sintering at 1200 °C. Bioactivity was tested via simulated body fluid (SBF) for 21 days. Finally, cell infiltration was tested *in vivo* with a subcutaneous-implantation rat model.

The relative porosity of prepared scaffolds reached ~70 %, with interlamellar spaces 10–20 μm. The obtained flexural strength was approximately 10 MPa, indicating sufficiently high mechanical stability considering the high porosity of the scaffolds. The SBF testing revealed high bioactivity of the CaP scaffolds with a fully grown apatite layer after 21 days. The *in vivo* cell infiltration was evaluated six weeks after the subcutaneous implantation. A thin fibroblastic tissue covered all the samples attaching them to the subcutaneous tissue. Inflammation nor other pathological response in the surrounding tissue was observed, also the blood counts did not show any significant changes compared to the sham-operated control group. The histological and microscopical observation revealed a high amount of fibroblasts in the inner part of the scaffolds. The presence of blood vessels was confirmed, together with immune system compartments.

Transparent ceramics of $LiAl_5O_8$ prepared by spark plasma sintering

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Transparent ceramics are a relatively new material form that serves as an alternative to the traditionally encountered glasses, polymers or highly transparent single crystals. They have found application in a variety of optical and electro-optical devices such as solid state lasers and scintillators, but also in some non-optical applications, e.g. armours. The fabrication of transparent ceramics usually involves a combination of chemical and physical processes, which are used to prepare a ceramic powder and compact the powder into a dense ceramic body. However, the optical properties of finished polycrystalline ceramics are closely related to their microstructure and to the presence of defects in it. Residual pores (located within grains or at grain boundaries), impurities or the actual grain boundaries (especially for optically anisotropic materials) are sources of light scattering, which deteriorates the optical properties of transparent ceramics. Therefore, transparent ceramics are commonly prepared from materials with an optically isotropic cubic structure using high purity powders, which leave porosity as the most significant factor for transparency.

In this work, the preparation of $LiAl_5O_8$ transparent ceramics is presented using spark plasma sintering (SPS). Powder precursors were prepared using two methods, namely sol-gel method and solid state reaction. Before sintering, the powders were heat treated at 1200 °C and their phase composition was verified by XRD to be pure cubic α-phase of $LiAl_5O_8$. The powders were compacted into dense ceramic bodies by SPS using a two-step sintering program. The sintered bodies were further processed by grinding and polishing to achieve a mirror finish and a thickness of approximately 1 mm. Based on the investigation of transmittance in the UV-vis and NIR-MIR spectral regions, transparent ceramics with superior transparency were obtained from powders prepared by solid state reaction and the optimal sintering temperature is 1400 °C.

Acknowledgement: This work was financially supported by the MVCR research agency (Grant no: VI20192022152).

Cold sintered $BaTiO_3$ - tailoring of phase transformation by post annealing

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The present study investigates the phase transformation and grain morphology of cold-sintered doped Barium titanate ($BaTiO_3$). $BaTiO_3$ is multifunctional electroceramics with high dielectric permittivity and often doped to achieve the desired properties such as relative permittivity and positive temperature resistivity and stability of the relative permittivity. The consolidation of $BaTiO_3$ is achieved at high temperatures >1000 °C. To reduce energy consumption, the research is driven to low-temperature synthesis methodologies. The drawback of low-temperature synthesis is the low density and the formation of $BaCO_3$ as the by-product, which is later removed by further heat annealing at 700 to 900 °C. The post annealing also influenced the phase transformation from pseudo-cubic to tetragonal or vice versa. Here the effect of post annealing conditions on the phase transformation of $BaTiO_3$ densified by the cold sintering process is studied. The $Sr(OH)_2.8H_2O$ was added as a dopant in $BaTiO_3$ and fabricated at 225 °C/1 hr, the pressure of 250 MPa was kept constant throughout the heating cycle. Then sintered samples were annealed at a temperature range of 500 to 1100 °C, after each heating cycle, the samples were analysed by XRD and SEM. During the investigation, it was found that cold sintering the Sr^{2+} ion impacted the post annealed sample's phase composition and phase transformation.

Dielectric properties of calcium and europium copper titanate ceramics prepared by a sol-gel method

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Calcium copper titanate is an inorganic compound with a chemical formula $CaCu_3Ti_4O_{12}$. It was first synthesized in 1967 by Alfred Deschanv and his colleagues, but it was not until 2000 that Mas Subramanian and his colleagues at DuPont Central discovered a dielectric permittivity in this material that was greater than 10 000 at room temperature. Since then, it has found a widespread use in various fields related to its dielectric properties [1, 2].

