

Seventh National Crystallographic Symposium with International Participation



PROGRAM and ABSTRACTS

organized under the auspices of the
Bulgarian Crystallographic Society (BCS) by:

Institute of Mineralogy and Crystallography
"Acad. Ivan Kostov" – BAS

Institute of Catalysis – BAS

University of Chemical Technology and Metallurgy

Institute of Optical Materials and Technologies
"Acad. Jordan Malinovski" – BAS

Institute of General and Inorganic Chemistry – BAS

Geological Institute "Strashimir Dimitrov" – BAS

Institute of Physical Chemistry "Rostislav Kaischew" – BAS

Sofia University "St. Kliment Ohridski"

Plovdiv University "Paisii Hilendarski"

October 3–5, 2018, Sofia, Bulgaria,
University of Chemical Technology and Metallurgy, Sofia, Bulgaria

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Georgi Avdeev, IPC – BAS

Aleksandar Nikolov, IMC – BAS

INVITED SPEAKERS

David L. Bish, *Indiana University, Bloomington, USA*
The Mars Science Laboratory Experience

Mira Ristic, *Division of materials Chemistry, Ruđer Bošković Institute, Croatia*
Synthesis and nano/microstructures of metal oxides: selected examples

Beatrix-Kamelia Seidlhofer, *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*
CALIPSOplus – overview and targeted research possibilities

Tzonka Mineva, *CNRS, Institut Charles Gerhardt Montpellier, France*
Computational studies of defect-containing perovskite crystals in relation to their proton conductivity

Juergen Eckert, *Department of Chemistry, University of South Florida, USA*
From Crystal Structures to Rotational Excitations of Bound H₂ by means of Computer Simulations

Vladimir Stilinović, *Department of Chemistry, University of Zagreb*
Halogen Bond – a Rival to Hydrogen Bond as Interaction of Choice in Crystal Engineering

Najaf Kakhramanov, *Institute of Polymer Materials, National Academy of Sciences of Azerbaijan*
Research and development of new types hybrid nanocomposites based on polyolefins and natural minerals of Azerbaijan

George Tzvetkov, *Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski”*
Imaging and spectroscopic microanalysis using synchrotron soft X-ray radiation

Angel Ugrinov, *Department of Chemistry and Biochemistry, North Dakota State University, USA*
Disordered Structures and the Fear to Publish them

Ana Proykova, *Faculty of Physics, Sofia University “St. Kliment Ohridski”*
Size-dependent emergence of crystallinity in molecular clusters

Hristo Kolev, *Institute of Catalysis, Bulgarian Academy of Sciences*
Structure and magnetic properties of ferromagnetic systems

Krastyo Buchkov, *Institute of Solid State Physics, Bulgarian Academy of Sciences*
Quantum Design PPMS-9T: cryostat system for electric, magnetic and thermal experiments at high magnetic fields in temperature range 2–400K

Boyko Tsyntsarski, *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences*
New carbon materials with graphite microstructure

SYMPOSIUM PROGRAM

Wednesday 3 October 2018

- 9:00–11:00 **Registration**
- 09:30–09:50 **Opening ceremony**
- 09:50–10:00 Awarding Dr. Mihail Maleev with the honorary sign of the BCS for overall contribution
- 10:00–10:40 **The Mars Science Laboratory Experience (Plenary lecture)**
Prof. David L. Bish, Indiana University, Bloomington, USA
- 10:45–11:15 **Coffee break**
- 11:15–11:55 **Imaging and spectroscopic microanalysis using synchrotron soft X-ray radiation (Keynote lecture)**
George Tzvetkov, Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski”
- 12:00–12:10 **Conference photo**
- 12:10–13:30 **Lunch Break**
- 13:30–14:10 **Disordered structures and the fear to publish them (Keynote lecture)**
Angel Ugrinov, Department of Chemistry and Biochemistry, North Dakota State University, USA
- 14:15–14:55 **Synthesis and nano/microstructures of metal oxides: selected examples (Keynote lecture)**
Mira Ristic, Division of Materials Chemistry, Ruđer Bošković Institute, Croatia
- 15:00–15:30 **CALIPSOplus – overview and targeted research possibilities**
Beatrix-Kamelia Seidlhofer, Helmholtz – Zentrum Berlin für Materialien und Energie GmbH, Germany
- 15:30–16:00 **Coffee break**
- 16:00–16:15 **The latest update on the Empyrean Platform Diffractometer with the relevant application**
Jamil Kassab, Malvern Panalytical – Sponsorship presentation
- 16:20–16:35 **Sponsorship presentation**
- 16:35–18:30 **Poster session 1 and Cocktail**

All posters should be placed in the poster area, but only posters with odd numbers will be presented.

Thursday 4 October 2018

- 9:30–10:10 **Computational studies of defect-containing perovskite crystals in relation to their proton conductivity (Plenary lecture)**
Tzonka Mineva, CNRS, Institut Charles Gerhardt Montpellier, France
- 10:15–10:55 **Crystal structures of some $A'B''VO_4$ vanadates: crystal structure determination from powder diffraction and phase transitions**
Gwilherm Nénert, Malvern Panalytical B. V., The Netherlands
- 10:55–11:30 **Coffee break**
- 11:30–12:10 **Size-dependent emergence of crystallinity in molecular clusters (Keynote lecture)**
Ana Proykova, Faculty of Physics, Sofia University “St. Kliment Ohridski”
- 12:10–13:40 **Lunch Break**
- 13:40–14:20 **Halogen bond – a rival to hydrogen bond as interaction of choice in crystal engineering**
Vladimir Stilinović, Department of Chemistry, University of Zagreb
- 14:25–14:55 **Research and development of new types hybrid nanocomposites based on polyolefins and natural minerals of Azerbaijan**
Najaf Kakhramanov, Institute of Polymer Materials, National Academy of Sciences of Azerbaijan
- 15:00–15:30 **Quantum Design PPMS-9T: cryostat system for electric, magnetic and thermal experiments at high magnetic fields in temperature range 2–400K (Thematic lecture)**
Krastyo Buchkov, Institute of Solid State Physics, Bulgarian Academy of Sciences
- 15:30–16:00 **Coffee break**
- 16:00–16:10 **Sponsorship presentation**
Darko Novakovic, ROFA Laboratory & Process Analyzers
- 16:10–16:20 **Sponsorship presentation**
- 16:30–18:30 **Poster session 2**
All posters should be placed in the poster area, but only posters with even numbers will be presented.
- 19.30–22:00 **Conference dinner**

Friday 5 October 2018

- 9:30–10:10 **From crystal structures to rotational excitations of bound H₂ by means of computer simulations (Keynote lecture)**
Juergen Eckert, Department of Chemistry, University of South Florida, USA
- 10:15–10:45 **Powder X-ray diffraction microstructural analysis of synthetic apatite subjected to thermal treatment and high energy dry milling**
Vladislav Kostov, Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences
- 10:45–11:15 **Coffee break**
- 11:15–11:40 **Structure and magnetic properties of ferromagnetic systems (Keynote lecture)**
Hristo Kolev, Institute of Catalysis, Bulgarian Academy of Sciences
- 11:40–12:05 **New carbon materials with graphite microstructure (Thematic lecture)**
Boyko Tsyntsarski, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences
- 12:05–12:30 **Challenges at characterization of particulate matter**
Zara Cherkezova-Zheleva, Institute of Catalysis, Bulgarian Academy of Sciences
- 12:30–14:00 **Lunch Break**
- 14:00–14:40 **Practical methods for structural characterization, physico-chemical properties, size and shape analyses of manufactured nanomaterials (Keynote lecture)**
Boris Shivachev, Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences
- 14:45–15:15 **Coffee break**
- 15:15 **Award for the best poster contribution, closing remarks**

Poster sessions 1 and 2

- P_1. R. Angelov, B. Georgieva, A. Slavov, I. Vasileva, T. Dodevska, D. Karashanova – Structural characterization of silver and gold nanoparticles synthesised by recycling of *Rosa Damascena* waste from oil industry in Bulgaria
- P_2. V. Angelov, E. Ivanov, R. Kotsilkova – TEM analysis of gold nanoparticles attached on the surface of organoclay and obtained by two different methods
- P_3. A. Anselmo, A. Vollmer, B. Seidlhofer, B. Schramm, M. Grobosch, M. Helm – CALIPSOplus – an integrating activity for advanced communities in Horizon 2020
- P_4. G. Atanasov, R. Rusev, O. Petrov, B. Shivachev, M. D. Apostolova – Evaluation of CA-4 benzoxazolone derivative 19Z's biological activity against tumor cell lines
- P_5. S. Atanasova-Vladimirova, I. Piroeva – Pyroxene composition: Evidence from the Vito-sha pluton, Western Srednogie Bulgaria
- P_6. A. Bachvarova-Nedelcheva, St. Yordanov, I. Stambolova, R. Iordanova, V. Blaskov – Sol-gel synthesis and properties of Sm modified TiO₂ nanopowders
- P_7. B. Barbov – Phenol removal using ANA-type zeolite synthesized from fly ash
- P_8. N. Bedeković, V. Martinez, V. Stilinović, D. Cinčić – Halogen bonding in the systems of benzoyl-4-pyridoylmethane and perhalogenated hydrocarbons
- P_9. T. Boyadzhieva, V. Koleva, R. Stoyanova – Crystal chemistry of mixed NH₄Mn_{1-x}Fe_xPO₄·H₂O ditmarites used as highly efficient precursors for synthesis of electrochemically active LiMn_{1-x}Fe_xPO₄ phospho-olivines
- P_10. B. Chen, A. Keulen, G. Ye – Development of MSWI bottom ash based geopolymer
- P_11. Z. Cherkezova-Zheleva, D. Paneva, M. Tsvetkov, E. Encheva, K. Strehina, N. Mirchev, M. Shopaska, J. Krstić, V. Radonjić – Green synthesis of iron oxide magnetic nanoparticles using different plant aqueous extracts and their photocatalytic properties
- P_12. Z. Delcheva, Ts. Stanimirova, N. Petrova – Thermal decomposition of new phase obtained at transformation of zinc hydroxysalt minerals
- P_13. K. Dikova, M. Tavlinova-Kirilova, K. Kostova, A. Chimov, R. Nikolova, B. Shivachev, V. Dimitrov – Synthesis of chiral aminoalcohol – configuration determination and catalytic application
- P_14. O. Dimitrov, I. Stambolova, S. Vassilev, T. Babeva – Deposition of nanosized ZrO₂ sol gel films using different stabilizing agents and study of the effect on the morphology and optical properties
- P_15. T. Dimitrova, V. Cvetkova, P. Marinova, P. Marinova, V. Karadjova – Synthesis, crystal growth and some characterization of mixed crystals M'₂Mg_(1-x)M_x''(SeO₄)₂·6H₂O (M' = K, NH₄, Rb, Cs, M'' = Co, Ni, Zn)
- P_16. L. Dimowa, N. Petrova, I. Piroeva – Comparative study of monocationic forms obtained by ion exchange of purified clinoptilolite tuff

- P_17. V. M. Dylgerov, L. T. Dimowa, R. Rusew, N. L. Petrova, R. P. Nikolova, B. L. Shivachev – Conformational polymorphism in (3-acetamidophenyl)boronic acid
- P_18. L. Fotović, V. Nemeč, V. Stilinović, D. Cinčić – The halogen bonding proclivity of the aldehyde group in cocrystals of 2-hydroxy-1-naphthaldehyde and perfluorohalogenobenzenes
- P_19. R. VI. Gavrilova, V. K. Lazarova – Complex study of phase transformations in wear-resistant cast alloys
- P_20. B. Georgieva, G. Gencheva – Complexes of “Platinum Blues” with creatine, creatinine and allantoin – formation of Pt^{III} species with electrochemical oxidation
- P_21. D. Goranova, R. Rashkov, H. Popova, V. Tonchev – Experimental and modeling study of Co-deposition of Ni-Cu alloys at low current densities
- P_22. P. Gorolomova, B. Krebs, R. Nikolova, B. Shivachev, S. Simova, G. Momekov, G. Gencheva – Crystal and molecular structure, spectroscopic properties and in vitro antiproliferative effects of new Au^{III} complexes with dipyrin-2-ylamine
- P_23. Ts. Ibrevva, Ts. Dimitrov, R. Titorenkova, I. Markovska, E. Tacheva, O. Petrov – Synthesis and characterization of willemite ceramic pigments in the system xCoO. (2–x)ZnO. SiO₂
- P_24. R. Ivanova, G. Issa, M. Dimitrov, J. Henych, M. Kormunda, D. Kovacheva, V. Štengl, T. Tsoncheva – Catalytic oxidation of ethyl acetate by copper modified Ce-Mn and Ce-Ti mesoporous nanostructured oxides
- P_25. M. Kamenova-Nacheva, I. Slavchev, V. Dimitrov, R. Nikolova, B. Shivachev, G. M. Dobrikov – Synthesis and X-ray crystallographic studies of ferrocenylmethylidene and arylidene substituted camphane based compounds
- P_26. N. Kaneva, A. Bojinova, K. Papazova, D. Dimitrov – Heterogeneous photocatalytic degradation of reactive Black 5 in aqueous suspension by La-modified ZnO powders
- P_27. D. Kichukova, D. Kovacheva, A. Staneva – Comparison of the properties of reduced graphene oxide obtained by different mild reducing agents
- P_28. I. Koseva, P. Tzvetkov, P. Ivanov, A. Yordanova, V. Nikolov – Rare Earth doped silicate glass-ceramics for LED application
- P_29. B. Kostova, V. Petkova, Y. Tzvetanova, E. Serafimova – Influence of gas mediums on the thermal decomposition of thaumasite from Igljika deposit, Bulgaria
- P_30. V. Kostov-Kytin, R. Nikolova, G. Avdeev – XRD study on the structural evolution of Zn-exchanged titanosilicate ETS-4 during thermal treatment
- P_31. V. Kurteva, B. Shivachev, R. Nikolova – Polydentate ligands combining pirlindole and piperazine fragments
- P_32. Ts. Lazarova, D. Kovacheva – A new phase obtained by oxidation of nanosized spinel MnFe₂O₄
- P_33. N. Lihareva, L. Dimowa, O. Petrov, Y. Tzvetanova, S. Vladimirova-Atanasova – Mechanism of Sr²⁺ uptake by clinoptilolite – kinetics and structural control

- P_34. D. Marinova, Tsv. Bancheva, M. Georgiev, D. Stoilova – Contribution to the study of iso-morphic inclusions in crystals. Synthesis and properties of mixed sodium manganese-sodium copper sulfate dihydrates with a kröhnkite-type structure
- P_35. D. Marinova, V. Kostov-Kytin, R. Nikolova, R. Kukeva, E. Zhecheva, R. Stoyanova – Crystal structure and redox properties of alluaudite $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$ as high-voltage electrodes for rechargeable batteries
- P_36. D. Marinova, M. Wildner, Tsv. Bancheva, M. Georgiev, D. Stoilova – Crystal structure of synthetic kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, and of limited solid solutions $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($0 < x \leq 0.18$) with a blödite type structure
- P_37. P. Markov, E. Grigorova, D. Nihtianova – TEM characterization of Mg_2NiH_4 based material prepared at low temperature
- P_38. I. Mihailova, L. Radev – Akermanite based bioactive ceramics: physicochemical and in-vitro bioactivity characterization
- P_39. N. Mirchev, M. Tsvetkov, G. Avdeev, K. Avramova, M. Gancheva – Thermoanalytical behavior of doped ZrW_2O_8 at elevated temperatures from 20 °C up to 800 °C
- P_40. M. Nedyalkov, E. Encheva, M. Tsvetkov, M. Milanova – The influence of the modifying Eu(III) on the $\alpha \rightarrow \beta$ phase transition temperature of zirconium tungstate
- P_41. A. Nikolov, R. Titorenkova, N. Velinov, Z. Delcheva, B. Chen – Characterization of a novel acid-activated geopolymers based on fayalite slag from local copper industry
- P_42. A. Nikolov, H. Nugteren, I. Rostovsky, Z. Delcheva – Synthesis of geopolymers using natural zeolite and sodium aluminate
- P_43. M. Panayotova, N. Mintcheva, O. Gemishev, G. Tyuliev, G. Gicheva, L. Djerahov – Preparation and antimicrobial properties of silver nanoparticles supported by natural zeolite clinoptilolite
- P_44. D. Paneva, Z. Cherkezova-Zheleva, V. Petkova, B. Kostova, H. Kolev, G. Avdeev, G. Stefanov – Investigation on crystallization and transformation processes in amorphous alloy $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$
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- P_46. T.M. Petrova, N.I. Velinov, I.B. Ivanov, T.T. Tabakova, V.D. Idakiev, I.G. Mitov – Structural characterization of $\text{Au}/\text{Cu}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ catalysts
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- P_48. R.I. Rusew, V.B. Kurteva, L.T. Dimowa, B.L. Shivachev – Synthesis and structure solution of novel quaternary ammonium salts of quinoline and 4,4'-bipyridine
- P_49. R.I. Rusew, B.L. Shivachev – New phenylboronic acid azo dye – structure determination and sugar sensing properties
- P_50. H.I. Sbirikova-Dimitrova, V. Ganev, B.L. Shivachev – Crystallization and crystal structure of lysozyme with nanosized titanium oxide

- P_51. E. Serafimova, V. Petkova – Spectroscopic analysis of sulphuric acid treated biodegradable waste
- P_52. V. Stefanova, E. Serafimova – Spectroscopic analysis of sewage sludge and fly ash from the biomass for land recultivation
- P_53. A. Stoyanova-Ivanova, I. Ilievska, V. Petrova, M. Gueorgieva, V. Petrov, L. Andreeva, A. Zaleski, V. Mikli – Physicochemical characterization on clinically retrieved Tritanium orthodontic archwires
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THE MARS SCIENCE LABORATORY EXPERIENCE

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The Mars Science Laboratory (MSL) began its journey to Mars in November, 2011, and landed in Gale crater on the night of 5 August, 2012. Gale crater is occupied by Mt. Sharp at the center, three times higher than the Grand Canyon is deep. MSL carries ten instruments on or inside the Curiosity rover, including a variety of cameras and radiation, weather, and chemistry analyzers. The rover also includes a device for analyzing gases in the Mars atmosphere and in soils and rocks (the SAM instrument) and an X-ray diffraction (XRD) and X-ray fluorescence instrument for detecting the minerals in soils and rocks using (CheMin). XRD is a well-established technique on Earth using large laboratory instruments and it can provide more accurate identifications of minerals than any method previously used on Mars. The MSL experience involved working on “Mars time” with a 24-hr, 39-min solar day (sol); if you went to work at 0800 today, you would go to work at 2000 in about two weeks. Work with Curiosity involves sending commands (~14 minutes from Earth to Mars) and receiving data, every day. The first photos from MSL showed a variety of volcanic rocks along with apparent sedimentary rocks that support the past existence of flowing water. Contrary to previous results, analyses of the atmosphere have not found compelling evidence of methane gas. Methane can have a variety of origins, including volcanic and biological, and its absence has important implications in the search for life. The CheMin instrument first analyzed a martian soil from a dune and found that it is very similar to soils on the flanks of Mauna Kea volcano in Hawaii. Unlike some several-billion-year-old conglomerates that Curiosity investigated, which are consistent with flowing water, the soil is representative of more modern processes on Mars. Subsequent XRD analyses of drilled rocks revealed the presence of phyllosilicates, which are consistent with formation in water. To-date, the materials analyzed by Curiosity are consistent with our ideas of the deposits in Gale Crater recording a transition through time from a wet to dry environment. The ancient rocks, such as the conglomerates and drill cores, suggest the past presence of liquid water, whereas minerals in the younger soil are consistent with little or no interaction with water. Curiosity continues to travel across the surface of Gale Crater to Mt. Sharp in search of evidence for past water and environments that may have once been habitable.

CALIPSOPLUS – OVERVIEW AND TARGETED RESEARCH POSSIBILITIES

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The Trans-national Access programme of the project CALIPSOplus (Convenient Access to Light Sources Open to Innovation, Science and to the World), funded by the European Commission within the EU Framework Programme for Research and Innovation Horizon 2020, supports access of European researchers to European and Middle Eastern light sources. The consortium consists of 19 partner organisations from 12 countries, involving a total of 14 synchrotrons and 8 free electron lasers totalling up to 82 500 hours of available experimental time.

Free access to the infrastructures is complemented by CALIPSOplus, which offers financial support to users coming from EU Member States or Associated States in the form of travel funding. CALIPSOplus also runs a special programme focused on leveraging scientific excellence across the EU and widening the use of light sources throughout the region. With the Twinning programme, researchers not yet active in synchrotron-based research are partnered with an experienced group for a hands-on introduction to the facilities. The short stay is fully financed. This programme aims at establishing and further developing new scientific communities, particularly from countries without own light source.

In this talk, a short overview of the project, the scientific infrastructures available and a variety of research opportunities will be presented, as well as a selection of scientific achievements relevant to the crystallography community.



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Keywords: synchrotron radiation, transnational access, european commission.

HALOGEN BOND – A RIVAL TO HYDROGEN BOND AS INTERACTION OF CHOICE IN CRYSTAL ENGINEERING

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The central issue of crystal engineering is recognition of specific intermolecular interactions, the study of their effect on the structure (and thus properties) of crystalline solids, and, eventually, rational design of solids with desired structures and properties through employing the knowledge of said interactions. Traditionally, hydrogen bond has been the main supramolecular interaction employed in crystal engineering, and the majority of the supramolecular synthons described and studied in the solid state have been based on it.

Over the past couple of decades, however, there has been a constant increase in the study of halogen bonds as alternative interactions in supramolecular chemistry and crystal engineering. Indeed, they have swiftly transformed from an obscure intermolecular interactions known only to a handful of experts into an indispensable tool of crystal engineering. The reason for this increase in interest of crystal engineering community for halogen bond lies in the properties of the halogen bond which are similar to those of hydrogen bond – both are strong and highly directional interactions which makes them efficient and reliable tools for crystal engineering.

In spite of general similarity, there are significant differences between the two interactions. Halogen bond is more directional than hydrogen bond due to the charge distribution on the halogen atom, making it more difficult to achieve a bifurcated bond. They are also more tuneable, as by changing halogens one can cover a very wide range of interaction energies.

Over the past several years our group has been studying some of these points through structural studies of halogen bonded cocrystals, using both the 'classical' halogen bond donor molecules (perfluorinated iodoarenes), as well as *N*-halogenoimides as extremely powerful organic halogen bond donors. The talk will cover some of our recent results on comparative studies of halogen and hydrogen bonds and halogen bond energetics,[1] geometries of halogen bonded synthons,[2,3] as well as interdependence between halogen bonds and other interactions in a crystal structure.[4]

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INVESTIGATION AND DEVELOPMENT OF NEW TYPES OF HYBRID NANOCOMPOSITES BASED ON POLYOLEFINS AND AZERBAIJAN NATURAL MINERALS

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The influence of organosilicon coupling agent (aminoethylaminopropyltrimethoxysilane) on the main physico-mechanical properties of hybrid nanocomposites based on low density polyethylene (LDPE) and Azerbaijan natural mineral – kaolin nanoparticles (particle size – 55–120 nm) is considered. Improving the properties of composites can be achieved through increase of the adhesion bond of nanoparticles with the polymer matrix. It is established that the use of a coupling agent promotes the hydrolysis process on the nanoparticles surface forming a monolayer that improves polymer-particle adhesion contact. It is this feature of the coupling agent that makes it possible to obtain hybrid polymer composites. In this connection, the most important step was the technique of introducing silane coupling agents into composites, through which the maximum effect on material properties is guaranteed. Zinc stearate and titanium dioxide (TiO₂) were used as associated components which improve the rheological characteristics to form fine spherulitic supramolecular crystal structure. In a wide range of concentrations, the influence of kaolin and clay nanoparticles on the strength properties of composites is studied. It is shown that with an increase in the nanoparticles concentration to 40 wt.%, accordingly, the need to increase the concentration of coupling agent to 3.0 wt.% grows up. The joint and separate influence of the ingredients – TiO₂ and zinc stearate on the change in the physico-mechanical characteristics of the filled composites is studied. A comparative analysis of the experimental data has convinced us that with an increase in the concentration of the above-mentioned ingredients in composites based on dressed kaolin, a noticeable improvement in their physico-mechanical properties is observed. The rise in the melt flow rate provides composites a technological advantage in their processing by extrusion and injection molding. The intended purpose of the structure-forming agent – TiO₂ in the composite is in the formation of additional heterogeneous crystallization centers, which are known to promote the spontaneous growth of crystalline formations during the melt cooling process. The latter circumstance reflects on the improvement of the quality of the developed composite materials.

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Keywords: hybrid nanocomposites, natural mineral, composite structure.

DISORDERED STRUCTURES & THE FEAR TO PUBLISH THEM

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Real crystals, grown in the laboratory or created by nature, are never perfect. They have defects and frequently parts of molecules (or whole molecules) are found in more than one crystallographically independent orientations. This leads to disorder, twinning, or the number of formula units in asymmetric unit (known as Z') to be bigger than 1. Roughly, half of all crystal structure analyses have problems and most of them involve disorder. Origin and classification of different types of disorders, as well as the different methods of treatments, are very well described in literature. Many different software and approaches have been developed for faster, automatic or semi-automatic solution of such problems, and yet, disordered crystallographic structures keep crystallographers busy for many hours and days. After all the hard work of solving the structure, the final and most challenging step is the validation and publication of reliable results. Validation of disordered structures has its limitations, due to lack of exact experimental evidence to prove the proposed model. The mathematical approach has many criteria such as thermal ellipsoids size, R-values of model error, maxima in residual electron density etc., which help crystallographers to judge the model, but the final decision how the new structure or discovery will be presented to the audience lies in the hands of the scientists involved in the particular research.

Today, most publications have more than one author and the main reason for that is the complexity of the presented research. Experts from different fields should be involved to comprehensively resolve each scientific problem. Crystallography, as one of the most powerful analytical methods, is part of that complex process and should be used to provide the necessary and correct evidence of the scientific topic developed in a publication. Disordered structures scare scientist with poor crystallographic knowledge. Such structures immediately open the door for discussions and concerns how to present, apply and publish the acquired results.

In my presentation, I will cover the basic concepts of disorder in small molecules single crystal analysis followed by a discussion how one can publish highly disordered structure without fear. I will provide examples and stories (some with unexpected end) collected during my professional work as crystallographer.

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Keywords: single crystals, disordered structures.

SIZE-DEPENDENT EMERGENCE OF CRYSTALLINITY IN MOLECULAR CLUSTERS

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Clusters consisting of N octahedral molecules AF₆ exhibit several structural phase transformations under the temperature of solidification – this is shown with Monte Carlo simulations, Molecular Dynamics calculations, and quantum computations (density-functional theory). The temperature is size-dependent, $T(N)$. The nature of the phase change (continuous/discontinuous) can only be identified if the following size-related prerequisites are simultaneously satisfied: a) specific number of molecules; b) specific ratio of the molecular size and the range of the potential. The structural transition below the freezing point of TeF₆ is discontinuous (with a latent heat) and the new phase is characterized with a partial order of the molecular axes of symmetry. A dynamic coexistence of phases in one solid-like molecular cluster has been observed using the phase trajectory computed with the isoenergetic molecular dynamics method. The phenomenon has been confirmed with constant temperature Monte Carlo computations. The observation of phase coexistence in an isolated small cluster is possible because of the special features of the cluster' potential energy surface that allow the phase trajectory to pass via the common (of the two-phases) saddle points more frequently that it would be possible for a large system. For example, the trajectory of a system containing the Avogadro number of particles would pass through such a point once in 10^{10} years. That is why the isolated large systems are observed in one of the available phases while a mixture of these systems reveals phase coexistence. The size-dependent temperature of cluster crystallization decreases if the Coulomb term in the interaction potential decreases. The explanation is that the small (in intensity) Coulomb term acts as an collective perturbation at very low temperatures and keeps the mutual order,

Despite the same molecular symmetry of SF₆ and TeF₆ (octahedral) the free clusters made of them have a different thermal behavior due to the ro-vibrational coupling that depends on both molecular symmetry and the symmetry of the environment surrounding it: while the clusters made of TeF₆ exhibit a two-stage orientation order transformation which converges into a single-stage continuous transformation for bulk, the SF₆ substances show weak discontinuous transition for both small and large systems.

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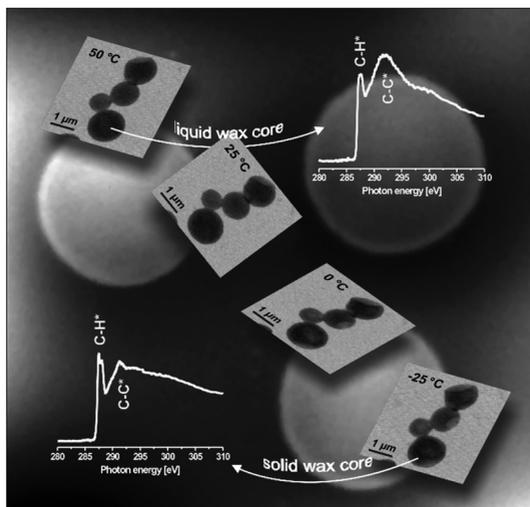
Keywords: phase transformation and phase coexistence in solid clusters, Molecular Dynamics, Monte Carlo, Density functional theory.

IMAGING AND SPECTROSCOPIC MICROANALYSIS USING SYNCHROTRON SOFT X-RAY RADIATION

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The recent advances in nanotechnology have led to the development of new experimental techniques to investigate nanoscale materials with unprecedented resolution. Combining soft x-ray absorption spectroscopy and zone plate imaging, scanning transmission X-ray microscopes (STXMs) provide both high chemical sensitivity and a spatial resolution less than 40 nm which allows gaining more detailed information on the variation in structures of such kind of materials. In STXM high-brilliance synchrotron radiation is focused by a Fresnel zone plate, and the sample is raster-scanned through the focal point while recording the intensity of transmitted X-rays in order to produce a 2-dimensional image. STXM can also be used for elemental mapping via near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, a fingerprint of the molecular composition in the sample. Here, few selected examples from modern material science will be presented to demonstrate the capabilities.



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Keywords: STXM, NEXAFS, nanomaterials, microanalysis.

SYNTHESIS AND NANO/MICROSTRUCTURE OF METAL OXIDES: SELECTED EXAMPLES

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Metal oxides are a class of materials exhibiting unique optical, magnetic, electrical and mechanical properties as a consequence of their ability to form very diverse crystal and electronic structures. These properties along with their high thermal stability make metal oxides to be very important materials for advanced applications as electronic components, catalysts, electrodes, sensors, etc. Generally, physical and chemical properties of solid materials are dependent on the particle's size and shape that can be controlled by synthesis route. However, the synthesis of solid nanostructures of desired size and morphology takes into account the careful control of various experimental parameters.

Metal oxides nanostructures can be synthesized using different chemical and physical methods. In this presentation, the focus will be given to the influence of experimental parameters on the chemical and nano/microstructural properties of selected metal oxides: zinc oxide [1, 2], nickel oxide [3] ruthenium oxide [4] and doped hematite [5, 6], produced either by wet chemical route or by electrospinning. Influence of manganese-ion dopant on the formation mechanism hematite [5] star-like nanostructures and its magnetic and optical properties will be discussed. In addition, the influence of chemical and electrospinning parameters on the formation and structural properties of single and composite metal oxides will be emphasized.

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Keywords: metal oxides. Nano/microstructure, electrospinning.

STRUCTURAL CHARACTERIZATION OF SILVER AND GOLD NANOPARTICLES SYNTHESISED BY RECYCLING OF *ROSA DAMASCENA* WASTE FROM OIL INDUSTRY IN BULGARIA

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Metal nanoparticles (NPs) with variety of shapes and sizes are one of the most studied nanomaterials due to their great potential for application in medicine, for biosensors, as catalyzers for elimination of biotoxins, for application in electrochemistry, etc. Despite the great number of chemical and physical methods for synthesis of NPs (chemical, electrochemical and photochemical reduction, gas-phase synthesis and deposition, laser ablation, sol-gel techniques, etc), the efforts of the scientists are focused on the development of new, perspective, cheap and environmentally friendly methods. Among them are so-called “green” methods for synthesizing metal NPs, which are based on the waste produced by agricultural and food industry. The rose oil industry is one of the most popular manufacturing in Bulgaria. More than 5500 tons of rose flower were processed in 2015 [1] and almost as much is the solid waste. In the same time, the rose wastes and waste waters are rich of polyphenols – compounds which are the main reducing agents of metal NPs “green” synthesis [2].

In this study we present “green” synthesis of Ag and Au NPs by reduction of AgNO₃ and HAuCl₄, respectively, using water extract of solid waste from *Rosa damascena* oil industry, pasteurized and live beer yeast and combinations thereof. The morphology, microstructure and phase composition of obtained by ten different recipes Ag and Au NPs are investigated by High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED) and X-ray diffraction (XRD). The size distribution of the NPs is realized using Image J software.

The indexing of SAED and XRD patterns shows the presence of Ag phase, both cubic and hexagonal and Au phase, cubic. The histograms from TEM analysis of Ag and Au NPs indicate average particles size in the interval 2–10 nm. The relation between synthesis conditions, phase composition and size distribution of Ag and Au NPs is followed and discussed.

Acknowledgement: The authors are grateful to the financial support of National Science Fund of Bulgaria; project DN 17/22/12.12.2017 “Valorization and application of essential oil industry wastes for “green” synthesis of metal nanoparticles”.

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Keywords: Ag and Au nanoparticles, green synthesis, *Rosa damascena* water extract, TEM, XRD.

TEM ANALYSIS OF GOLD NANOPARTICLES ATTACHED ON THE SURFACE OF ORGANOCLAY AND OBTAINED BY TWO DIFFERENT METHODS

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The Turkevich method was applied for the synthesis of gold nanoparticles using trisodium citrate as a chemical reducing agent. But in this study two different approaches have been developed. In the first approach we have prepared concentrated solutions of HAuCl_4 and sodium citrate, and in the second approach we have prepared dilute solutions. In the first method for the preparation of the suspension of organoclay is used i-propanol and in the second method is used distilled water. TEM analysis shows that in the first approach gold nanoparticles form larger agglomerates on the surface of organoclay. In contrast, the second method produces relatively uniform and small gold nanoparticles with sizes of about 30 nm, which are homogeneously dispersed on the clay surface.

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Keywords: organoclay, gold nanoparticles.

CALIPSOplus – AN INTEGRATING ACTIVITY FOR ADVANCED COMMUNITIES IN HORIZON 2020

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The Trans-national Access programme of the project CALIPSOplus (Convenient Access to Light Sources Open to Innovation, Science and to the World) provides supported access of European researchers to European and Middle Eastern light sources [1]. This project is funded by the European Commission within the EU Framework Programme for Research and Innovation H2020.

CALIPSOplus dedicates particular attention to leveraging scientific excellence across the EU and to widening the use of light sources throughout the region. A Twinning programme has been set up aiming at establishing and further developing new scientific communities, particularly from countries without own light source [2]. In the Twinning programme, potential users are partnered with host groups that share their know-how and expertise in applying the available experimental techniques to common research areas. Scientists new to research with



synchrotron-based techniques have the opportunity to participate in a fully-financed hands-on introduction to the facilities.

[1] <http://www.calipsoplus.eu/calipsoplus-in-a-nutshell/>

[2] <https://www.helmholtz-berlin.de/user/user-info/eu-support-programmes/>

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Keywords: synchrotron radiation, trans-national access, European commission.

EVALUATION OF CA-4 BENZOXAZOLONE DERIVATIVE 19Z'S BIOLOGICAL ACTIVITY AGAINST TUMOR CELL LINES

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Combretastatin A-4 is a naturally occurring compound with pronounced cytotoxic activity against endothelial and rapidly dividing tumor cell lines. The relatively simple cis-stilbene structure allows synthesis of numerous CA-4 structural analogs. This presents an opportunity for better understanding of structure-activity relationship and discovery of new, more efficient anti-tumor drugs. In our studies, we investigate the biological activity of new combretastatin A-4 derivatives in which ring B is replaced with benzoxazolone [1] and/or thiazolone fragments.