$CaCu_3Ti_4O_{12}$ perovskite-type phase possesses promising dielectric properties; however, the giant permittivity phenomenon in this material has not been satisfactorily described yet. One of the positive factors could be the presence of secondary phases or substitution of calcium in a dodecahedral position by europium(II). This rare earth cation shows similar ionic radius and electronegativity but differs in valence shell configuration. Such a substitution has not been studied yet more detailed. We prepared a series with a composition of $CaCu_3Ti_4O_{12}$, $Eu_{0,4}Ca_{0,6}Cu_3Ti_4O_{12}$ and $EuCu_3Ti_4O_{12}$. A sol-gel method was used to synthetize precursors, followed by sintering in a temperature range of 1000 °C–1120 °C. Europium was substituted in full stoichiometry of Ca^{II} with the aim to observe whether i) Eu^{II} is stabilized in the perovskite structure and/or ii) possible secondary phases induced by the excess of Eu^{III} positively affect the dielectric characteristics. Samples were characterized by XPS, XRD and SEM. Influence of the microstructure and phase composition on the dielectric properties of the samples (in relation to the sintering temperature) is discussed. Secondary phases and microstructure played an important role in improving the permittivity values. The obtained values of permittivity measured at room temperature are giant up to higher frequencies but differ significantly for some compositions.

We found out that the stoichiometric excess of europium in the fully substituted sample produces secondary phases that could be one of the reasons why dielectric characteristics of this sample were much better than those without europium substitution. The sample $EuCu_3Ti_4O_{12}$ pressed by isostatic pressing and sintered at 1120 °C showed a giant permittivity together with very low losses: ε = 20 874 and $tan\ \delta$ = 0.041 (at 10 kHz). These results confirm the published results describing a positive influence of secondary phases on the dielectric behavior.

References:

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ABSTRAKTY

Soutěžní sekce

(Sklářská)

The effect of TRIS-HCl buffer on *in vitro* testing of bioactive glasses

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In vitro tests are a vital part of testing biomaterials. They provide initial information about the reactivity of the given material in a living organism. Bioactive glasses are one of the most desirable materials in the field of tissue engineering. Thanks to their properties, ion exchange can occur in the human body's environment leading to the formation of an apatite layer rich in calcium and phosphorus. This allows a strong bond to form between bone and implant. A series of previously made experiments show that in vitro testing of glass materials, whether according to ISO 23317:2014 using simulated body fluid (SBF) solution with TRIS buffer or using other commercially available buffers (HEPES, MOPS, DMEM, etc.), gives false positive results.

This work is focused on the behaviour of the bulk Bioglass samples in different solutions (SBF (ISO 23317:2014), SBF without TRIS buffer, TRIS+HCl) and on the biomineralization of the hydroxyapatite layer. Monitoring the kinetics of the process during the entire experiment will provide us with a comprehensive overview of the behaviour of the given material in a living organism. To achieve that, the AAS, UV-VIS, and ICP-OES analyses of leachates were combined with the appearance of the Bioglass samples and chemical composition of the formed layers (cross section SEM-EDS).

The results clearly show that the presence of TRIS buffer has an adverse influence on the in vitro tests because it interacts with the glass samples, accelerating their dissolution and promoting the formation of hydroxyapatite.

Acknowledgment: This work was supported from the grant of Specific university research – grant No A1 FCHT_2022_002 and No A1 FCHT_2023_005.

Deposition of a solution-processed thin films of As-S-Se system, prepared from modified $As_{50}Se_{50}$ chalcogenide glass solution

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Chalcogenide glasses are semiconducting materials that contain one or more 16. group element (S, Se, Te) as their main component. They are widely studied for their desirable properties, such as a wide IR transparency window, high refractive index, and high optical nonlinearity.[1] Chalcogenide glasses can be used in the form of bulk material (e.g. lenses, windows, fibers) or as a thin film deposited on a transparent substrate. Thin films are traditionally prepared by physical vapor deposition methods such as thermal evaporation, sputtering, or laser ablation. [1,2] Alternatively, thin films can also be prepared from a solution of chalcogenide glass in an amine or amine-based solvent. Thin films can be deposited from the solution by various techniques, including spin-coating or dip-coating [1,3]. Solution-based methods are cheaper, because they do not need expensive high-vacuum equipment. The solution path also enables modification of the source solution by adding new components (doping) or mixing several chalcogenide glass solutions of different compositions.