MTT test for antiproliferative activity of benzoxazolone analogue 19Z showed it has an IC₅₀ value of 1 μM for HepG2 and 0.7 μM for K562 cell lines. IC₅₀ for endothelial cell line is 10 μM. Since the main target molecule of CA-4 is known to be the colchicine site in the β subunit of α/β-tubulin dimer – the main building component of microtubules which play key role in cell division, a flow cytometry analysis was done to screen for potential cell cycle disturbances. The results confirmed that 19Z induces mitotic block in the G2/M phase. The structure and conformation of 19Z was confirmed by X-ray crystallography. Molecular modeling analysis confirmed that 19Z binds well in the colchicine site of tubulin and forms hydrogen bonds with tubulin aminoacids sidechain groups.

This primary studies on the biological activity of 19Z confirm that it's able to induce relevant cytotoxic effects against tumor cells. Future work on CA-4 analogues containing this pharmacologically relevant modifications could result in synthesis of new more effective cancer drug formulations.

Acknowledgement: The authors are grateful to the BAS for the financial support under Grant DFNP-17-124/2017 and to Bulgarian Science Fund [Contract DN19/13, 2017].

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Keywords: combretastatin A-4, benzoxazolone, cytotoxicity.

PYROXENE COMPOSITION: EVIDENCE FROM THE VITOSHA PLUTON, WESTERN SREDNOGORIE BULGARIA

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The Vitoshka volcano-plutonic edifice crops out in the western part of the Srednogorie structural zone. The plutonic body is composed of gabbros, anorthosites, monzonite, quartz monzonite, monzogabbro, quartz monzogabbro, syenites, quartz syenite and late veins of aplitic quartz syenitic composition, intruded in the Late Cretaceous volcano-sedimentary sequence. The major rock-forming mineral phases are plagioclase, K-feldspar, amphibole, clinopyroxene and biotite. Common accessory minerals include apatite, titanite, magnetite, ilmenite and zircon. Secondary minerals are epidote, chlorite, actinolite and clay minerals.

Within the Vitoshka pluton, clinopyroxenes are observed as small crystals and in most of the samples, they are completely replaced by a successive generation of green to brown amphiboles. Clinopyroxenes display diopsitic to augitic compositions within the range of $En_{36}Fs_{15}Wo_{49}$ to $En_{44}Fs_{13}Wo_{43}$, according to the calculation proposed by Morimoto (1988). They are characterized by Ca-rich (CaO – 19.57–24.73), Na-poor ($Na_2O < 0.67$) and high-Mg (Mg# – 67–80) and low-TiO₂ (<0.56 wt%) composition.

In all rock types clinopyroxenes temperatures of crystallization ranged from 1209–1179 °C for gabbro to 1167–1072 °C for quartz syenite (Putirka, 2008).

The low-Ti and high-Mg content of the clinopyroxenes suggest that the Vitoshka pluton was formed by the presence of depleted mantle source for the parental magma.

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Keywords: clinopyroxene, diopside, augite, Vitoshka pluton.

SOL-GEL SYNTHESIS AND PROPERTIES OF Sm MODIFIED TiO₂ NANOPOWDERS

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The present investigation deals with the sol-gel synthesis and properties of TiO₂/Sm³⁺ nanopowders. The gels were prepared using Ti(IV) butoxide and Ti(IV) isopropoxide with isopropanol as solvent. The titanium(IV) alkoxide/solvent ratio was kept 1:1 and no water was added during the sol-gel synthesis. The aging of gels was performed in air for several days in order to allow further hydrolysis.

By XRD was investigated the phase formation of the gels upon heating in the temperature range 200–700 °C. It was established that the heat treated up to 300 °C gels exhibit a predominantly amorphous phase. The amount of amorphous phase gradually decreases with increasing the temperature and the first TiO₂ (anatase) crystals were detected about 400–500 °C. The average crystallite size of TiO₂ (anatase) (calculated using Sherrer’s equation) in the powdered samples heat treated at 400 °C is about 10 nm. By DTA was established that the decomposition of the organics is accompanied by strong weight loss occurred in the temperature range 200–300 °C. The completeness of the hydrolysis – condensation reactions was verified by IR and UV-Vis analyses.

It was established the impact of samarium on the thermal properties, structure and morphology of the obtained nanopowders.

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Keywords: sol-gel, powders, thermal stability, X-ray diffraction.

PHENOL REMOVAL USING ANA-TYPE ZEOLITE SYNTHESIZED FROM FLY ASH

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The thermal power plants, based on coals, are the main source of fly ash (FA). Depending on the type of source and the composition of the coal being burned, the components of the solid by-products could vary considerably, but all FA includes substantial amounts of silica (both amorphous and crystalline) and alumina, both of them being endemic ingredients in many coal-bearing rock strata. FA is a fine powder captured from flue gas streams by dust collecting systems prior to their release into the atmosphere FA is generally stored in landfills. The disposal of FA creates ecological risks because of the acidification and the infiltration of heavy metals and radioactive components into the soil. The production of zeolite from FA would result in a good ingredient of high value as additive to cement. An attempt to find a common solution for this environmental problem is reported in the present work.

It was successfully synthesized zeolite Analcime (ANA) from FA produced by combustion of coal in three thermal power plants using a one-stage process – hydrothermal synthesis. Initial synthetic gels were obtained by preparing of mixture with ratio Sodium hydroxide/FA in the range of 2.0 to 1. By decreasing the amount of NaOH, crystallization of zeolites ANA, SOD and NaP begins. In order to obtain the mono-phase product zeolite analcime, additional silica powder was added to the synthesis mixture. The obtained samples were characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscopy. They was investigated for the purification of phenol-contaminated water.

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Keywords: synthesis, zeolites, fly ash, phenol.

HALOGEN BONDING IN THE SYSTEMS OF BENZOYL-4-PYRIDOYLMETHANE AND PERHALOGENATED HYDROCARBONS

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Halogen bond is an attractive interaction between an electrophilic region on a halogen atom in a molecular entity (halogen bond donor) and a nucleophilic region in another, or the same, molecular entity (halogen bond acceptor) [1]. Alongside hydrogen bond, it is a widely used tool for constructing supramolecular assemblies in the solid state, where perhalogenated hydrocarbons have been highlighted as the most frequently used halogen bond donors [2]. On the other hand, potential for using b-diketones for the synthesis of a halogen-bonded structures in the solid state has scarcely been investigated to date, indicated by only 6 structures deposited with the CSD.^[3] In this contribution we are presenting crystal structures of a novel asymmetric b-diketone, benzoyl-4-pyridoylmethane (**b4pm**) and cocrystals derived from **b4pm** and five usual halogen bond donors: iodopentafluorobenzene (**ipfb**), 1,2-, 1,3- and 1,4-diiidotetrafluorobenzene (**1,2-tfib**, **1,3-tfib** and **1,4-tfib**) and 1,3,5-triiodo-2,4,6-trifluorobenzene (**1,3,5-titfb**). These binary solids have been prepared both by crystallization from solution and liquid-assisted grinding (LAG). All five cocrystals are assembled by C—I⋯N halogen bonds involving pyridyl nitrogen and iodoperfluorobenzene iodine. Furthermore, cocrystals derived from **1,3-tfib** and **1,2-tfib** have additional C—I⋯O halogen bonds, involving oxygen atoms from b-diketo group and the other iodine atom. Most of the obtained cocrystals are of 1:1 stoichiometry except (**b4pm**)₂(**1,4-tfib**), where stoichiometry is 2:1 as a result of **1,4-tfib** bridging two diketone molecules via C—I⋯N halogen bonds. All obtained compounds have been characterized by X-ray powder diffraction, thermogravimetry and differential scanning calorimetry.

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**CRYSTAL CHEMISTRY OF MIXED $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4\cdot\text{H}_2\text{O}$
DITTMARITES USED AS HIGHLY EFFICIENT PRECURSORS
FOR SYNTHESIS OF ELECTROCHEMICALLY ACTIVE
 $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ PHOSPHO-OLIVINES**

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Dittmarite-type compounds, $\text{NH}_4\text{MPO}_4\cdot\text{H}_2\text{O}$ ($\text{M}^{2+} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$), are a typical example of two-dimensional structure materials with valuable properties like ion-exchange, interlayer ionic mobility, sorption, supercapacitive behaviour and etc.

In the present contribution two main topics have been addressed: (i) To gain a deep understanding of the solid solution formation between $\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O}$ and $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$. The choice of just those members of the dittmarite-family is purposeful and it is dictated from the second topic: (ii) To demonstrate the ability of $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4\cdot\text{H}_2\text{O}$ mixed crystals to act as highly effective precursors for a fast low-temperature synthesis of electrochemically active olivine phase $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ through an ion-exchange reaction. The study is focused on the effect of Mn/Fe substitution on the crystal structure, spectroscopic and morphological characteristics of both $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4\cdot\text{H}_2\text{O}$ and $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ with emphasizing on the relationship "precursor design – product design". The different aspects of the cation substitution in the precursors $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4\cdot\text{H}_2\text{O}$ and target $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ products such as crystallochemistry, long-range and local structure, intermolecular interactions and morphology have been studied by combination of Rietveld analysis based on powder XRD data, IR and EPR spectroscopies and microscopic methods which are highly complementary in describing crystal chemistry of solid solutions. The electrochemical activity of a solid solution $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ as an electrode in a model two-electrode lithium cell of the type $\text{Li}|\text{LiPF}_6$ (EC:DMC)| $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ has been also manifested.

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Keywords: Solid solutions; *Cation substitution*; Dittmarites; Phospo-olivines; Li-ion battery.

QUANTUM DESIGN PPMS-9T: CRYOSTAT SYSTEM FOR ELECTRIC, MAGNETIC AND THERMAL EXPERIMENTS AT HIGH MAGNETIC FIELDS AND TEMPERATURE RANGE 2–400 K

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The Quantum Design: Physical Properties Measurements System (PPMS) is versatile cryostat instrument with advanced capabilities for magnetic, thermal and electric experiments at high magnetic fields ($\pm 9\text{T}$) and wide temperature range (2–400 K). We will present the features of the main experimental modules and a measurement examples and analysis of the properties of innovative materials in various structural forms.

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Keywords: electric, thermal, magnetic measurements, low temperatures and high magnetic fields.

DEVELOPMENT OF MSWI BOTTOM ASH BASED GEOPOLYMER

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A variety of characterization techniques were used in this study to evaluate the application potential of both low- and high-Fe containing municipal solid waste incineration (MSWI) bottom ash in geopolymer. Due to the removal of the glass, ceramic and natural stony materials in the separation process, slag is the main component in as-received bottom ash. The results suggest that the bottom ash with low-Fe content has advantage over that with high-Fe content as geopolymer precursor, due to its lower metallic Al content. However, H₂ gas induced matrix expansion occurred upon the alkali activation of low-Fe containing bottom ash. The 28-day compressive strength of synthesized geopolymer specimens is very low, owing to the residual pores formed in the redox reaction of metallic Al at high pH.

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Keywords: MSWI bottom ash, geopolymer, metallic Al.

CHALLENGES AT CHARACTERIZATION OF PARTICULATE MATTER

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Nowadays, the particulate matter (PM) has been recognized as one of the major air pollutants with established scientific evidences on risks to human health. Major interdisciplinary and multiyear research efforts have to be done to improve scientific understanding of airborne PM and its effects on human health. This new information will help to reduce uncertainties in the framework for assessing the public health risks from emissions of airborne particles and their gaseous precursors. The aim of our project is to investigate PM samples collected in Sofia, to identify global and regional particle sources in order to develop tools needed to formulate effective control strategies. This study reports a detailed examination of the challenges ahead for Particulate Matter physicochemical characterization. Several different approaches have been utilized in this regard starting from standard mineral techniques such as powder XRD, FTIR and SEM microscopy to non-standard techniques such as Mössbauer spectroscopy, DRIFT and XPS. In particular, the study has focused on the smallest magnetic grains (<30 nm), which are most likely to be inhaled into the human lung. These PM have to be characterized using low-temperature Mössbauer measurements. On the other hand, the presence of multiple phases presented in PM and also their small size makes difficulties in their identification. Therefore the preparation of standard procedures and methodology for investigation and control of PM is both challenge and priority.

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Keywords: particulate matter (PM), physicochemical characterization, PM collected in Sofia, global and regional particle sources.

GREEN SYNTHESIS OF IRON OXIDE MAGNETIC NANOPARTICLES USING DIFFERENT PLANT AQUEOUS EXTRACTS AND THEIR PHOTOCATALYTIC PROPERTIES

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Recently, there is an increased interest of research groups and tendency of using green and sustainable methods of metallic nanoparticles (NPs) preparation due to their environmentally friendly protocols, low cost and simplicity. The NPs synthesized by biosynthesis method, are promising candidate in various biomedical and ecological applications like utilizing as recyclable magnetic photocatalysts for degradation of organic pollutants. The one-step green synthesis of iron oxide magnetic nanoparticles has been done in this study using aqueous extracts of different plants as a reducing and capping agent. The formation of NPs was observed by the addition of ammonia in the mixture of leaf extract and precursor ferro- and ferric salts. Characterization of physicochemical properties of the samples was done using X-ray, FTIR, UV-VIS and Moessbauer spectroscopy. It was obtained that phase composition and dispersity of prepared NPs depends on the leaf extract used. In case of Green tea and Green Coffee preparation of single spinel phase of partially oxidized magnetite was registered. Use of Carob tree and Salvia extracts lead to synthesis of spinel phase and iron oxyhydroxide. Ferrihydroxide phase was obtained by Bay Leave extract. Photocatalytic properties of materials were tested in Methyl Orange degradation reaction.

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Keywords: green synthesis, iron oxide magnetic nanoparticles, plant extracts and photocatalytic properties.

THERMAL DECOMPOSITION OF NEW PHASE OBTAINED AT TRANSFORMATION OF ZINC HYDROXYSALT MINERALS

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The hydroxyl-salt minerals are normally stable over a small range of external conditions (such as Eh, pH, T, P, concentration of solutions, component ratio, impurities, etc.) as well as they are commonly associated with many other minerals of similar compositions in same parageneses. In contrast to the stable rock-forming minerals the hydroxyl-salt minerals react to slight environmental changes through changes in the crystal structure. Therefore, they are converted easily (and very often reversibly) into each other under environmental changes.

The zinc hydroxyl-salts and their thermal decomposition product show some useful properties: ion exchange and sorption properties, photocatalytic properties, flame retardant properties as well as their applicability as precursors of nanostructured ZnO for various applications.

A phase obtained by mixing of synthetic NO₃ – simonkolleite in aqueous 1M Na₂SO₄ solution for 24h at room temperature was investigated by various methods: XRPD, IR, DTA-TG (DTG) – MS and SEM – EDAX. Based on X-ray data, the resulting zinc hydroxysalt phase has a basal distance of about 18Å. The results of the SEM-EDAX chemical analysis showed that the composition of the phase was as follows: ZnO ~ 65.6 wt%, SO₃ ~ 14.6 wt% and H₂O (OH) ~ 20 wt%. The thermal decomposition of the phase was studied in details in regard to the thermal events, the released volatiles and solid residues. Effects of dehydration (25–200 °C), dehydroxylation (200–350 °C) and SO₂ release (700–1000 °C) were observed on the thermal curves. The intermediate and final decomposition products were characterized by XRD and SEM – EDAX. The ZnO obtained during thermal decomposition as intermediate and final product is of interest in regard to both changes in nano-dimensionality and degree of crystallinity.

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SYNTHESIS OF CHIRAL AMINOALCOHOL – CONFIGURATION DETERMINATION AND CATALYTIC APPLICATION

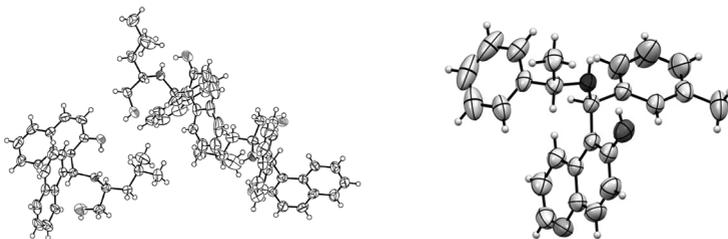
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The multicomponent reaction between 2-naphthol, aryl aldehydes and ammonia or amines yields aminobenzyl-naphthols in a process known as the Betti reaction. The replacement of ammonia with chiral amines results in diastereoselective formation of aminobenzyl-naphthols, which are easily isolated as pure diastereoisomers. These are useful as ligands in asymmetric synthesis.

The synthesis of chiral aminobenzyl-naphthols is demonstrated by using 1-naphthaldehyde, 3-methylbenzaldehyde and 2-naphthol or 6-hydroxyquinoline as naphthol component; (S)-(+)-leucinol and (S)-phenylethylamine were the amine-component. The reactions proceed highly diastereoselective leading to the formation of functionalized isomeric aminobenzyl-naphthols. The individual diastereoisomers could be isolated in pure form using chromatography. The configuration of the new stereogenic centres was determined by using of advanced NMR methods. The structure of the main isomer was determined by X-ray crystallography and confirms the applicability of the NMR approach for configuration assignment.



Structures of new compounds synthesized through Betti-condensation

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Keywords: (Betti condensation, aminobenzyl-naphthol, NMR spectroscopy, X-ray crystallography).

DEPOSITION OF NANOSIZED ZrO₂ SOL GEL FILMS USING DIFFERENT STABILIZING AGENTS AND STUDY OF THE EFFECT ON THE MORPHOLOGY AND OPTICAL PROPERTIES

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Thin nanosized ZrO₂ films were obtained by sol gel method (dip coating technique). The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The optical properties were also investigated. In order to study the effect of the precursor solution on the phase composition, morphology and the optical properties three stabilizing agents (acetyl acetone, acetic acid and nitric acid) and their combinations were applied. The XRD data revealed tetragonal crystalline phase. The films are relatively dense, homogeneous, without visible cracks.

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Keywords: nano films, sol gel, zirconium dioxide, morphology.

SYNTHESIS, CRYSTAL GROWTH AND SOME CHARACTERIZATION OF MIXED CRYSTALS $M'_2Mg_{(1-x)}M_x''(SeO_4)_2 \cdot 6H_2O$ ($M' = K, NH_4, Rb, Cs, M'' = Co, Ni, Zn$)

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Crystals of the family of crystallographic Tutton salt with the general formula $M'_2M''(XO_4)_2 \cdot 6H_2O$ in which M' is a monovalent cation such as K^+ , NH_4^+ , Rb^+ , Cs^+ , M'' is a divalent cation such as Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Cd^{2+} and $X=S$ and Se has been investigated by various experimental techniques in order to understand their physical properties and potential technological applications.

Tutton's salts are potential conductors due to the existence of comparatively strong hydrogen bonds.

Nowadays, the applications of pure salt compounds as well as the ones doped with transition metals are very highly valued.

The idea is finding a new mixed material with the same structure, which shows further optical, electrical and magnetic properties than the undoped salt.

Polycrystalline samples of mixed crystals were grown from an equimolar aqueous solution been by the slow evaporation method at room temperature. The mixed crystals, $M'_2Mg_{(1-x)}M_x''(SeO_4)_2 \cdot 6H_2O$ ($M' = K, NH_4, Rb, Cs, M'' = Co, Ni, Zn$) characterized by XRD, FT-IR analysis, Raman and SEM.

The crystal chemistry of was investigated by single-crystal structure analysis to determine the effects of the chemical variation of M'' on the structural environment. The crystal composition reveals the co-existence of magnesium and transition metal in the mixed crystal.

Small variations in cell parameter values, slight shifts in characteristic vibrational patterns in FT-IR confirm the crystal stress to the lattice developed as a result of incorporation of transition metal – into the crystalline matrix.

The surface morphological changes are observed by scanning electron microscopy.

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Keywords: Tutton's salt crystal growth, mixed crystals, XRD, FT-IR spectroscopy.

COMPARATIVE STUDY OF MONOCATIONIC FORMS OBTAINED BY ION EXCHANGE OF PURIFIED CLINOPTILOLITE TUFF

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Clinoptilolite tuff from Beli Plast deposit (Bulgaria) was used as starting material to obtain monomineral clinoptilolite (cpt) sample. The tuff was purified in order to remove the co-occurring minerals [1]. The resulting sample contains >99% cpt. Ion exchange procedure was performed at 90 °C in 1M solution of Na, Ca, K and Mg nitrates for 6 days, by using four of the most common cations in the natural cpt structure: Na⁺, K⁺, Ca²⁺, and Mg²⁺. According EDS analysis ion exchanged forms are almost mono-cationic: Na – 4.44, K – 5.25, Ca –2.50 and Mg – 2.26 per unit cell. The comparison between the purified cpt powder pattern and Na, Ca, and Mg ones reveals that the intensity of the 020 reflection do not change. The line 020 is the most influenced one by cation exchange as it was discussed [2]. The lowering of {F(020)}² can be achieved if cpt undergoes ion exchange with heavy cations. Therefore, no change in the intensity of 020 reflections can be expected for Na, Ca and Mg forms. Only the potassium form shows negligible intensity decrease of 020 reflection. The results of DTA analysis show endothermic effects for all exchanged samples related to dehydration processes. According to TG analysis, the Mg form contains 24.76 water molecules followed by Ca-cpt (24) and the smallest amount is contained in the K form (14.92). The preliminary structural refinement carried out shows that the exchangeable cations occupy the positions that they prefer in the natural cpt, but also distribute in other positions.

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[2] O.E. Petrov. In D.W. Ming, F.A. Mumpton, Eds., *Natural Zeolites'93* (1993) 271.

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Keywords: ion exchange, structural refinement, clinoptilolite.

CONFORMATIONAL POLYMORPHISM IN (3-ACETAMIDOPHENYL) BORONIC ACID

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This study focuses on the structural peculiarities of two conformational polymorphs of (3-acetamidophenyl)boronic acid. The two polymorphs were generated by crystallization from different solvents e.g. chloroform and ethanol. The crystal structures of both polymorphs have been characterized by single-crystal X-ray diffraction analyses, DTA/TG, FTIR and *in situ* powder diffraction. Single crystal analyses showed that compound **1** crystallizes in the triclinic system space group $P\bar{1}$ while compound **2** crystallizes in the monoclinic crystal system, space group $P2_1/c$. The DFT calculations showed that the energy difference between the *trans* and

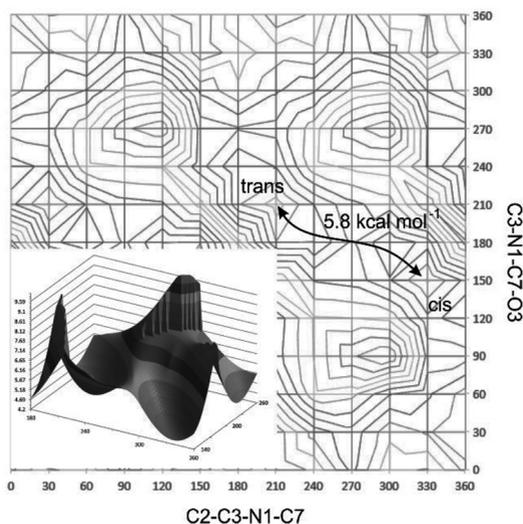


Fig. 1. Potential energy surface showing the barrier between *trans*/*cis* conformers.

cis conformers is not considerable ($0.9 \text{ kcal mol}^{-1}$ in favor of the *trans* conformer) Fig. 1. The computed barrier of rotation of $5.8 \text{ kcal mol}^{-1}$ between the two conformers is not excessively high (*cis* to *trans* rearrangement). The DTA/TG and FTIR spectra of the two polymorphs are nearly identical and therefore they are not very suitable for differentiation.

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Keywords: boronic acid, conformational polymorphism, single crystal, FTIR, DTA.

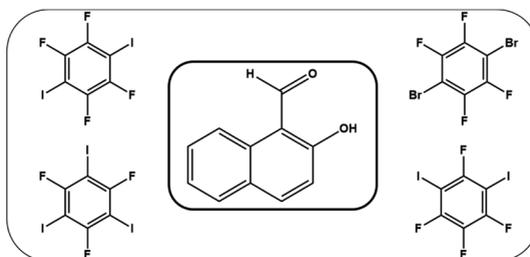
THE HALOGEN BONDING PROCLIVITY OF THE ALDEHYDE GROUP IN COCRYSTALS OF 2-HYDROXY-1-NAPHTHALDEHYDE AND PERFLUOROHALOGENOBENZENES

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Throughout our previous work, we have become increasingly interested in the carbonyl oxygen atom as a halogen bond acceptor. In our present work [1], we have decided to test the halogen bonding proclivity of the aldehyde group oxygen atom in competition with the hydroxyl group oxygen atom, and have selected 2-hydroxy-1-naphthaldehyde as the model compound. For cocystal cofomers we have selected haloperfluorinated benzenes, as they are reliable halogen bond donors [2].

We performed a series of mechanochemical experiments, which yielded cocystals with tetrafluoro-1,4-diiodobenzene, tetrafluoro-1,3-diiodobenzene, 1,4-dibromotetrafluorobenzene and trifluoro-1,3,5-triiodobenzene. In order to explore the stoichiometric ratio of the cofomers in the cocystal, powder X-ray diffraction and differential scanning calorimetry experiments were performed. Single crystals were obtained by solution-based methods, and their crystal and molecular structures were determined by single crystal X-ray diffraction. In cocystals containing linear halogen bond donors, molecules participate in $C-I \cdots O_{\text{aldehyde}}$ halogen bonds, while in the cocystal with tetrafluoro-1,3-diiodobenzene the molecules participate in $C-I \cdots O_{\text{hydroxyl}}$ and $C-I \cdots I$ halogen bonds.



[1] V. Nemeč, L. Fotović, T. Frišćić and D. Cinčić, *Cryst. Growth. Des.*, 17 (2017) 6169.

[2] C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst. B*, 72 (2016) 171.

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Keywords: halogen bonding, perfluorohalogenobenzenes, aldehyde group, 2-hydroxy-1-naphthaldehyde.

COMPLEX STUDY OF PHASE TRANSFORMATIONS IN WEAR-RESISTANT CAST ALLOYS

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Metal alloys for producing the cast parts working under abrasion, impact loads and corrosive environments must have optimal mechanical properties in service conditions. This necessitates research on their thermal stability, wear resistance, non-magnetism, corrosion resistance, and so on.

Improving the overall complex of properties of conventional alloys is achieved by introducing additional elements in their composition. The goal is to reduce the amount of used precious metal in the production of a particular part or machine, longer alloy life and lower cost of production.

These criteria motivate the purpose of this study - a complex investigations of the transformations in the distribution and the amount of the separated second phase in the metal matrix has been carried out.

Materials from Fe-Cr, Fe-Ni-Cr, Fe-C-Cr-Mn base systems have been studied to show the capacity for the large-scale applications. These are iron-based alloys with a under-eutectic or over-eutectic carbon content, additionally doped with chromium and manganese, vanadium or nickel.

Test specimens obtained after homogenization are accepted as standards. Metallographic examinations is performed at each stage of the study, macrohardness is measured using a Rockwell standard method, an X-ray analysis with a description of the available phases is applied. The microhardness of the matrix structure and the formed secondary phases is measured also.

The structural changes as a result of the applied modes of heat treatment – homogenization and aging at different retention times, are traced and analyzed. Data on the thermal stability of the alloys has been received and enriched with respect to the performance properties of this type of materials.

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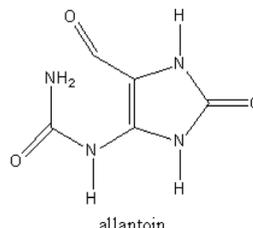
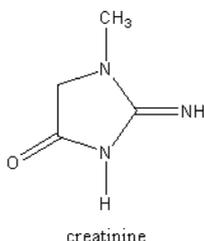
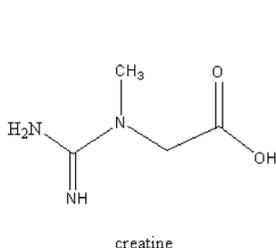
Keywords: wear-resistant cast alloys, heat treatment, structure transformations.

COMPLEXES OF “PLATINUM BLUES” WITH CREATINE, CREATININE AND ALLANTOIN – FORMATION OF Pt^{III} SPECIES WITH ELECTROCHEMICAL OXIDATION

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The metal complexes called “Platinum blues” are compounds that can be activated in the reducing environment of cancer cells. Nowadays, the trend in the field of medicinal inorganic chemistry has been toward molecularly targeted metal-based drugs obtained by functionalizing complexes with biologically active ligands.



The presented study deals with the reproducible synthesis of stable high oxidation paramagnetic oligonuclear platinum complexes with bioligands creatine, creatinine and allantoin. Intermediates Pt^{III} are now attracting attention in pathways associated with anticancer activity. It was found that the chemical and electrochemical oxidation leads to formation of platinum oligonuclear species with different chain lengths and formal Pt^{II}/Pt^{III} ratio. The selection of the conditions for the electrochemical generation of a Pt^{III} species is a prerequisite for directed synthesis of complexes with controlled chain length and the formal oxidation state of the platinum ions. The determined values of the formal redox potentials are in the range: $-0,2$ V to $0,5$ V. These values indicate that the obtained complexes will be relatively resistant to reducing influences and it can be assumed that they will be delivered to the tumor cells as active species. The solid state structure of the newly synthesized complexes was studied by IR, UV/Vis and electrochemical methods for analysis.

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Keywords: “Platinum Blues”, electrochemical synthesis, solid state structure.

EXPERIMENTAL AND MODELING STUDY OF CO-DEPOSITION OF Ni-Cu ALLOYS AT LOW CURRENT DENSITIES

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We present results from experimental and modeling study of co-deposition of Ni–Cu alloys far from equilibrium at lower current densities [1]. The influence of the initial concentration of Ni ions in the bath on the resulting morphologies and elemental distribution is studied. Different contents of nickel are detected, depending on the current density, concentration of nickel ions in the electrolyte and natural convection. The results reveal that Ni content increases twice with current density raising from 1 to 2 A dm⁻² and there is a difference of about 10 wt.% Ni along the coating surface. The increase of the nickel ion concentration in the electrolyte leads to a smooth surface and to the enhancement of the nickel content in the alloy at current density 1 A dm⁻². While at 2 A dm⁻² the roughness increases resulting in a typical dendritic morphology at low concentration of the nickel ions, which is changed to a cauliflower-like structure with increasing the nickel ion concentration. It was found that generally and independent of the varied factors, the distribution of the copper is predominant in the convex parts of the deposit, while the nickel deposits in the concave regions. This observation is considered a transcription of the principal expectation that copper deposits in a diffusion-limited mode, while the nickel still discharges in a kinetics-limited regime. We suggest an original computational model based on Cellular Automata that rationalizes the findings on the deposition regimes. It predicts that Cu is in the core of the dendritic structure having a branched geometry, while Ni forms a sort of a leveling layer on the fractal skeleton of Cu. The observed morphologies show that this leveling effect of Ni is enhanced by increasing the initial concentration of Ni ions. The model is expected to be valid for electrochemical deposition at lower interval of current densities when Ni could be still considered as depositing in kinetics-limited regime. With the increasing current density, Ni inevitably enters the diffusion-limited regime of deposition, and this may change the resulting complex morphology as well as its elemental distribution.

Acknowledgement: The authors are grateful for financial support to Project BG05M2OP001-2.009-0023, “Establishment and development of scientific potential for the specializations of physical chemistry and electrochemistry”, funded by the Operational Program “Science and Education Smart Growth”, co-funded by the European Union through the European Structural and Investment Funds.

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Keywords: co-deposition, diffusion-limited vs. kinetics-limited regime; computer modeling; cellular automata.

CRYSTAL AND MOLECULAR STRUCTURE, SPECTROSCOPIC PROPERTIES AND *IN VITRO* ANTIPROLIFERATIVE EFFECTS OF NEW Au^{III} COMPLEXES WITH DIPYRIDIN-2-YLAMINE

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The gold(III) complexes have great potential as anticancer agents, because there are many experimental evidences which proved that their growth inhibition effects pass through a variety of DNA-independent mechanisms.

In this study we present the synthesis, structural characterization and cytotoxic studies of two Au^{III}-complexes of dipyrindin-2-ylamine (dpa). The complex cation [Au(dpa)Cl₂]⁺, *Au1*, was obtained in acidic medium and isolated as compounds: [Au(dpa)Cl₂]Cl, *Au1a*, (orthorhombic Pnma space group, *a* = 27.5104(17), *b* = 12.3308(16), *c* = 8.2024(12) Å), and [Au(dpa)Cl₂]₂[AuCl₄], *Au1b*, (monoclinic P2₁ space group, *a* = 8.9273(6), *b* = 12.0903(10), *c* = 16.4352(14) Å, β = 105.684(3)°). A neutral complex with a composition [Au(dpa-H)Cl₂], *Au2*, was produced in alkaline medium (pH=9.5). The structures of the complexes have been characterized by X-ray diffraction, spectroscopic methods and DFT calculations. The ligand is coordinated in a bidentate mode respectively: symmetrically through the pyridine N-atoms in *Au1* and asymmetrically via a pyridine N-atom and the N-atom from the deprotonated amine group in *Au2*. The new compounds exhibited prominent antiproliferative effects against a panel of human tumor cell lines in a micromolar range of concentrations as the difference in activity is a function from the mode of the ligand coordination.

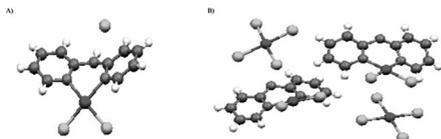


Fig. 1. Crystal structures of Au^{III} – complexes of dpa:
A) Au1a and B) Au1b.



Fig. 2. Molecular structure of Au2, optimized at RB3LYP DFT functional.

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Keywords: gold(III) complexes, structural characterization, DFT calculations.

SYNTHESIS AND CHARACTERIZATION OF WILLEMITE CERAMIC PIGMENTS IN THE SYSTEM $x\text{CoO} \cdot (2-x)\text{ZnO} \cdot \text{SiO}_2$

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Zinc silicate α -willemite ($\text{Zn})_2\text{SiO}_4$ is an orthosilicate with rhombohedral symmetry (space group R-3). Cobalt doped willemite is a pigment with application in high-temperature ceramics and glaze production. The aim of this study is to obtain single phase Co-doped willemite ceramic pigments with various concentration of cobalt in order to determine the optimal composition and temperature of sintering producing a pigment with the most intense blue color and good mechanical performance. For the purpose, a full series of cobalt containing willemite ceramic pigments with composition $x\text{CoO} \cdot (2-x)\text{ZnO} \cdot \text{SiO}_2$, where $x = 0.125, 0.250, 0.375, 0.50, 0.625, 0.75, 0.875$ and 1 , were synthesized via solid-state high temperature sintering. CoO , ZnO and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ are used as starting materials. NaF was used as a mineralizer. Synthesis was carried out in a laboratory muffle furnace in porcelain crucibles with a heating rate of $300\text{--}400\text{ }^\circ\text{C/h}$ in air with isothermal retention of 1 hour at the final temperature. The powder mixtures were sintered at $800, 900, 1000, 1100$ and $1200\text{ }^\circ\text{C}$. The resulting ceramic pigments were examined by powder X-ray analysis, infrared spectroscopy, electron microscopy, and the color was determined spectrophotometrically. The results reveal that even at $800\text{ }^\circ\text{C}$ α -willemite is synthesized. The disadvantage at low temperatures is the presence of a minimal amount of other phases such as ZnO , ZnAl_2O_4 and Co_3O_4 detected by powder x-ray and infrared spectroscopy. The amount of such phases decrease with temperature of sintering and ceramic pigments obtained at $1000\text{ }^\circ\text{C}$ contains only $(\text{Co}, \text{Zn})_2\text{SiO}_4$ with mean particle size of about 90 nm . The structural incorporation of cobalt is monitored by the position of the peaks in the infrared spectra. The pigment with the composition $0.375\text{CoO} \cdot 1.625\text{ZnO} \cdot \text{SiO}_2$ sintered at $1000\text{ }^\circ\text{C}$ has the brightest blue color as defined after spectrophotometric measurements of the coloring efficiency. It was proved that the synthesized pigments are suitable for application in sanitary ceramics and glaze tiles.

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Keywords: willemite, cobalt doped willemite, pigments, infrared spectroscopy, color measurements.