This work deals with the preparation of As-S-Se chalcogenide glass thin films deposited from $As_{50}Se_{50}$ glass solution modified with elemental sulfur. Four sulfur-modified solutions were prepared from $As_{50}Se_{50}$ solution in ethylenediamine ($As_{45}S_{10}Se_{45}$, $As_{40}S_{20}Se_{40}$, $As_{35}S_{30}Se_{35}$, $As_{30}S_{40}Se_{30}$). Thin films of all compositions, including unmodified $As_{50}Se_{50}$, were deposited in specular optical quality using the spin-coating technique. Refractive index, optical band gap, organic residua content, structure, and chemical resistance were studied in dependence on the annealing temperature, composition, and stoichiometry.

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Dissolution kinetics of phosphate glasses

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In general, phosphate glasses are mainly used for the manufacturing of laser glass, thanks to their refractive indices values and high transparency for UV radiation, or for glass solders production – here, their low softening temperature is important. Another significant usage can be found in biomedical or agricultural applications. Phosphate glasses are known for their ability to be dissolved in water, or even on exposure to humidity. Among many factors affecting solubility, the fundamental one is the glass composition. By changing the composition, the glass solubility can be tuned to desired levels.

This work aims to prepare and characterize the novel phosphate glasses in the system P_2O_5 SiO_2-K_2O-CaO. Four different types of glass with variable chemical composition were prepared by melting in an electric furnace at 1200 °C for 2 hours. The molten glass was mixed two times during the melting process and cast into stainless steel moulds. The glass was then annealed at 400 °C for 1 hour and then cooled slowly to room temperature overnight.

To observe dissolution kinetics, a static leaching test was utilized. This test consisted in leaching the crushed glass (particle size 0.3–0.5 mm) in demineralized water at laboratory temperature for 24 hours and 7 days. Leachates were collected during the test for further analyses. The concentration of leached elements was evaluated via ICP-OES, pH values were assessed with a laboratory pH meter. The dissolution kinetics parameters were determined by the means of the mathematical model.

Results showed that all prepared glasses exhibit dissolution in water. Using the obtained data, the normalized leached amounts of Si, Ca, P, K and the rates of dissolution were computed and the dissolution behaviour of prepared glasses was compared with each other. Due to fast dissolution, further experiments with shorter sampling intervals are necessary.

Acknowledgment: This work was supported from the grant of Specific university research – grant No A1 FCHT_2022_002 and No A1 FCHT_2023_005.

Directed Energy Deposition 3D Glass Printing for Realizing Customized Optical Sensors

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Additive manufacturing or 3D printing enables the realization of customized designs; 3d glass printing is a promising technique to realize customized glass structures and designs that can operate as optical sensors. The current knowledge of additive technologies for glass components does not yet allow for large-scale research and application deployment. There are several research directions for obtaining glass products using additive technologies. In the framework of fundamental research, the principle of micro-fusion of optical fibers using CO_2 laser and the use of Directed Energy Deposition (DED) technology is being investigated.

This Ph.D. thesis/study aims to realize 3D glass printing by studying the possibilities of using DED technology to print 1D, 2D, and 3D glass structures and exploring the possibilities and challenges of using several glass fibers to realize the printing. The study also aims to realize optical sensing functional parts or devices that can be hard to obtain using other fabrication techniques and to reach optimized printing conditions that would assure the quality and homogeneity of the printed structure.

Preparation of $CuCr_2O_4$ nanofibers using crystallization in molten glass

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Spinels play significant roles in many fields of industry. They have very variable properties and due to the ability to form solid solutions, they show varied magnetic, optical, electrical and other properties and thus a wide range of applications, from data storage in information technology and telecommunications to capacitors for energy storage or batteries used in electric cars. Based on the structure, spinels are divided into three types: normal, inverse and complex. In the case of $CuCr_2O_4$, it is a normal spinel with significant magnetic and electrical properties.

A widely used method for the preparation of nanofibers is electrospinning. The major components include a high voltage source, spinning nozzle and conductive collector. The preparation of nanofibers consists of three steps, namely suspension preparation followed by electrospinning and thermal calcination. The suspension contains an inorganic precursor and an organic polymer (usually PVP, PVA or TEOS).