CATALYTIC OXIDATION OF ETHYL ACETATE BY COPPER MODIFIED Ce-Mn AND Ce-Ti MESOPOROUS NANOSTRUCTURED OXIDES

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Ceria-based materials continue to be investigated for their structural and chemical reduction behaviour and non-stoichiometry, oxygen storage capacity and metal-ceria interactions. These materials show promising application as catalysts for environmental protection [1]. In the current investigation mesoporous ceria-titania and ceria-manganese binary oxides were used as a host matrix of nanosized copper oxide species. The aim of the study is to elucidate the influence of the second metal oxide on the structural, redox and catalytic properties of the supports. The obtained composites were characterized by Nitrogen physisorption, X-ray diffraction, UV-Vis, Raman spectroscopy as well as temperature-programmed reduction with hydrogen. Their application as catalysts was investigated for the complete oxidation of ethyl acetate as a representative air pollutant.

Acknowledgements. Financial support from project DM-09/4/2016, Financial support by Program for career development of young scientists, BAS (project DFNP 17-65/26.07.2017) and Bulgarian Academy of Science – Czech Academy of Sciences bilateral project is gratefully acknowledged.

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Keywords: mesoporous nanostructured ceria-titania, ceria-manganese oxides, total oxidation of ethyl acetate, copper oxide.

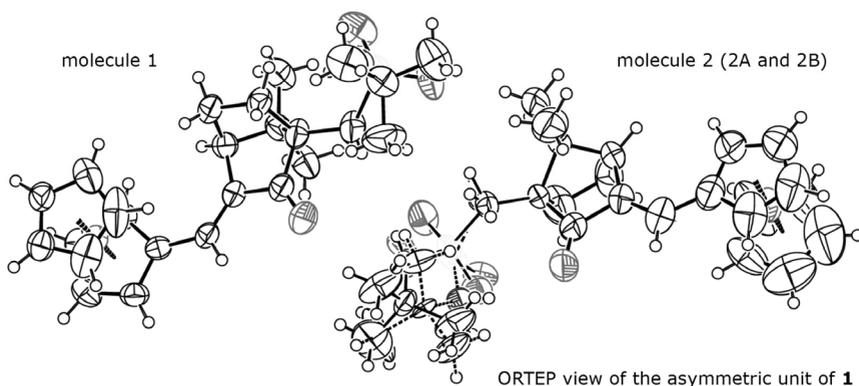
SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STUDIES OF FERROCENYLMETHYLIDENE AND ARYLIDENE SUBSTITUTED CAMPHANE BASED COMPOUNDS

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Compounds possessing bicyclic skeleton have shown promising biological activities as antioxidant, anti-inflammatory, anticancer or anti-infective agents [1]. Herein we present a small library of (+)-camphor-derived compounds realizing structural diversity through variation of substituents (i.e. sulfonamide groups, ferrocenyl-methylidene and arylidene moieties and heterocyclic substituents [2].



The configuration and regiochemistry of one of the synthesized compounds (**1**, Figure) has been unambiguously deduced from the X-ray crystallographic studies of single crystals.

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Keywords: ferrocenylmethylidene, sulfonamide, X-ray, stereochemistry.

HETEROGENEOUS PHOTOCATALYTIC DEGRADATION OF REACTIVE BLACK 5 IN AQUEOUS SUSPENSION BY La-MODIFIED ZnO POWDERS

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La-modified ZnO powders with different concentration (0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol%) are prepared by simply hydrothermal method. The obtained homogeneous charge is annealed at 100, 200, 300, 400 and 500 °C. The structural and photocatalytic properties are characterized by X-ray diffraction, Scanning electron microscopy, BET surface area and UV–vis spectroscopy. The result of XRD La³⁺ is successfully doped into ZnO lattice. It is found out that the crystallite size of La-modified ZnO is smaller as compared to pure ZnO and decreases with the increasing La content. Surface area (BET) measurements show higher surface areas and pores volume for La–ZnO catalysts in comparison to pure ZnO. The photocatalytic investigations revealed that all the lanthanum-modified ZnO powders exhibited excellent photocatalytic degradation of Reactive Black 5 compared with the ZnO under UV light irradiation. The optimal concentration and annealing temperature are experimentally established. The result showed that La³⁺ doping concentration had a remarkable effect on the efficiency of photocatalytic activity, with the optimal doping content being determined to be 2 mol% at 100 °C in terms of the photocatalytic activity efficiency.

Acknowledgements: Authors are grateful to Operational program “Science and Education for Smart Growth”, project BG05M2OP001-2.009-0028, DFNI-T02/16, Russian Presidential Program of engineer advanced trading and Horizon 2020 project ID: 692146-H2020-eu.4.b “Materials Networking”.

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Keywords: zinc oxide, lanthanum, Reactive Black 5, photocatalysis.

COMPARISON OF THE PROPERTIES OF REDUCED GRAPHENE OXIDE OBTAINED BY DIFFERENT MILD REDUCING AGENTS

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The preparation of reduced graphene oxide (rGO) by chemical reduction of graphene oxide (GO) usually involves highly toxic reducing agents which are harmful to the environment and human health. In the present study a relatively “green” approach for preparation of rGO is implemented, which involves the use of mild but nontoxic reducing agents. As soft reducing agents urea, ascorbic acid, glycine and citric acid are used. For some samples hydrogen peroxide is used as an additional reducing component. All samples were characterized by: powder X-ray diffraction (XRD), low temperature nitrogen adsorption, Raman and IR spectroscopy, as well as by Scanning and Transmission Electron Microscopy (SEM, TEM).

The results of all methods applied show that reduced graphene oxide (rGO) obtained by glycine-assisted reduction have characteristics superior to that of materials obtained by using the other reducing agents studied.

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Keywords: reduced graphene oxide, mild reducing agents.

STRUCTURE AND MAGNETIC PROPERTIES OF FERROMAGNETIC SYSTEMS

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Interest on the epitaxial growth thin films of 3d elements and its alloys is triggered from the opportunity to stabilize new phases with novel properties that can be used in Electronics and Magnetoelectronics/Spintronics.

In this work we present the structure of thin $\text{Fe}_x\text{Co}_{1-x}$ alloy films grown on Cu(001) as a function of the film thickness d and the Fe concentration x . The geometrical structural information has been determined by Low-Energy Electron Diffraction whereas electronic structure is derived from Appearance Potential Spectroscopy (APS) that gave us additional insight in the structural order of the films. Theoretical approach of APS was necessary for better understanding of spectroscopic results.

In the investigated thin films we were able to distinguish three different regions of structural order as a function of x and d . In the first region, where the concentration of Co dominates, an fcc-structure is observed. In the second region a mixture of fcc- and bcc-order was identified in the alloy. For very high Fe concentrations the fcc-structure recovers for films thinner than 13 ML.

Combining our results with data from the literature [1, 2] we were able to construct a comprehensive phase diagram of the studied thin $\text{Fe}_x\text{Co}_{1-x}$ films at room temperature.

Acknowledgements: Author gratefully acknowledges the financial support of the Bulgarian National Science Fund at the Ministry of Education and Science – Project № DCOST 01/22/2017. Many thanks to M. Donath, G. Rangelov and J. Braun for the discussions and help during my PhD Thesis.

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Keywords: thin films, Fe-Co alloys, phase diagram.

RARE EARTH DOPED SILICATE GLASS-CERAMICS FOR LED APPLICATION

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Light emitting diodes are of special interest and extensive study as they are environmental friendly and efficient energy saving devices.

Rare Earth doped glasses from the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{LiBO}_2$ are prepared with concentration of the dopants 0.5 at.% for Tb^{3+} and 0.1 at.% for Eu^{3+} . Glass-ceramics are obtained after thermal treatment of the parent glass at two different temperatures (580 and 630 °C) and for three different durations (2, 5 and 24 hours). The crystallizing phases, the crystallization degree and the particle size are determined.

The main crystallizing phase after thermal treatment with different duration and time is LiAlSiO_4 in two different crystallographic modifications – Eucryptite and Pseudocryptite. The ratio between these two phase modifications depends on the nature of the Rare earth ion. After longer thermal treatment the quantity of Pseudocryptite decreases. X-ray analyses show the presence of additional phases whose quantity is less than 5%. The crystallinity of all samples is about 90%. The particle size depends slightly on the Rare earth ion and varies between 80 and 120 nm according to the thermal treatment regime.

Emission and excitation spectra of the glass-ceramics show the characteristic peaks of Tb^{3+} and Eu^{3+} . The main emission peak of Tb^{3+} is ${}^5D_4 \rightarrow {}^7F_5$ transitions at 545 nm, corresponding to green color. Other transitions are located at 417, 440, 465, 488, 586 and 621 nm. The Tb^{3+} excitation spectra, cover the range from 300 to 500 nm. The sample show characteristic transitions of Tb^{3+} , attributed to the f–f transitions. The strongest peak is located at 379 nm corresponding to the ${}^7F_6 \rightarrow {}^5D_3$ transition. The main emission peak of Eu^{3+} is ${}^5D_0 \rightarrow {}^7F_2$ transitions at 613 nm, corresponding to orange-red color. Other transitions are located at 590, 653 and 702 nm. The Eu^{3+} excitation spectra, cover the range from 300 to 500 nm. The samples show characteristic transitions of Eu^{3+} , attributed to the f–f transitions. The strongest peak is located at 393 nm corresponding to the ${}^7F_0 \rightarrow {}^5L_6$ transition.

CIE coordinates of the samples show different emission colors which depend on the active ion and thermal treatment regime.

The obtained results show that as prepared terbium doped glass-ceramics could be used as a blue-green phosphor. Europium doped glass-ceramics could be used as an orange-red phosphor. Different emission colors could be obtained by using different thermal treatment regimes.

INFLUENCE OF GAS MEDIUMS ON THE THERMAL DECOMPOSITION OF THAUMASITE FROM IGLIKA DEPOSIT, BULGARIA

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The mineral thaumasite belongs to the ettringite group and is with theoretical formula $\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)(\text{CO}_3)\cdot 12\text{H}_2\text{O}$. The investigated sample is from Iglika magnesiumian skarn deposit, where the skarns are with an extremely monticellite composition. The Iglika deposit is located in the Srednogorie structural-metallogenic zone in SE Bulgaria [1, 2].

The mineral identification were made via X-ray powder diffraction analysis and IR spectroscopy measurements and the results are comparable to those published in the literature [3, 4]. The thermal analysis in two gas mediums – air and argon, were made to obtain the thermal decomposition of thaumasite. We measured mass losses, thermal effects as well as temperature intervals (under 1000 °C) of dehydration, decarbonization and desulphurization. The TG-DTG-DSC investigations are with mass-spectroscopy gas phase analysis.

The obtained new data allow compare the reaction mechanisms of thaumasite thermal dissolution in oxygen and inert mediums. The results can find widespread application in thermal chemistry investigations of cement minerals and composites in the order to define their physical-chemical, structural and thermal properties.

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Keywords: thaumasite, thermal decomposition, thermal analysis.

XRD STUDY ON THE STRUCTURAL EVOLUTION OF Zn-EXCHANGED TITANOSILICATE ETS-4 DURING THERMAL TREATMENT

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In situ time-resolved powder X-ray diffraction technique has been applied to investigate the structural evolution of Zn-exchanged titanosilicate ETS-4 upon heating within the temperature interval from 25 to 375 °C. The facilities of the Rietveld method as implemented in the software package GSAS [1, 2] have been used to control the plausibility of the obtained crystal-chemical characteristics at each stage. Previous single crystal structure determination of the title compound has served as initial model for the refinement procedure held on a sample at room temperature. Subsequently, the structure model of each increasing temperature step has been taken from the previous refinement. The structural evolution has been evaluated in terms of the unit cell parameters changes, water molecules site occupancies (during the dehydration period), the titano-silicate framework flexibility (pore sizes), and possible atomic motion during the thermal treatment. The obtained results have been interpreted with emphasis on the elastic properties of the studied titanosilicate structure and its thermal stability.

Acknowledgment: Part of the results in this work has been achieved in fulfillment of a project financed by the National Science Fund of Bulgaria under contract No. DNTS/Russia 02/8 from 15.06.2018.

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Keywords: Zn-ETS-4, Rietveld refinement, structural evolution.

POWDER X-RAY DIFFRACTION MICROSTRUCTURAL ANALYSIS OF SYNTHETIC APATITE SUBJECTED TO THERMAL TREATMENT AND HIGH ENERGY DRY MILLING

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Samples of nano-sized synthetic fluor-hydroxylapatite – $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F})_2$ heated within the temperature range 400–910 °C and samples of sintered biphasic calcium phosphates hydroxyapatite – $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and β -tricalcium phosphate – $\text{Ca}_3(\text{PO}_4)_2$ subjected to high energy dry milling for different durations have been studied by powder X-ray diffraction analysis. Descriptions of the microstructural characteristics of the apatite material at different stages of both treatment procedures as well as their evolution are in the focus of the investigations. The analysis of diffraction-line broadening has been performed using Rietveld refinement as implemented in the FullProf program [1]. Various size and strain models have been applied to handle the distinct anisotropy observed in certain crystallographic directions. Certain trends and consistencies of patterns in terms of domain sizes and microstrain have emerged for the studied material. The obtained results are explained and interpreted in the light of the up-to-date views and theories on crystal growth and imperfections and modern PXRD microstructural approaches.

Acknowledgment: These investigations have been performed in fulfillment of a project supported by a bilateral contract between the Bulgarian and Estonian Academies of Sciences.

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Keywords: apatite, Rietveld refinement, microstructural analysis.

POLYDENTATE LIGANDS COMBINING PIRLINDOLE AND PIPERAZINE FRAGMENTS

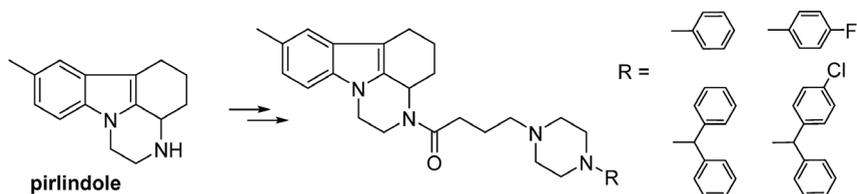
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Pirlindole, known also as pyrazindole, is a tetracyclic compound with antidepressant properties [1], which is clinically used psychotropic drug nowadays. From the other side, piperazine derivatives have shown remarkable variety of biological activity profiles [2]. In a search of novel efficient biologically active compounds, we decided to combine both fascinating units in a common molecule.

Herein, we present the synthesis and solution and solid state characterization of a series of compounds, possessing bridged pirlindole and piperazine fragments.



The target products were obtained from pirlindole in moderate overall yields *via* a two-step protocol and were characterized by NMR in solution and single crystal XRD of selected samples in solid state. The ligands (R = Ph and 4-FPh) crystallize in *P*-1 space group with a single molecule in the asymmetric unit and almost identical unit cell parameters, e.g. they are isostructural. It was found that piperazine substituent does not influence significantly the reaction output and preferred geometry.

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Keywords: pirlindole, piperazine, NMR, single crystal XRD.

A NEW PHASE OBTAINED BY OXIDATION OF NANOSIZED SPINEL MnFe_2O_4

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In a bulk form MnFe_2O_4 is a partially inverse spinel where about 80% of Mn^{2+} ions are located at tetrahedral (A) site while only 20% of them are located at octahedral (B) site. MnFe_2O_4 can be used as catalyst, as adsorbent for removing heavy metals in water, as ferrofluid, in biomedicine, in energy storage device and others. Solution combustion synthesis is used for the preparation of nanosized MFe_2O_4 with a mixture of two types of fuel glycine and glycerol in a 0.75:0.25 ratio. The resulting material was characterized by X-ray diffraction (XRD). As-prepared sample is single phase spinel with unit cell parameter 8.470 Å and mean crystallite size of about 40 nm. After the thermal treatment in argon flow at 400 °C for 2 hours, the unit cell parameter increases to 8.488 Å and the average crystallite size decreases to 35 nm. Additional thermal treatment at 400 °C of the same sample in air atmosphere resulted in a new diffraction pattern indicative for structural transformation. The detailed analysis of the newly obtained diffraction pattern shows that the positions and the intensities of the lines in it can not be unambiguously attributed to the known phases in the Mn-Fe-O system. Indexing the entire set of diffraction lines with Topas 4.2 gave a solution with a good confidence factor within a rhombohedral space group (unit cell parameters $a = 6$ Å and $c = 28.6$ Å). On the basis of systematic extinction possible space groups were R3, R3m and R-3m. Close values of unit cell parameters (R-3m, $a = 6.05$ Å, $c = 28.06$ Å) were found for Aerugite, cobaltian, $\text{Co}_{0.5}\text{As}_3\text{O}_{16}$ (65630-ICSD) thus its structure was used as a starting model for searching the structure of the new phase. Preliminary structural data will be presented. The new structure is closely related to that of the spinel. It was found that the oxygen layer packing sequence remained unchanged, but the displacement at the oxygen positions resulted in the lowering of cubic symmetry to hexagonal. The arrangement of the cation positions also remains close to that of the spinel, alternating the Oh_3 layers and T_2O layers. Due to the supposed oxidation of the cations, the composition of the new phase should be close to that of the $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and is supposed to be cation deficient. Unlike the maghemite where cation vacancies are distributed while preserving the cubic symmetry, in the current structure they seem to be located in one position (the octahedral position in one of the T_2O layers).

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Keywords: MnFe_2O_4 , solution combustion synthesis, spinel structural transformation, XRD.

MECHANISM OF Sr²⁺ UPTAKE BY CLINOPTILOLITE – KINETICS AND STRUCTURAL CONTROL

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One of the most abundant and harmful isotopes in radioactive wastes is ⁹⁰Sr. Its removing from contaminated media in the environment is very important. For improving the retention performance of sorbents it is necessary to know the property and characteristics of interaction between cations and sorbent.

In this study, kinetic data of strontium uptake by clinoptilolite was used in order to investigate the kinetics and mechanism of the process. Two kinetic models – pseudo-first and pseudo-second-order ones were applied for study of the overall kinetic rate. It was found, that pseudo-second-order kinetics described the experimental data fully.

Two diffusion models: external mass transfer and intraparticle diffusion, were applied for depicting the mechanism of interaction controlling the rate of uptake. It was found that the uptake is complex. On every step of strontium sorption the kinetics is not governed by any of both mechanisms, but contributions from the two models may have impact on the run of the process.

In order to identify the location of Sr²⁺ inside the zeolite structure, powder XRD analysis combined with Rietveld refinement were applied. Therefore, it is possible to depict the sites in the zeolites cages, where the cations are sorbed and their displacement with time of contact was followed. Thus, it is possible to check the existence and physical meaning that is attributed to different time step of kinetic study according to the applied models. The approach allows to study the transfer mechanism and to evaluate the importance of the diffusion effect.

According to EDS data the four samples shows presence of exchanged cation (Sr²⁺) as the values are: 0.22, 0.41, 0.48 and 2.05 per unit cell for samples at 16, 35, 95 min and 4 cycles exchanged process, respectively. According to the Rietveld analyses, strontium cations occupy the position of sodium (M1) in the clinoptilolite structure up to 35 min. Between 35 and 95 min strontium cations start to occupy the position of calcium (M2). For the 4 cycle exchanged sample the amount of Sr²⁺ increases significantly (1.02 per unit cell) in the position (M2).

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Keywords: clinoptilolite, strontium, ion exchange, Rietveld refinement.

CONTRIBUTION TO THE STUDY OF ISOMORPHIC INCLUSIONS IN CRYSTALS. SYNTHESIS AND PROPERTIES OF MIXED SODIUM MANGANESE-SODIUM COPPER SULFATE DIHYDRATES WITH A KRÖHNKITE-TYPE STRUCTURE

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On the basis of the solubility diagram of the $\text{Na}_2\text{Cu}(\text{SO}_4)_2\text{-Na}_2\text{Mn}(\text{SO}_4)_2\text{-H}_2\text{O}$ system at 25 °C combined with X-ray powder diffraction, it has been found that kröhnkite and Mn-kröhnkite form limited solid solutions, irrespective of their isostructureness. The reason for this finding is due to the different effective ionic radii of Cu^{2+} and Mn^{2+} ions (0.73 vs. 0.83), the different lattice parameters b , β and unit cell volumes, and the influence of the Jahn-Teller effect on the distortion of the MO_6 polyhedra.

The neat compounds $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{Mn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and solid solutions $\text{Na}_2\text{Cu}_{1-x}\text{Mn}_x(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ were characterized by means of vibrational spectroscopy, X-ray powder diffraction, TG-DTA-DSC methods. The vibrational spectra are interpreted in the light of the crystal structure of the salts. A correlation diagram between the point group symmetry, site symmetry of the sulfate ions and the factor group symmetry is presented. The phase transitions of the solid solutions were monitored by means of powder X-ray diffraction at elevated temperature. The enthalpies of dehydration (ΔH_{deh}) and of formation (ΔH_f) of the neat compounds and solid solutions have been calculated. Two types of anhydrous solid solutions are obtained after heating the hydrated solid solutions at 350 °C. The solid solutions $\text{Na}_2\text{Cu}_{1-x}\text{Mn}_x(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($0 < x \leq 0.08$) form anhydrous compounds with a saranchinaite-type structures. However, the included Jahn-Teller copper ions in $\text{Na}_2\text{Mn}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($0 < x \leq 0.16$) change the alluaudite structure of $\text{Na}_2\text{Mn}(\text{SO}_4)_2$.

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Keywords: kröhnkite-type solid solutions, solubility diagram, Jahn-Teller effect, vibrational spectroscopy, anhydrous solid solutions.

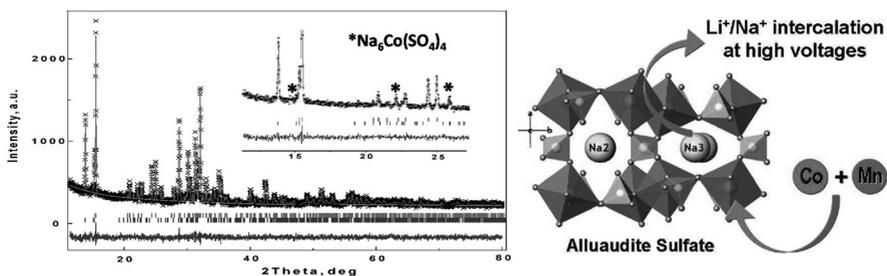
CRYSTAL STRUCTURE AND REDOX PROPERTIES OF ALLUAUDITE $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$ AS HIGH-VOLTAGE ELECTRODES FOR RECHARGEABLE BATTERIES

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Double sulfates of sodium and transition metals, having alluaudite structure, are predicted to be new class of high-voltage electrodes for Li/Na-ion batteries. Herein we provide a first experimental evidence for operation of sodium cobalt-manganese sulfate, $\text{Na}_{2+2\delta}(\text{Co}_{0.63}\text{Mn}_{0.37})_{2-\delta}(\text{SO}_4)_3$ at potentials higher than 4.0 V vs Li/Li^+ . Through detailed diffraction and spectroscopic analysis, it is found that the high-voltage operation of the alluaudite-type salt is a result of the unique interplay between the reduced cationic deficiency on the 8f alluaudite site, redox properties of Co and Mn ions and stability of the alluaudite structure during Li^+/Na^+ migration. This first experimental evidence will open new perspectives for design of high-voltage electrode materials for rechargeable batteries.



Rietveld refinement plot of $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$ calculated in the $C2/c$ space group together with $\text{Na}_5\text{Co}(\text{SO}_4)_4$ (some of its strongest lines are denoted by asterisks in the inset of the figure).

On the right, a motive from alluaudite structure with schematic mechanism of intercalation process.

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Keywords: alluaudite structure, $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$, high-voltage electrode.

CRYSTAL STRUCTURE OF SYNTHETIC KRÖHNKITE, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, AND OF LIMITED SOLID SOLUTIONS $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($0 < x \leq 0.18$) WITH A BLÖDITE TYPE STRUCTURE

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Based on different experimental methods – crystallization processes in aqueous solutions, infrared spectroscopy, single crystal X-ray diffraction and TG-DTA-DSC measurements, it has been established that copper ions are included in sodium cobalt sulfate up to about 18 mol%, thus forming limited solid solutions $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($0 < x \leq 0.18$) with a blödite-type structure. In contrast, cobalt ions are not able to accept the coordination environment of the copper ions in the strongly distorted $\text{Cu}(\text{H}_2\text{O})_2\text{O}_4$ octahedra, thus resulting in the crystallization of Co-free kröhnkite. The formation of $[\text{Cu}(\text{H}_2\text{O})_4(\text{SO}_4)_2]$ clusters in the blödite structure changes both the profile and the numbers of the infrared bands in the region of the asymmetric stretches of the sulfate ions. DSC measurements reveal that the copper concentration increase leads to increasing values of the enthalpy of dehydration (ΔH_{dehy}) and decreasing values of the enthalpy of formation (ΔH_f).

The crystal structures of synthetic kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, as well as of three Cu^{2+} -bearing mixed crystals of Co-blödite, $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ with $x_{(\text{Cu})}$ ranging from 0.03 to 0.15, have been investigated from single crystal X-ray diffraction data. The new data for the structure of synthetic kröhnkite facilitated to clarify structural discrepancies found in the literature for natural kröhnkite samples, traced back to a mix-up of lattice parameters. The crystal structures of Co-dominant $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ solid solutions reveal an influence of the Jahn-Teller-affected Cu^{2+} guest cations up to the maximum content of $x_{(\text{Cu})} = 0.15$. The response of the $\text{MO}_2(\text{H}_2\text{O})_4$ octahedral shape by increased bond-length distortion with Cu-content is clear-cut (but limited), mainly concerning the M–OH₂ bond lengths, whereas other structural units are hardly affected.

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Keywords: kröhnkite structure, $\text{Na}_2\text{Co}_{1-x}\text{Cu}_x(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ solid solutions, Jahn-Teller effect, vibrational spectroscopy.

TEM CHARACTERIZATION OF Mg₂NiH₄ BASED MATERIAL PREPARED AT LOW TEMPERATURE

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Mg₂Ni is attractive material for hydrogen storage because of its fast hydrogen sorption kinetics and relatively high theoretical absorption capacity. However, some disadvantages like high hydrogen sorption temperatures and consuming time and energy synthesis procedures [1], makes its practical application difficult. In our study we are synthesized Mg₂NiH₄ at milder temperature and for shorter period of time. A mixture of MgH₂ and Ni in weight ratio 1:1 is prepared by ball milling under Ar in a planetary mill for 1 h. The received mixture after ball milling was put in the Sievert's type device reactor for investigation of hydrogen sorption characteristics. Structure, phase and surface composition of the starting compounds and the sample before and after hydriding are determined by XRD and TEM for the sample after hydriding. The X-ray diffraction patterns of ball milled MgH₂:Ni does not indicate a presence of MgO. The MgH₂ contents some traces of Mg and the main phase is tetragonal MgH₂. The detected phases in ball milled sample are MgH₂, Ni and some unhydrided Mg. There is no presence of new phases after ball milling. After hydriding of the mixture at 573 K and P = 1 MPa contains as main phases tetragonal MgH₂ and monoclinic Mg₂NiH₄, respectively. Some unhydrided magnesium, nickel and MgO are detected also. TEM (SAED, HRTEM) results showed the following phase composition of the sample after hydriding: predominant monoclinic Mg₂NiH₄, orthorhombic Mg₂NiH₄, tetragonal MgH₂ and traces of Mg, Ni (both of them hexagonal, and also traces of MgO, NiO (both of them cubic). The histogram from TEM analysis of hydrided MgH₂:Ni indicated average particles size of 7 nm. The formation at such low temperature of mainly monoclinic phase, but also some orthorhombic Mg₂NiH₄ during cycling has great effect on hydrogen sorption properties of magnesium. The most of the methods of Mg₂NiH₄ synthesis published in the literature are done at higher temperatures and more complicated procedures.

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Keywords: TEM analysis; structure Mg₂NiH₄; hydrogen storage.

AKERMANITE BASED BIOACTIVE CERAMICS: PHYSICO-CHEMICAL AND IN-VITRO BIOACTIVITY CHARACTERIZATION

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Ceramics with chemical composition corresponding to akermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) was synthesized by sol gel technique. The obtained dried gel was subjected at two-step thermal treatment firstly at $700\text{ }^\circ\text{C}$ for 2 hours and then at 1000 , 1100 , $1300\text{ }^\circ\text{C}$ respectively for 2 hours. X-ray diffraction showed the structure evolution depending on temperature. The characteristics of the crystallization proceeding in $\text{CaO} - \text{MgO} - \text{SiO}_2$ system provide the synthesis of materials of an identical chemical but various phase composition, structure and relevant properties. All obtained samples between 700 and $1300\text{ }^\circ\text{C}$ were polyphases. The quantity of akermanite was increased with the temperature.

The structural behavior of the synthesized after two-step thermal treatment at 700 and $1300\text{ }^\circ\text{C}$ ceramics was examined by means of X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Akermanite, as the main crystalline phase, merwinite and diopside, as the minor phases, were identified. The XRD results were in good agreement with FTIR analysis.

The main purpose of the paper was the evaluation of the in vitro bioactivity of ceramics in static conditions for different periods of time – 7, 14 and 28 days in Simulated Body Fluid (SBF). The formation of carbonated apatite layer on the surface of the immersed samples was verified by FTIR, SEM and Energy Dispersive Spectroscopy (EDS) techniques. The change of ions concentrations in SBF was also carried out by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

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Keywords: $\text{CaO} - \text{MgO} - \text{SiO}_2$, ceramics, akermanite, in vitro bioactivity.

THERMOANALYTICAL BEHAVIOR OF DOPED ZrW_2O_8 AT ELEVATED TEMPERATURES FROM 20 °C UP TO 800 °C

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The ZrW_2O_8 compound has a negative coefficient of thermal expansion and phase transition in the temperature range of 20 to 800 °C. 0.1 mol Dy and Ce were added during its synthesis. Analyses indicate that the introduced modifiers slightly change their thermal behavior. Their impact is shown by decreasing the decomposition temperature to the constituent oxides, shifting the temperature of the phase transition to lower temperatures, and lowering the thermal stability of the samples.

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Keywords: ZrW_2O_8 , negative thermal expansion, phase transition.

THE INFLUENCE OF THE MODIFYING Eu(III) ON THE $\alpha \rightarrow \beta$ PHASE TRANSITION TEMPERATURE OF ZIRCONIUM TUNGSTATE

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The research on tungstates is focused on obtaining both nanoparticles and monolithic ceramics composites, as well as on testing their properties such as photocatalytic, conductivity, etc. The introduction of ions of different radius and charge leads to a disorder in the crystalline structure and consequently to the change of the tungstates properties. It is known that the tungstates of Zr and Hf have a negative coefficient of thermal expansion [1]. Small amounts of the modifying agent may influence the phase transition temperature and the temperature expansion coefficient [2], respectively. In order to investigate the influence of the Eu(III) on the Zr tungstate properties, hydrothermal method was used to obtain pure and Eu(III) modified ZrW_2O_8 . The content of the modifying ion applied was 1, 2 and 5 mol%. The samples obtained possess phase homogeneity as shown by the XRD and the $\alpha \rightarrow \beta$ phase transition temperature of ZrW_2O_8 was followed by high temperature XRD and TG/DTA.

Acknowledgements: The financial support from the Bulgarian Fund of Scientific Investigations, project ДМ 19/5 is acknowledged.

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Keywords: Zr tungstate, Eu(III) modification, XRD, TG/DTA.

CRYSTAL STRUCTURES OF SOME A'B^{II}VO₄ VANADATES: CRYSTAL STRUCTURE DETERMINATION FROM POWDER DIFFRACTION AND PHASE TRANSITIONS

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The crystal chemistry of A'B^{II}XO₄ (A^I = alkali ion, B^{II} = alkali-earth ion, X = P, V, As) is very rich and leads to numerous polymorphic phases which belong to 8 different structures types: olivine, arcanite, glaserite, tridymite, α -K₂SO₄, β -Na₂SO₄ and γ -Na₂SO₄ [1]. Among the various families (X = P, V, As); the phosphates have been the most widely investigated. Besides the purely interest from a crystal chemistry point of view, the research activities related to this family of materials is driven mainly due to their ferroelectric and ferroelastic properties and possible applications as phosphors for LEDs [1, 2].

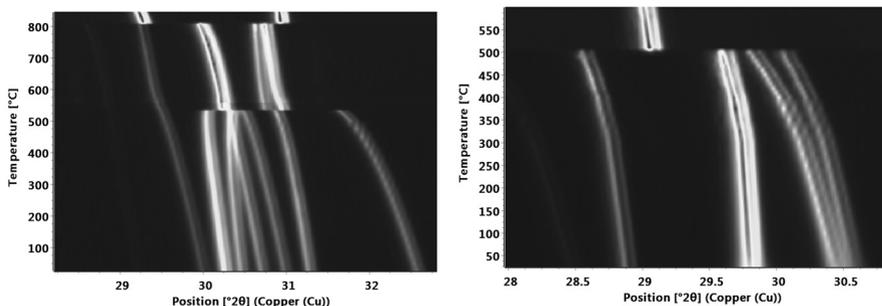


Fig. 1. Phase transitions in NaSrVO₄ (left, [4]) and AgPbVO₄ (right, [6])

While the phosphates family has been widely investigated, this is much less the case for the vanadates and arsenates. In this contribution, we report results on the crystal structures of new vanadates which exhibits new crystal structure type never reported previously in the A'B^{II}XO₄ series and rich phase diagrams as function of temperature [4–6].

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CHARACTERIZATION OF A NOVEL ACID-ACTIVATED GEOPOLYMERS BASED ON FAYALITE SLAG FROM LOCAL COPPER INDUSTRY

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The smelting process of the copper industry produce vast amounts of waste slag. In the present study the copper by-product from Aurubis (Pirdop, Bulgaria) was used as geopolymer precursor. The geopolymers are class of inorganic polymers used as binder to produce materials with high compressive strength, chemical resistance, thermal stability, low CO₂ footprint, possibility of utilizing industrial waste materials, etc. The X-ray fluorescence and powder diffraction analysis showed that the slag contains significant amount of iron presented by minerals fayalite and magnetite. The slag was homogenized with phosphoric acid activator solution to prepare fresh geopolymer paste. Rapid exothermic reaction takes place and the material hardens in minutes. Boric acid was successfully used to control the setting time of the geopolymer paste. The obtained inorganic polymer material is characterized with XRD, FTIR, Raman, DTA and Mössbauer spectroscopy. In conclusion, our study shows that the waste slag from local copper industry could be used as potential geopolymer precursor to produce building materials. This novel method could reduce the huge amounts of fayalite slag generated for the last decades.

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Keywords: geopolymer, copper slag, fayalite, acid-activated, inorganic polymer, iron silicate fines.

SYNTHESIS OF GEOPOLYMERS USING NATURAL ZEOLITE AND SODIUM ALUMINATE

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The geopolymers are novel class of inorganic materials consisting of chains, sheets or networks made of covalently bonded mineral molecules. The main precursors of the geopolymers are reactive aluminosilicate material and hardener solution. Natural zeolite clinoptilolite based geopolymers were synthesized using alkali aluminate solution, including aluminate anodizing waste solution. The effect of calcination at 900 °C of the clinoptilolite sample was investigated. The structure and physical properties of the samples were studied by: powder X-ray diffraction (XRD), thermal analysis (DSC–TG (DTG)) and scanning electron microscopy (SEM). Alkali aluminate activated clinoptilolite geopolymers are characterized by sufficient compressive strength, low density and acceptable shrinkage. The obtained clinoptilolite geopolymer contains an X-ray amorphous phase and certain amount of newly formed phillipsite and zeolite NaP. The presence of zeolite phases in the geopolymer agglomerate could be beneficial in products with specific qualities.

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Keywords: geopolymer, metazeolite, sodium aluminate, clinoptilolite.

PREPARATION AND ANTIMICROBIAL PROPERTIES OF SILVER NANOPARTICLES SUPPORTED BY NATURAL ZEOLITE CLINOPTILOLITE

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Nanocomposites consisting of natural zeolite and metal nanoparticles provide unique properties and various applications. Zeolite acts as microporous support that can embed and stabilize silver particles, control their size and distribution, and ensure the preparation of hybrid materials with enhanced properties.

Silver nanoparticles (AgNPs) supported by the natural Bulgarian zeolite clinoptilolite have been prepared by ion exchange of silver ions (Ag⁺) followed by thermal treatment of the silver-loaded zeolite. The Ag⁺ immobilization by the zeolite has been investigated at different concentrations of silver nitrate solution in a series of zeolite mass to solution volume (m:v) ratio. The effect of temperature and heating time on the immobilization of AgNPs by the zeolite and reduction of Ag⁺ and were also studied.