The aim of this work was to prepare the $CuCr_2O_4$ crystals and from them prepare nanofibers containing the spinel. The method for the preparation of the material was based on the crystallization in molten glass, which is a method that has not yet been published in the literature and, in the case of spinel crystallization during vitrification of high-level waste glasses, is considered rather as an undesirable phenomenon. Melted glass containing spinel crystals was grounded into fine powder from which the suspension was prepared for the electrospinning. The glass was analyzed using XRF and XRD, and also using optical confocal and scanning electron microscopy.

Acknowledgment: This work was supported from the grant of Specific university research – grant No A1_FCHT_2022_002 and No A1 FCHT_2023_005.

ABSTRAKTY

Nesoutěžní sekce

Skla systému TeO_2-ZnO-La_2O_3 dopovaná Er^{3+}

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Telluričitá skla vykazují vysoký nelineární index lomu, vysokou optickou propustnost od ultrafialové do střední infračervené spektrální oblasti, relativně vysokou chemickou odolnost, nízké fononové energie, což v kombinaci s jednoduchou přípravou a možností jejich dopování vysokými koncentracemi lanthanoidů je činí slibnými materiály pro fotonické aplikace [1, 2]. Cílem práce byla příprava vybraných skel ternárního systému TeO_2-ZnO-La_2O_3 dopovaných ionty Er^{3+} ve formě Er_2O_3 a studium jejich fyzikálně-chemických vlastností s důrazem na vlastnosti optické. Vedle vlivu chemického složení hostitelské matrice na výsledné vlastnosti, byla pozornost věnována odhalení závislosti koncentrace Er^{3+} iontů ve vybraných sklech na mechanismus upkonverzní fotoluminiscenční (PL) emise.

Studované vzorky skel byly charakterizovány z hlediska jejich chemického složení (EDX mikroanalýza), měrné hmotnosti ρ (Archimédova metoda, ρ ≈ 5,40–5,61 g cm^{-3}), teploty skelného přechodu T_g (DSC kalorimetrie, T_g ≈ 360–420 °C), ověřen jejich amorfní stav (XRD analýza), struktury skelné sítě (Ramanova spektroskopie), disperze indexu lomu $n(\lambda)$ (spektroskopická elipsometrie, n ≈ 1,96-1,99 při λ ≈ 1550 nm). Dále byla měřena spektra optické propustnosti (UV Vis NIR spektroskopie) a spektra fotoluminiscenční emise v ustáleném stavu a časově rozlišená spektra při excitaci laserem o vlnové délce λ ≈ 977 nm.

Přídavek La_2O_3 do skel na bázi TeO_2-ZnO vede ke zvýšení jejich měrné hmotnosti, molárního objemu, teploty skelného přechodu a k vyšší rozpustnosti iontů Er^{3+}. Optimální koncentrace přídavku La_2O_3 do studovaných skel TeO_2-ZnO je <10 mol.%, aby nedocházelo k jejich odskelnění. Substitucí La_2O_3 za ZnO dochází k transformaci strukturních jednotek [TeO_4] na jednotky [TeO_{3+1}] a [TeO_3]. U všech skel byla pozorována PL Stokesova emise z elektronových přechodů Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (λ ≈ 1,56 μm) a PL anti Stokesova emise ve viditelné oblasti spektra z elektronových přechodů Er^{3+}: $^2H_{11/2}/{}^4S_{3/2} \rightarrow {}^4I_{15/2}$ (λ ≈ 520–550 nm) a Er^{3+}: $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (λ ≈ 670 nm). Na základě dat PL emisních spekter a dob dohasínání elektronových přechodů Er^{3+} byl stanoven mechanismus upkonverzní PL emise. Studovaná skla se jeví slibnými hostitelskými materiály pro dopování ionty lanthanoidů s potenciálem v optických aplikacích.

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Poděkování: Tato práce vznikla za podpory Ministerstva školství, mládeže a tělovýchovy ČR z projektu LM2018103, dále děkuji projektům SG2023 a VA390011.

Characterization and thermal analysis of oxide glasses

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This work is focused on studying surface morphology and characterization of corrosion products. Based on composition of industrially produced glasses I will derive composition of studied glasses. Those glasses are prepared in laboratory conditions by melting of oxide powders in furnace. Fifteen glasses in total are prepared for examination. Our research is aimed to describe dependance among the most important physicochemical properties and composition or temperature. We plan to study Archimedes method density, low temperature viscosity, thermal expansions related to above and below glass transition point, refractive index by which we can determine whether glass is crystalline or not. In later stages during my experiment we will pay special attention to chemical durability against water and surface tension determined by Sessile drop test. [1]

Characterization of prepared glasses will provide solid bases for actual experiment. I tend to gain better understanding of surface corrosion what helps to prevent and eliminate corrosion itself. Results will serve us as proposal for new composition of industrially produced glasses with better corrosion resistance.

At current stage, I would like to highlight composition of prepared glasses, findings from Archimedes method density compared to theory, determination of glass transition temperature by differential thermal analysis (DTA) and coefficient of thermal expansion by thermomechanical analysis (TMA). I want to characterize and compare those results for 5 glasses containing lower and higher amounts of silica oxide as network-forming agent and natrium oxide as modifier. [2, 3].

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Acknowledgment: This work was supported by The Slovak Grant Agency for Science under grant No. VEGA 2/0091/20, APVV 21-0016.

Vlastnosti hydraulického pojiva připraveného z metakaolinu, anhydritu II a vápna

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V dnešní době, kdy je kladen důraz na udržitelnost, ekologii a s tím spojené snižování emisí CO_2, se stává aktuálním tématem příprava nových hydraulických pojiv, která by mohla alespoň částečně nahradit stávající vysoko-emisní portlandský cement. Vhodným materiálem pro jejich přípravu se ukazují být kalcinované jíly, které se ve velkém množství ukládají jako odpadní skrývkový materiál, zejména po těžbě uhlí či dalších nerostných surovin. Pro kalcinaci jílů za účelem získání pucolánových vlastností jsou oproti cementu potřebné podstatně nižší kalcinační teploty pohybující se v rozmezí 500-900 °C, tím se snižuje celková energetická bilance a uhlíková stopa. Pojiva s přídavkem kalcinovaných jílů jsou proto do budoucna schopna nahradit dnes zatím dostupné pucolány jako je struska a popílek, běžně používané do směsných cementů, jejichž množství se bude vzhledem k ekologii v budoucnu postupně snižovat.

Tato práce se zabývá přípravou nového hydraulického pojiva připraveného na bázi metakaolinu, anhydritu II a vápna. Během výzkumu byla navržena a připravena řada směsí obsahujících plastifikátor a konstantní vodní součinitel. Následně byla vytvořena tělesa tvaru kostek o hraně 20 mm, na kterých byla v časových intervalech zkoušena pevnost v tlaku, a získané výsledky byly porovnány s portlandským cementem. Dále bylo pro směsi stanoveno fázové složení pomocí rentgenové difrakce a bylo sledováno zejména množství amorfní fáze a ettringitu, jakožto hlavní krystalické fáze hydratovaného pojiva. Pro další charakterizaci pojiva byla měřena pórovitost pomocí MIP a na vybraných vzorcích byly navíc pořízeny SEM snímky.

Poděkování: This work was supported from TAČR FW01010195 – Advanced and innovative processing technologies for strategic utilization and storing of coal combustion products (CCPs); 2020–2023. This work was supported from the grant of Specific university research – grant No A1 FCHT_2022_002 and No A1 FCHT_2023_005.

Adsorpce fosfátů a amonných iontů na odpadní stavební kaly

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Ve vyspělých zemích vede stavební průmysl k vyčerpávání přírodních zdrojů a produkci několika miliónů tun odpadu. Stavební odpad v různých odvětví stavebnictví (výroba betonu, umělého kamene atd.) zahrnuje také vysušené práškové stavební kaly (WBS) [1,2]. V současnosti jsou využívány různé separační a recyklační procesy, které jsou účinné, ale pro udržitelný rozvoj sami o sobě nedostatečné, protože stále značná část odpadů je odvážena bez dalšího využití na skládky [2,3]. Odpadní stavební kaly mají slibné povrchové vlastnosti a chemické složení (obsah Si, Ca, Al a Fe), toto z nich dělá vhodné kandidáty pro jejich uplatnění v environmentálně přátelských technologiích [3].

Pro práci byly použity dva vybrané odpadní stavební kaly: i) kal z výroby a opracování předpojatých betonových sloupů (B); ii) kal z výroby technického kamene (TS), v jejich původní i povrchově modifikované podobě pomocí železa (B_{Fe} a TS_{Fe}) pro sorpci fosfátů a amonných iontů z kontaminovaných vodných systémů. Experimenty byly provedeny na modelovém roztoku simulující reálnou odpadní vodu o koncentraci 1,7 $mmol \cdot l^{-1}$ (NH_4^+) a 0,2 $mmol \cdot l^{-1}$ (PO_4^{3-}). V této práci byly sledovány selektivní, následné a simultánní adsorpce PO_4^{3-} a NH_4^+. Experimentální data byla proložena Langmuirovou adsorpční izotermou pro stanovení sorpčních parametrů ($q_{max.}$ — maximální rovnovážný obsah iontů v pevné fázi, Q_t —teoretická sorpční kapacita, K_L — Langmuirova adsorpční konstanta, R^2 —korelační faktor).