The structure and surface chemistry of as-prepared nanocomposites, morphology and size distribution of the obtained AgNPs were characterized by set of methods including XRD, XPS, SEM, TEM, and BET. The impact of initial AgNO₃ concentration, m:v ratio, temperature and treatment time on the degree of silver ions loading as well as the deposition of AgNPs on zeolite has been analyzed.

The zeolite supported AgNPs have been tested as antibacterial agents. The nanocomposites have shown a dose- and time-dependent antimicrobial activity against *Escherichia coli* bacteria. The synthesized AgNPs-clinoptilolite composites could find an application in the water disinfection.

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Keywords: silver nanoparticles, nanocomposites, AgNPs-zeolite, antimicrobial activity.

INVESTIGATION ON CRYSTALLIZATION AND TRANSFORMATION PROCESSES IN AMORPHOUS ALLOY $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$

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Amorphous Fe-Si-B-C alloy ribbons are widely used for different industrial applications. Elements like Ni, Co, Mo (critical raw materials) are added to iron-based amorphous alloys to improve their properties. They have an amorphous structure which is thermodynamically unstable. In the process, the materials undergo changes that lead to a stable transition and a change in the phase composition. Formation of crystallite phases as a result of heating in such materials gives rise to loss of their advanced properties. The combination of several metalloids is intended much easier glass-formers, but complicates the crystallization process. We use amorphous $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$ ribbons produced by the melt spinning technique as a model system for the study of crystallization. Thermal treatment up to 1000 °C in vacuum was performed in apparatus for *in situ* high temperature X-Ray Diffraction analysis. Material obtained after this experiment was investigated also by ⁵⁷Fe Mössbauer spectroscopy. Both analyses show transformation of amorphous iron-based alloys and decomposition to crystal phases. Crystallization process was registered additionally by thermal analysis (TG, DTG and DSC). The thermal treatment above the crystallization temperature of the amorphous $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$ alloy results in formation of multiphase crystalline structure composed by α -Fe and iron borides and silicides-Fe₃(B,Si). Mössbauer data show rearrangement of iron neighbors as a result of thermal treatment.

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Keywords: Fe-Si-B-C amorphous alloys, crystallization, *in situ* high temperature XRD.

INVESTIGATION OF RARE EARTH DOPED ZINC BOROPHOSPHATE GLASSES

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In recent decades, rare earths are becoming a vital wealth of advanced materials and technologies (catalysts, alloys, magnets, optical components and lasers, electronics, economical lighting, conversion of wind and solar energy). It could say that they are like jewels for functional materials of the future [1, 2].

The present research is focusing on the synthesis and characterization of rare earth doped ZnO-rich borophosphate glasses ($67.5\text{ZnO} - 18\text{B}_2\text{O}_3 - 14-x\text{P}_2\text{O}_5 - 0.5\text{RE}_2\text{O}_3$). The ratio of the main components – ZnO, B_2O_3 , P_2O_5 , the content of the dopant rare earth element (Sm, Eu, Gd, Tb, Nd), and the conditions of synthesis and analysis are set on the basis of literature data and our previous studies.

The density of the obtained materials is measured, the molar volume is calculated, the chemical durability in acid, neutral and alkaline medium is determined. The structure of the synthesized compositions was investigated by powder X-ray diffraction, differential scanning calorimetry and infrared spectroscopy, and their optical properties – by photoluminescence analysis.

The obtained compositions are amorphous, homogeneous, non-hygroscopic and predominantly transparent glasses.

The synthesized rare earth doped zinc borophosphate glasses have a potential for practical application in optical devices.

Acknowledgement: This study was supported by the "Scientific Research" fund at University of Plovdiv, Bulgaria, Grant № ФП17-ХФ-013.

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Keywords: rare earths, doped zinc borophosphate glasses, x-ray powder diffraction, photoluminescence.

STRUCTURAL CHARACTERIZATION OF Au/Cu_{1-x}Mn_xFe₂O₄ CATALYSTS

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The spinel ferrites are known that have many important properties as magnetic, optical, catalytic etc., which provokes the scientific interest. The magnetite (Fe₃O₄) is the main active phase in Fe-containing catalysts of the high temperature first stage of water-gas shift reaction (WGSR), which performs at 350–450 °C to reduce CO content to 1–3%. It is known that in some cases multi-component ferrites has better catalytic behaviour than single component ferrite. Moreover, it is known that the iron oxide modified by gold shows high catalytic activity at low temperature.

The aim of the present work is to study structural characteristics of gold modified copper-manganese ferrite catalysts. Object of the investigation are materials with compositions Au/Cu_{1-x}Mn_xFe₂O₄ (0 ≤ x ≤ 1) before and after catalytic test in WGSR, where final phases have been formed.

Structural characteristics of samples were determined by X-Ray diffraction and Mössbauer spectroscopy. Spinel ferrite phase and gold phase were proved in all synthesized samples. In copper-rich composition additional phase of CuO is present. In Au/CuFe₂O₄ simultaneous presence of spinel phase with cubic and tetragonal symmetry was found. The cation distribution in octahedral and tetrahedral position in spinel lattice and presence of superparamagnetic particles were evaluated by Mössbauer spectroscopy. Catalytic activities in WGSR of studied samples during second day, when working catalytic phases have been formed are determined in following order: Au/Cu_{0.2}Mn_{0.8}Fe₂O₄ ≥ Au/Cu_{0.5}Mn_{0.5}Fe₂O₄ > Au/Cu_{0.8}Mn_{0.2}Fe₂O₄ > Au/CuFe₂O₄ ≥ Au/MnFe₂O₄. After WGSR were found changes in phase composition and structure of both gold and ferrite phases. Full or partial alloying of gold with copper was evidenced. The main transformation in samples in reaction atmosphere is reduction of the ferrite phase. In mixed copper-manganese ferrite the result of this reduction is formation of metallic copper and copper and/or manganese substituted magnetite. Simultaneous presence of both phases could be considered as a reason for better catalytic activity of mixed ferrites.

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Keywords: copper-manganese ferrites, gold catalysts, Mössbauer spectroscopy, WGSR.

SYNTHESIS, STRUCTURE AND PROPERTIES OF HYBRIDS DOPED WITH COPPER IONS IN THE SILICA-HYDROXYPROPYL CELLULOSE SYSTEM

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In the present study, the formation of copper-doped hybrids and their structure were examined. The hybrids were synthesized by sol-gel method based on silica derived from tetraethylorthosilicate (TEOS), hydroxypropyl cellulose (HPC) and different sources of copper – $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The quantity of organic substance was 5 wt.% and the amount of copper was varied from 0.5 to 5 wt.%. The principles of the hybrids formation were developed using structural data from Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Differential thermal analysis (DTA/TG). The XRD analysis showed that all samples are in amorphous state. The IR spectra are characterized with typical bands for silica network ($\sim 460, 650, 795, 960, 1085, 1200$ and 3480 cm^{-1}), and vibration of Cu-O bonds ($460\text{--}480 \text{ cm}^{-1}$). Using optical absorption spectra (UV-Vis) the band gap energy was determined. The obtained materials were tested as antibacterial agents. *Bacillus subtilis* and *Escherichia coli* K12 were used as model microorganisms.

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Keywords: sol-gel method, silica hybrid materials, copper ions.

SYNTHESIS AND STRUCTURE SOLUTION OF NOVEL QUATERNARY AMMONIUM SALTS OF QUINOLINE AND 4,4'-BIPYRIDINE

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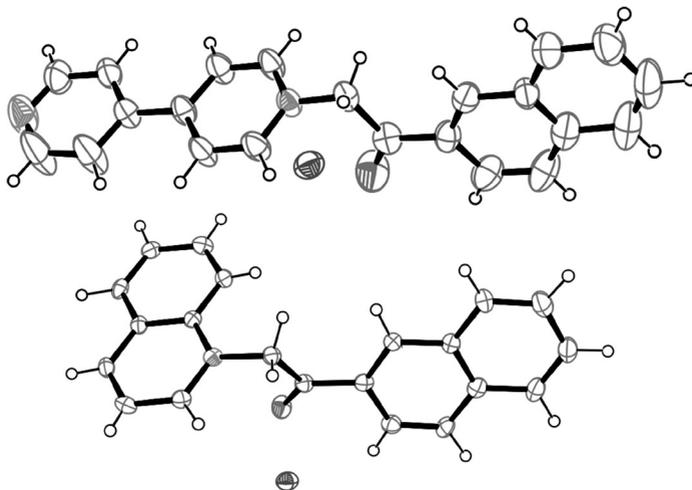
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Quaternary ammonium salts (QASs) have found various applications as surfactants, phase-transfer catalysts, antimicrobial and bactericidal agents, fabric softeners, etc. In addition, they compose the cationic part of the majority ionic liquids. QASs are usually synthesized via Menshutkin method.

Here we report on the facile synthesis of novel quaternary ammonium salts of quinoline and 4,4'-bipyridine with 2-bromoacetyl-naphthalene using modified Menshutkin method. The structures were characterized by single crystal X-ray diffraction, FTIR and DTA/TG analysis.



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Keywords: quaternary ammonium salts, 4,4'-bipyridine, quinoline, 2-bromoacetyl-naphthalene.

NEW PHENYLBORONIC ACID AZO DYE – STRUCTURE DETERMINATION AND SUGAR SENSING PROPERTIES

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Blood glucose levels can be monitored by different sensor systems that, by their mechanism of action, are divided into enzymatic and non-enzymatic. Enzyme-loaded sensors such as glucose oxidases and glucose dehydrogenases work on the principle of electrochemical analytical measurement. However, these sensors have a number of disadvantages such as temperature and pH sensitivity. More recently, non-enzymatic boronic acid-based fluorescence sensors have been developed [1, 2]. The sensors action is based on the ability of boronic acids to form five- or six-membered cyclic boronate esters with saccharides. This determines the use of boronic acids as effective colorimetric, fluorescence and electrochemical sensors for various saccharides. In this work we report the synthesis and UV-Vis spectroscopic changes of a new aminophenyl boronic acid azo dye upon glucose and fructose binding.

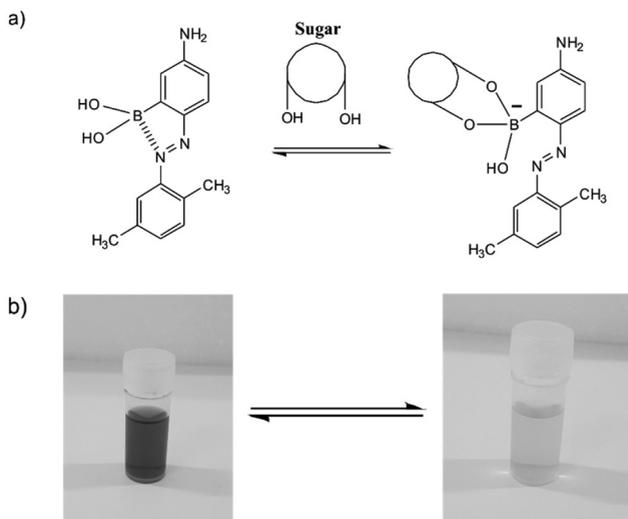


Fig. 1. Proposed mechanism of the sugar induced spectral change [3] (a) and visible representation of the color change (b)

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CRYSTALLIZATION AND CRYSTAL STRUCTURE OF LYSOZYME WITH NANOSIZED TITANIUM OXIDE

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Lysozymes are ancient and important components of the innate immune system of animals that hydrolyze peptidoglycan, the major bacterial cell wall polymers [1]. Lysozyme directs the formation of titanium nanoparticles under ambient conditions and is simultaneously entrapped while in the active bactericidal form. The ability to encapsulate an active antimicrobial protein within inorganic nanoparticles provides an opportunity to create bio-nanomaterials that resist bacterial activity, for use as broad-spectrum antifouling materials [2]. One of the approaches for the development of new antibacterial compounds focuses on the design and screening of compounds that interact with Lysozyme. We report on the interaction of Lysozyme with Titanium oxide (Figure 1a). The Titanium binds successfully with the enzyme and interacts within the complex. Single crystal of Lysozyme complex with Titanium were grown (Figure 1b) in the presence of TiO_2 . The initial crystallization conditions included 20 mg/ml Lysozyme in TiO_2

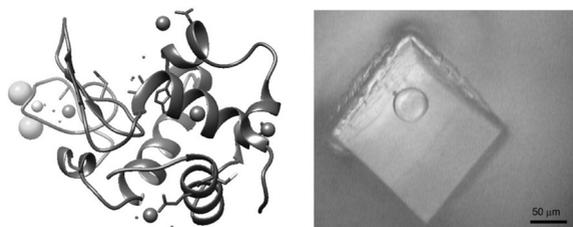


Fig. 1. a) Crystal structure of **6G5C** and b) Crystals after Laser ablation (LA-ICP-MS).

2.56 mg/ml (JRC NM-101), well/solution: Sodium chloride (NaCl), Sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) buffer (pH 5.0), 25% (v/v) Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$). The crystals were colorless and diffracted up to 1.8 Å resolution and the structure was solved by MR. The observation of structural and chemical adjustments was assessed by single crystal diffraction, LA-ICP-MAS and cyclic voltammetry.

Acknowledgements: The authors are grateful to the Bulgarian national Science fund grant T02/14 for the financial support.

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Keywords: lysozyme, titanium, XRD, LA-ICP-MAS.

SPECTROSCOPIC ANALYSIS OF SULPHURIC ACID TREATED BIODEGRADABLE WASTE

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This work is devoted to study the possibilities to minimize biodegradable waste generated by poultry farms by developing and offering new approaches to convert them into useful products through which a closed life cycle is implemented [1, 2].

That raises animal hygiene and environmental problems [3, 4]. In Bulgaria there are only few realized practices for use of poultry bio-waste as a secondary raw material or energy resource [4]. This problem has not found the best solution and globally yet.

The proposed new solution is constructed on the basis of biodegradable waste from poultry farms wastes and ash from paper industry. The aim is to do integrated recovery of several wastes. These spectroscopic analysis have attempted application of the solid phase poultry waste and identifying the phases in it, in order to obtain organic products for agriculture.

On the basis of developed compositions, treated with sulfuric acid in various ratios new products were obtained. So the results of this paper have shown the possibility to realize integrated recovery of several wastes.

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Keywords: biodegradable waste, IR, XRD, SEM.

SPECTROSCOPIC ANALYSIS OF SEWAGE SLUDGE AND FLY ASH FROM THE BIOMASS FOR LAND RECUITIVATION

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The purpose of this study is to investigate the possibilities for recultivation of soils contaminated with heavy metals from the mining industry in the Chelopech area and to suggest a suitable improver for contaminated soil from waste products with purpose for waste utilization and improving the soil structure and stoking with nutrients [1, 2].

This has led to the need to explore opportunities for ruthless recultivation as a technological approach to managing environmental rehabilitation. A number of studies such as chemical analysis, infrared spectroscopy, etc., are used to investigate the possibilities of various soil improvers and additives to intensify the formation of soil organic matter and soil humus [3].

The analyzes determine the sewage sludge from WWTPs and fly ash from biomass as suitable soil improvers for the restoration of disturbed terrains from copper mining due to Ca and Mg content which are important for the neutralization of soils and the presence of microelements such as B, Cu, Fe, Mo, Mn and Zn needed for vegetation development [3,4]. A conducted infrared spectroscopy proves a rich content of proteins, carbohydrates, lipids and their products in this improvers.

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Keywords: IR, soil, heavy metals, mining, recultivation.

PHYSICOCHEMICAL CHARACTERIZATION ON CLINICALLY RETRIEVED TRITANIUM ORTHODONTIC ARCHWIRES

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Different teeth benefit from different tooth moving forces. TriTanium has three distinct thermally activated force regions which place the correct force in the anterior, bicuspid, and posterior arch-regions to efficiently level, align and torque [1]. During treatment in the leveling phase of fixed appliance for teeth alignment in the frontal area light forces are required and for the lateral section – greater forces. This study aims to identify the chemical composition, structure and thermal behavior of clinically retrieved (up to 6 and 9 weeks) Tritanium (0.016 × 0.022 inches) archwires. The studies were made in the three regions of elasticity: anterior – encompasses the four incisions, middle – encompasses the canine tooth and the premolars and the posterior – the molars. To achieve the aim the following methods are used: XRD, EDX, SEM and DSC. The EDX analysis shows that Ni and Ti are the main elements in the composition of the examined archwires and the ratio of elements 1:1 is kept during treatment. The room temperature XRD patterns show typical peaks for a Ni-Ti alloy with austenite type structure. SEM micrographs show different morphology in the 3 zones of the investigated archwires. The DSC measurements were conducted in the –50 °C to +50 °C temperature range. The DSC analyses of the clinically retrieved Tritanium archwires revealed three phase transitions (austenite, martensite and R-phase) in the 3 zones. The results obtained within this study contribute to the establishment of some peculiarities related to the thermal behavior and the shape-memory effect of the investigated archwires.

Acknowledgements: This work was a part of a bilateral project between BAS and EAS Tallinn University of Technology (Estonian projects TAR16016 and IUT-T4).

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Keywords: Tritanium orthodontic archwires, XRD, SEM, DSC.

IR-SPECTRAL STUDIES OF VITREOUS AND CRYSTALLINE MATERIALS IN THE $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$ SYSTEM

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Two series of glasses with compositions $x\text{Bi}_2\text{O}_3 \cdot 70\text{B}_2\text{O}_3 \cdot (30-x)\text{Na}_2\text{O}$ ($x=5, 10, 15, 20$ and 25 mol%) and $x\text{Bi}_2\text{O}_3 \cdot 30\text{B}_2\text{O}_3 \cdot (70-x)\text{Na}_2\text{O}$ ($x = 10, 20, 30, 40, 50$ and 60 mol%) were prepared using a conventional melt quenching method. The structure of the vitreous and crystalline materials is studied by means of IR spectroscopy. The IR spectra are recorded in the $2000-400$ cm^{-1} range. The spectra of crystals are defined with large number and sharp absorption bands while the spectra of the glasses are with more defused character. The structural investigation showed the presence of BO_3 , BO_4 and BiO_6 groups in the glass structure. Weak chemical bonds, such as B-O-Bi and Bi-O-Bi between them were also confirmed by IR-spectroscopy.

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Keywords: IR spectra, bismuthate glasses, bismuthate crystals, structure.