Kaly B, B_{Fe} a TS_{Fe} se ukázaly jako slibné a velmi účinné sorbenty pro sorpci PO_4^{3-} a bylo možné tyto adsorpce přizpůsobit Langmuirově adsorpčnímu modelu. TS spontánně uvolňoval PO_4^{3-} do roztoku a nedocházelo k adsorpci. Adsorpce NH_4^+ probíhala s nižšími sorpčními účinnostmi (< 60 %) než sorpce PO_4^{3-}, TS se ukázal jako nejúčinnější sorbent. Adsorpce NH_4^+ na TS mohla být přizpůsobena Langmuirově adsorpčnímu modelu. Při adsorpci opačně nabitých iontů na sorbenty dříve nasycené adsorpcí PO_4^{3-} nebo NH_4^+ (tj. adsorpce NH_4^+ na B, B_{Fe} a TS_{Fe} nasycené PO_4^{3-} a adsorpce PO_4^{3-} na TS nasycené NH_4^+) se účinnost sorpce zvýšila oproti adsorpci na původní nenasycené sorbenty v důsledku vytvoření nových aktivních míst na povrchu sorbentu. Současná adsorpce PO_4^{3-} a NH_4^+ byla účinnější ve srovnání s účinností selektivní iontové adsorpce.

Nakonec byly provedeny výluhové testy podle normy ČSN EN 12457 pro B/B_{Fe} a TS/TS_{Fe} před a po sorpci NH_4^+ a PO_4^{3-}, které prokázaly poměrně vysoké uvolňování NH_4^+ a PO_4^{3-} z původní a nasycených sorbentů, což otvírá možnosti pro aplikace těchto kalů například do zemědělských půd pro zvýšení jejich kvality a nutričních hodnot.

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Poděkování: Tento výstup vznikl v rámci projektu Specifického vysokoškolského výzkumu – projekt č. A1_FCHT_2023_005.

Nové sklokeramické materiály v systéme Al_2O_3-RE_2O_3 so zaujímavými optickými vlastnosťami

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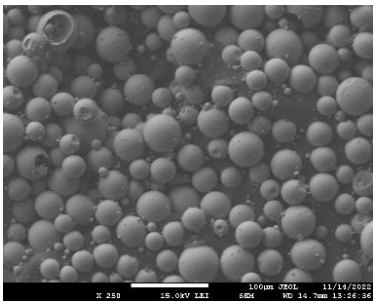
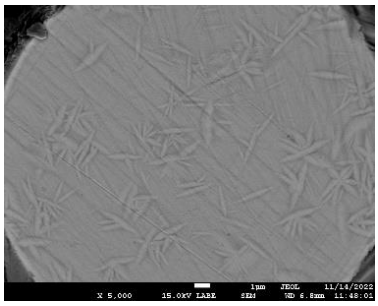
Medzi pomerne dobre preskúmané materiály v systéme Al_2O_3-RE_2O_3 patria ytrito-hlinitý granát $Y_3Al_5O_{12}$ (YAG) a ytrito-hlinitý perovskit $YAlO_3$ (YAP). Tieto materiály dopované iónmi vzácnych zemín majú potenciálne využitie pri konštrukcii polovodičových laserov, okenných materiálov, pre svietidlá a telekomunikačných optických vlákien. Materiály dopované Er^{3+} iónmi vykazujú up-konverznú emisiu zeleného a červeného žiarenia [1] a ich optické vlastnosti možno zlepšiť súčasným dopovaním Yb^{3+} iónmi, keďže tieto majú jednoduchú elektrónovú štruktúru, vďaka ktorej môžu fungovať ako senzibilizátory [2]. V súčasnosti sa skúma možnosť nahradiť YAG a YAP materiály hlinitanovými sklami [1]. Hlinitanové sklá vykazujú vysokú chemickú a tepelnú odolnosť a v porovnaní s YAG a YAP majú vyššiu priepustnosť pre IČ žiarenie a väčšiu schopnosť absorbovať dopanty oxidov vzácnych zemín. Výroba hlinitanových skiel je náročná, lebo neobsahujú žiaden sklotvorný oxid, majú vysoké teploty tavenia a vysoký sklon ku kryštalizácii. Možným ekonomickým aj technologickým riešením sa javí plameňová syntéza. [1].

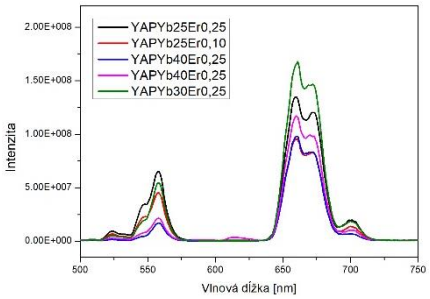
V tejto práci popisujeme prípravu a skúmanie optických vlastností Er^{3+} a Yb^{3+} iónmi dopovaných mikroguľôčok so zložením ytrito-hlinitého perovskitu. Prekurzorové prášky pre plameňovú syntézu sme pripravili Pechiniho sol-gél metódou. Základnú charakteristiku pripravených mikroguľôčok sme uskutočnili pomocou röntgenovej práškovej difrakcie (RTG), infračervenej spektroskopie (IČ), Ramanovej spektroskopie a riadkovacej elektrónovej mikroskopie (SEM). IČ a Ramanova spektroskopia potvrdili prevažne amorfný charakter pripravených mikroguľôčok. V RTG záznamoch sme pozorovali okrem amorfného pleca v intervale 25-40°2theta aj slabé difrakcie typické pre kryštalické fázy YAG a YbAG. SEM ukázala prítomnosť čiastočne alebo plne kryštalických mikroguľôčok s prevažujúcimi ihličkovitými kryštálmi (**Obr.1**). V DTA záznamoch všetkých vzoriek sme pozorovali jeden exotermický efekt s maximom pri teplote 926-927 °C. Na základe vykonanej RTG analýzy vzoriek po termickej analýze možno tento efekt prisúdiť kryštalizácii YAP, YAG a Yb_2O_3. UV-VIS spektroskopia ukázala charakteristické emisie Er^{3+} iónu v zelenej oblasti spektra pri 525-567 nm a v červenej pri 625-725 nm (**Obr.2**).



Obr. 1a: SEM snímka systému YAPYb40Er0.1 (50 mol.% Al_2O_3, 10 mol.% Y_2O_3, 40 mol.% Yb_2O_3 a 0.1 mol.% Er_2O_3)



Obr. 1b: Detailná SEM snímka YAPYb40Er0.1 kryštalickej mikroguľôčky (leštený prierez)



Obr. 2: UV-VIS spektrá pripravených systémov

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Poďakovanie: Tento príspevok vznikol vďaka finančnej podpore projektu FunGlass (Horizon 2020, číslo grantu No 739566), a projektov VEGA 2/0028/21, VEGA 2/0141/21 a APVV-19-0010.

Porovnanie statického a dynamického korózneho testovania žiaruvzdorných materiálov

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Žiaruvzdorné materiály nachádzajú svoje uplatnenie v širokej plejáde energetického priemyslu. Nároky na ich kvalitu sa odvíjajú od prevádzkových podmienok - záťaže, ktorej sú vystavené (teplota/výkyvy teploty, typ a prúdenie korózných médií ai.). Vplyv týchto faktorov sa testuje a výsledky vedú k objasneniu procesu korózie žiaruvzdorných materiálov. K štúdiu mechanizmu a predikcie správania sa žiaruvzdorných materiálov pri záťaži je vyvinutý rad korózných testov. Pre pochopenie termodynamických aspektov sa využívajú statické korózne testy a na sledovanie kinetických javov sa používajú dynamické korózne testy.

Práca porovnáva výsledky statického téglikového korózneho testu s výsledkami dynamického testu, ktorý je vyvíjaný za účelom overovania rezistencie materiálov pre vymurovky atakované lietavým podielom popolov, tvoriacich sa pri spaľovaní biomasy. Jedná sa o test v usporiadaní: korózne médium - frakcia popola je nanášané prúdom horúcich spalín na vypálenú keramickú vzorku. Usporiadanie testu simuluje podmienky v spaľovacej komore kotla na biomasu.

Testovaný bol korundový žiarobetón (AK SC 20) na báze andaluzitu s prímesou 20 hm.% SiC viazaný hydraulickou cementovou väzbou po primárnom výpale pri teplote 1450 °C. Ako korózne médium bol použitý popol z tkanivového filtra z tepelného agregátu na spaľovanie biomasy s obsahom 18.8 hm. % K_2O, 32.7 % CaO, 4.6 % SiO_2, (14.4 % SO_3, 21 % strata žiarom).