CRYSTAL STRUCTURE OF A NEW STILBAZIOLIUM TOSYLATE WITH ENLARGE CONJUGATED SYSTEM

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Stylbazolium dyes are of interest in the field of organic non-linear optical (NLO) materials. A new stylbazolium salt 4-[(*E*)-2-(2-hydroxynaphthalen-1-yl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate hydrate (D13) having enlarged π -conjugated system was synthesized and characterized by single crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with $a = 13.635$ (2) Å, $b = 6.6532$ (8) Å, $c = 27.213$ (4) Å, $V = 2407.1$ Å³, and $Z = 4$ (at 300° K). The unit cell contains 4 molecules of the dye and 4 molecules of water, participating in H-bonds and weak intermolecular interactions (Fig. 1). In the crystal structure, the H-bonds are carried out between the phenolic OH group and the water molecule, and it in turn forms H-bonds with two tosylate anions.

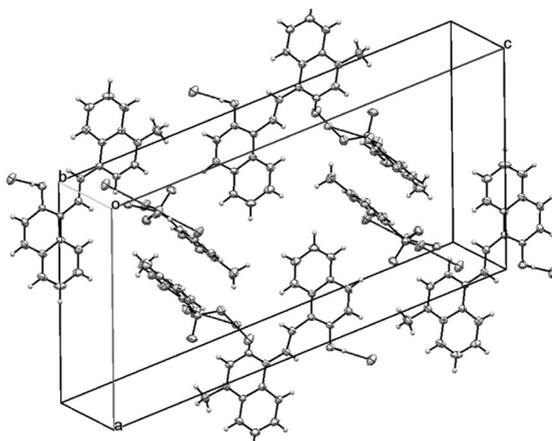


Fig. 1. Three-dimensional arrangement of the molecules in the crystals of the dye.

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Keywords: Crystal structure; Stylbazolium dye; Bond Lengths Alternation (BLA).

COMPARISON OF [Al]ZSM-5 AND [Ga]ZSM-5 ZEOLITES – SYNTHESIS AND CATALYTIC APPLICATIONS

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Zeolites are crystalline aluminosilicates, composed of TO_4 tetrahedra (T = Si, Al) with O atoms connecting neighboring tetrahedral, that contain pores and cavities of molecular dimensions. Many occur as natural minerals, but it is the synthetic varieties which are among the most widely used sorbents, catalysts and ion-exchange materials in the world. The isomorphous substitution of Si^{4+} or Al^{3+} by Ga^{3+} is interesting from practical point of view. Catalytic processes for fine chemical productions and oxidation reactions are amenable to the employment of tuned and novel zeolites. The phenomenon of isomorphous substitution is well-known in the field of mineralogy. By isomorphous substitution, framework atoms of crystalline compounds are replaced by atoms of other elements without changing the type of the crystal structure.

This study reported on the hydrothermal synthesis of AlZSM-5 and GaZSM-5 zeolite from systems containing tetrapropylammonium bromide as an organic structure determining agent. The crystallization conditions were optimized by varying the heating time for both systems. AlZSM-5 was obtained from a system $50SiO_2 : Al_2O_3 : 5.0Na_2O : 5.0TPABr : 2000H_2O$ after 72 hours at a crystallization temperature $170^\circ C$. Pure GaZSM-5 is obtained from an initial gel $30SiO_2 : Ga_2O_3 : 4.4Na_2O : 18TPABr : 1000H_2O$ after 114 hours and crystallization temperature $150^\circ C$. Post synthesis treatment is applied in order to increase the specific surface area and providing easy access to the active zeolite centers. Secondary pores in crystals were formed by etching at room temperature with solution of NH_4F and 0,25M HF acid, varying the time of treatment. All samples have been characterized by X-ray diffraction analysis, scanning electron microscopy (SEM), infrared spectroscopy (IR), solid-state nuclear magnetic resonance (NMR) spectroscopy and physical absorption-desorption of nitrogen.

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Keywords: zeolite synthesis, ZSM-5, Post-synthesis treatment, fluoride etching.

SOLID STATE STRUCTURE OF PARAMAGNETIC COMPLEXES OF HEMATOPORPHYRIN IX

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Solid state structure of a series paramagnetic Pt^{III}, Pd^{III}, Au^{II} and Cu^{II} complexes of hematoporphyrin IX (Hp) has been studied by EPR spectroscopy and magnetochemistry. The uncommon oxidation state +3 of platinum was additionally proved by X-ray photoemission spectroscopy. The mode of ligand coordination was investigated using IR and UV/Vis spectroscopy. The composition of the obtained stable compounds was found using thermal and microelemental C,H,N,M analysis. The metal ions in the complexes have distorted octahedral or square-planar (Cu^{II}) coordination formed by the binding of donor atoms from Hp and small ligands as Cl⁻, NH₃ and H₂O. The ligand Hp possesses several donor functional groups. The nitrogen donor atoms of the imino (>N) and aza (=N-) groups of the pyrrole rings, as well as the outside COO⁻ groups determine the nature and the size of three different coordination modes. The metal ions choose a different mode of coordination as a function of their nature and properties. Coordination through two N-atoms of adjacent pyrrole rings to the metal ions in cis-position leads to the formation of so called “sitting atop” (SAT) complexes. This mode of Hp coordination was observed at the complexes cis-Pt^{III}(NH₃)₂((N,N)Hp_{-3H})(H₂O)₂·H₂O (**Pt1**) and cis-[Pd^{III}₂((N,N)(O,O) Hp_{-3H})Cl₃(H₂O)₅].2PdCl₂ (**Pd1**). Metalloporphyrin-type complexes with coordination via the four pyrrole N-atoms in the porphyrin framework are typical of all metal ions studied, namely [Pt^{III}((N₄)Hp_{-3H})(H₂O)₂].H₂O (**Pt2**), [Pd^{III}((N₄)Hp_{-2H})Cl(H₂O)].H₂O (**Pd2**), [Au^{II}((N₄)Hp_{-2H})]·2H₂O (**Au1**) and [Cu^{II}((N₄)Hp_{-2H})]·2H₂O (**Cu1**). Coordination through the side chains deprotonated propionic COO⁻ groups, outside the porphyrin macrocycle is established in the complexes [Pt((O,O)Hp_{-2H})Cl(H₂O)₃] (**Pt3**) and **Pd1**. The latter compound has a dinuclear Pd^{III}-Hp-Pd^{III} structure with differently bounded Pd^{III} ions: one Pd^{III} is coordinated to the deprotonated COO⁻ groups and the second Pd^{III} – to two adjacent pyrrole N-atoms on the top of the porphyrin ring. The in-depth study of the biological behavior of various representative compounds from the series unambiguously highlights their advantages as non-classical metal based anticancer agents, stemming from their unique structure.

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Keywords: platinum(III), palladium(III), gold(II), copper(II), octahedral complexes, hematoporphyrin IX.

NEW CARBON MATERIALS WITH GRAPHITE MICROSTRUCTURE

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The object of this investigation is synthesis of porous carbon materials from different polymer waste materials. The carbon composites were synthesized by thermo-oxidation treatment with mineral acids at 200 °C and subsequent carbonization at 600 °C, was applied to produce porous carbon materials. Some samples were subjected to graphitization at 1500 °C. For other samples hydrolysis at 800 °C was used as additional procedure to increase the porosity. The structure and properties of obtained carbon materials were studied by SEM, XRD, Raman spectroscopy, BET, etc.

Results: New carbon materials with high mechanical strength were produced using precursors obtained after thermo-oxidation treatment of polymer precursors with mineral acids. The composition and properties of the modified pitches allow foam formation without using pressure and stabilization step.

The chemical composition of the initial mixture significantly affects the physicochemical properties of the obtained nanocarbon. Increasing oxygen content leads to formation of nanoporous carbons with large surface area and oxygen functionalities of basic nature.

The investigation of the relation between the properties of the precursor and the structure of the carbon composites indicate, that the precursor composition affects the synthesis procedure, and consequently, the final characteristics of the product.

Conclusions: The results show that porous carbons synthesized from polyethylene wax and phenolformaldehyde resin are characterized by high surface area and high mechanical strength, which imply their possible application as adsorbents, constructive materials, etc.

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Keywords: carbon composites; carbon foam; graphite; nanocarbon; polymer waste.

FRAMEWORK ELASTICITY OF THE Mn-ETS-4

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The framework elasticity of Mn-exchanged titanosilicate ETS-4 has been investigated by single crystalline X-ray diffraction. One and the same single crystal sample has been analyzed subsequently at 290 K, 150 K, and 290 K. Crystal structure data at 150 K reveal certain shrinkage of the titanosilicate framework without affecting its overall topology. Only partial relaxation of the structure was observed when the crystal was studied back at room temperature.

Acknowledgement: Part of the results in this work has been achieved in fulfillment of a project financed by the National Science Fund of Bulgaria under contract No. DNTS/Russia 02/8 from 15.06.2018.

THE DEGREE OF STRUCTURAL DISORDER IN APATITE FROM TOOTH ENAMEL

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Dental enamel is the most crystalline and mineralized hard tissue in the body, composed of carbonated hydroxylapatite with traces of organic compounds. The degree of disorder for biological apatite is determined generally by the Ca-deficiency and the amount of carbonate and hydroxyl ions incorporated in the structure of apatite. Raman and infrared micro-spectroscopy were applied to determine the presence of hydroxyl group, the type of carbonate substitution and the degree of atomic order on molecular structural level.

Spectra were collected along the profile, oriented perpendicular to the enamel-dentine junction and parallel to the apatite rods. Not only the relative amount of carbonate groups but the carbonate environment in different crystallographic sites were determined by the spectral features. The degree of structural disorder was evaluated through broadening of the Raman peak at 960 cm^{-1} ($\nu_1\text{ PO}_4$), changes of the intensity ratio of the peaks at 960 cm^{-1} ($\nu_1\text{ PO}_4$) and 1070 cm^{-1} ($\nu_1\text{ B-type CO}_3$) stretching modes, changes of the intensity ratio of the carbonate ($\nu_1\text{ B-type CO}_3$) and hydroxyl stretching peaks. The results obtained reveal that the degree of structural disorder of enamel increases in depth along the profile from the surface to the enamel–dentine junction. The degree of carbonate isomorphic substitution gradually increases in this direction, while the degree of hydroxylation decreases. A negative correlation between carbonate groups replacing phosphate groups in the structure and hydroxyl ion was established.

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Keywords: enamel, carbonated hydroxylapatite, Raman, Infrared micro-spectroscopy.

1, 3, 5-TRIAMINO-1, 3, 5-TRIDEOXY-CIS-INOSITOL-CHARACTERIZATION IN SOLID STATE AND IN SOLUTION

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The ligand 1,3,5-triamino-1,3,5-trideoxy-cis-inositol (*taci*) possesses six donor atoms and has tridentate nature. It is known with its remarkable versatility due to the two chair conformations providing different binding modes: (i) N, N,O-; (ii) N,O, O-, (iii) N,N, N- or (iv) O,O,O. These four binding modes are all restricted to facial coordination.

The present study is dedicated to the X-Ray and NMR characterization of the ligand- *taci* in solid state and solution as well as its coordination behavior is discussed on the basis of different Pt⁴⁺-complexes.

The compound 2,4,6-triaminiumcyclohexane-1,3,5-triol sulfate chloride crystallizes in trigonal space group P31c with 1/3 of the formula unit in the asymmetric unit of the structure, depicted on Fig.1. The ligand adopts a chair conformation with axial OH-groups and equatorial protonated amine groups. The complex with composition $Pt(taci)(taci-_{2H}(OH)(NHCO_2)_2].2H_2O$ crystallizes in orthorhombic space group Pnma with one half formula unit in the asymmetric unit of the structure (Fig. 1). There are two *taci*-molecules, coordinating the platinum center. The first one coordinates the platinum via three N-donor atoms from its three axial NH₂-groups. In the second *taci* molecule the two of the NH₂-groups are blocked with CO₂-molecules and the coordination mode in this case is via the asymmetric site of *taci*- with two O-donor atoms from the deprotonated axial OH-groups and one N-donor atom from the free equatorial NH₂-group, resulting in octahedral geometry around the metal atom.

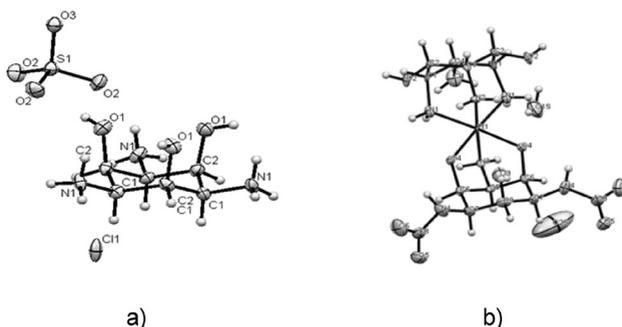


Fig. 1. Structure of a) $taci-_{3H}.SO_4.Cl.H_2O$ and b) $[Pt(taci)(taci-_{2H}(OH)(NHCO_2)_2].2H_2O$.

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Keywords: X-Ray, Pt(IV)-complexes.

X-RAY PHOTOELECTRON SPECTROSCOPY AND SCANNING ELECTRON MICROSCOPY INVESTIGATION OF STRONTIUM-SUBSTITUTED BARIUM TITANATE OBTAINED FROM OXIDE GLASSES

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Barium titanate and perovskite materials derived hereof, such as barium-strontium titanate are of great interest due to their potential applications as resistive sensors, capacitive elements, parts of opto-electronic systems, as well as of devices operating at microwave frequencies.

The present work reports on the synthesis of multi component oxide glasses with large concentrations of BaO, TiO₂, Fe₂O₃ and additions of up to 3 mol% SrO. The valence states of Sr, Ba and Ti in the glasses are determined by X-ray photoelectron spectroscopy (XPS) and correspond to those required for the precipitation of Ba_{1-x}Sr_xTiO₃. From the prepared glasses, after appropriate thermal treatment, strontium-substituted barium titanate crystallizes. The phase composition of the obtained glass-ceramics is studied by X-ray diffraction (XRD) and shows crystallization of solid solutions of cubic Ba_{1-x}Sr_xTiO₃. The microstructure of the prepared glass-ceramics is investigated by means of scanning electron microscopy (SEM) and reveals formation of bright droplet-like structures in a dark matrix which, according to the findings of XRD, can be attributed to the crystallization of strontium-substituted barium titanate in an amorphous glass matrix.

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Keywords: barium-strontium titanate, crystallization, XPS, SEM.

***IN SITU* IMMOBILIZATION OF TYROSINASE ONTO POLYMER THIN FILMS BY QUARTZ CRYSTAL MICROBALANCE TECHNIQUE**

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In this study tyrosinase (EC 1.14.18.1) was *in situ* covalently immobilized onto thin and ultrathin polymer films by quartz crystal microbalance technique (QCM). The optimal parameters of poly-(acrylonitrile-co-acrylamide) films were determined by surface plasmon resonance (SPR). By QCM technique was proved that the enzyme was effectively immobilized onto films for 4 hours. Atomic Force Microscopy (AFM) was used for visualization of enzyme attachment onto polymer surface.

Our previous experience and obtained results suggest optimization for biosensor construction. Obtained biosensors successfully can be used for hazardous materials determination.

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Keywords: tyrosinase immobilization, biosensors, hazardous materials determination, QCM.

STRUCTURAL AND LUMINESCENCE STUDIES OF CHROMIUM DOPED NANOSIZED $\text{Sc}_{2-x}\text{In}_x(\text{WO}_4)_3$ SOLID SOLUTIONS

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Chromium (III) doped nanosized $\text{Sc}_{2-x}\text{In}_x(\text{WO}_4)_3$, ($x=0\div 2$) solid solutions were prepared by co-precipitation/calcination method. The obtained powders were characterized using XRD, EPR, absorption and luminescence spectra. X-ray analysis showed that scandium rich solid solutions are with orthorhombic symmetry and indium rich with monoclinic symmetry. The calculated crystallites size ranged from about 20 nm to 110 nm, except for $\text{Sc}_2(\text{WO}_4)_3$ characterized by considerably larger sizes. EPR analysis proved presence of isolated Cr^{3+} ions in crystal field with rhombic symmetry. The absorption and luminescence spectra revealed presence of Cr^{3+} in sites with weak and strong crystal field, depending on doping concentration and composition of solid solutions. The influence of crystal symmetry on emission intensity was established. At room temperature, broadband emission is observed only, revealing a potential application of the considered class of compounds as host matrixes for tunable lasers application.

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Keywords: tungstate, chromium (III), EPR, luminescence.

STUDY OF THE CONFIGURATION OF AMINO BENZYL NAPHTHOLS BY NMR AND X-RAY SPECTROSCOPY

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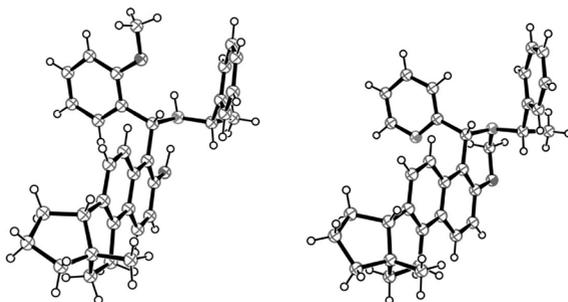
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The three component Betti-type condensation of aldehydes, 2-naphthols and chiral amines is an excellent tool for synthesis of chiral 1,3-aminonaphthols. By using of chiral amines, chiral nonracemic aminobenzyl naphthols could be synthesized with high diastereoselectivity. The structural diversity of the 1,3-aminonaphthols synthesized is realized by variation of the components. These compounds may possess more than one stereogenic center and are suitable building blocks for various asymmetric syntheses.

We are presenting here the synthesis of aminobenzyl naphthol derivatives through condensation between steroidal 2-naphthol analogue, (S)-(-)-1-phenylethylamine and aromatic aldehydes. The condensation reaction is stereoselective and the individual diastereoisomers have been isolated in pure form.

The configurations of the newly formed stereogenic centres were determined through application of advanced NMR experiments and was proved by X-ray crystallography.



Structures of new compounds synthesized through Betti-condensation determined by X-ray crystallography

Acknowledgements: This work was promoted by the Support Program of Young Scientists and Scholars of BAS (DFNP-149/2016); Bulgarian National Science Fund (DRNF-02/1/2009).

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Keywords: Betti condensation, aminobenzyl naphthol, NMR spectroscopy, X-ray crystallography.

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