Statický korózny test bol realizovaný na téglikoch odliatych zo žiarobetónu (ϕ 25 mm, hĺbka 33 mm) naplneného 11,2 g popola za podmienok: 1450°C/výdrž 15 hodín.

Dynamický korózny test bol realizovaný na doske žiarobetónu (110 x 110 x 20 mm) za vyhrievania v peci pri 1450 °C nanášaním popola horúcimi spalinami v 9 sekvenciách. (1 sekv.: dávkovanie ≈ 1 g popola/ 1 min, interval medzi dávkovaním 19 min, odhadovaná rýchlosť prúdu je 2,75 m/s. Celková doba testu 180 min.

Testované žiarobetóny boli po rozrezaní v priečnom reze hodnotené vizuálne a korózne rozhranie bolo podrobené EDX analýze. Prvkové mapy ukázali výraznejšie a širšie korózne rozhranie pod nálepom taveniny vytvorenej v dynamickom teste, oproti statickému. Vďaka rýchlemu nábehu na teplotu a dobu testu sú dynamické skúšky energeticky a časovo menej nákladné. Výhodou je aj kontinuálna kontrola podmienok a možnosť pozmeniť podmienky - režim testu. Dynamické korózne testy sa viac približujú reálnym pracovným podmienkam.

Poďakovanie: Práca je podporovaná grantovou agentúrou VEGA – MŠVVaŠ SR a SAV cez projekt No.1/0060/22.

Preparation of nickel-containing mixed oxide catalysts and their performance in the total oxidation of volatile organic compounds

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Volatile organic compounds (VOC) are important air pollutants as they contribute to ozone/smog formation and can be harmful for human health. The VOC in air can be removed applying the catalytic total oxidation to carbon dioxide and water as the final products; transition metal oxides are often used as catalysts in this process [1]. Combination of more transition metal cations in oxide catalysts can be beneficial due to the synergistic effect [2]. The present work focused on catalytic performance of oxide catalysts containing nickel in combination with other transition metal cations, namely Co, Cu, and Mn.

The binary (Ni-Co, Ni-Cu, and Ni-Mn) and ternary (Ni-Co-Mn and Ni-Cu-Mn) mixed oxide catalysts were obtained by heating (4 h at 500 °C in air) of precursors prepared by coprecipitation of aqueous nitrate solutions containing the above mentioned transition metal cations in various molar ratios. The prepared catalysts were characterized by elemental analysis (AAS), powder XRD, and temperature programmed reduction (H_2-TPR). The catalytic performance was studied in the total oxidation of ethanol.

Formation of NiO and CuO mixtures was observed in the Ni-Cu samples, whereas mixed oxides (Co_2NiO_4, Ni_6MnO_8, and $NiMnO_3$), together with single-component oxides (NiO and Mn_2O_3) were found in the Ni-Co and Ni-Mn samples. Mixed oxides with spinel structures together with other oxide phases ($NiMnO_3$, CuO) were identified in the Ni-Cu-Mn samples; mixtures of NiO, $(Ni,Cu)_6MnO_8$, and CuO were found in samples with high Ni or Cu content. Various mixed oxides with spinel structure were obtained by heating of ternary Ni-Co-Mn precursors.

The T_{50} and $T_{90}(CO_2)$ temperatures (the temperatures required to achieve 50% and 90% conversion of ethanol and all organic compounds to CO_2, respectively) were chosen as a measure of catalyst activity. The most active catalysts were the Ni-Mn (Ni:Mn molar ratio 1:1) and Ni-Co-Mn (Ni:Co-Mn molar ratio 1:1:1) catalysts ; T_{50} of 91 and 89 °C and $T_{90}(CO_2)$ values of 172 and 183 °C were found for the deep oxidation of ethanol on these catalysts, respectively. Acetaldehyde and carbon monoxide were detected as the main byproducts of ethanol oxidation on these catalysts. Both catalysts showed similar maximum acetaldehyde formation (about 550 ppm at 115 °C) but increased CO formation was observed on the Ni-Co-Mn (177 ppm at 190 °C) compared to that on the Ni-Mn catalyst (70 ppm at 180 °C). In contrast, much lower CO concentrations were measured during ethanol oxidation over the Ni-Cu and Ni-Cu-Mn catalysts containing copper.

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