

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

ORGANISING COMMITTEE

Chairpersons

Zara Cherkezova-Zheleva, IC – BAS

Peter Tzvetkov, IGIC – BAS

Members

Irena Mihaylova, UCTM, Sofia

Daniela Kovacheva, IGIC – BAS

Daniela Karashanova, IOMT – BAS

Boris Shivachev, IMC – BAS

Rositsa Nikolova, IMC – BAS

Thomas Kerestedjian, GI – BAS

Ivanina Sergeeva, GI – BAS

Ognyan Petrov, IMC – BAS

Yana Tzvetanova, IMC – BAS

Petar Georgiev, Sofia University

Vassil Delchev, Plovdiv University

Biliana Georgieva, IOMT – BAS

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

Morning session:

Chairpersons: Zara Cherkezova-Zheleva, Petar Tzvetkov

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 the 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**

Afternoon session:

Chairpersons: Boris Shivachev, Rositsa Nikolova

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**
Bas ter Mull, Malvern Panalytical – Sponsorship presentation

16:15–19:15 **Poster session 1** (All posters should be placed in the poster area, but only posters with odd numbers will be presented.)

19:15–21:15 **Cocktail**

Thursday 4 October 2018

Morning session:

Chairpersons: Galina Gencheva, Vanya Kurteva

- 9:30–10:00 **Computational studies of defect-containing perovskite crystals in relation to their proton conductivity (Plenary lecture)**
Tzonka Mineva, CNRS, Institut Charles Gerhardt Montpellier, France
- 10:00–10:45 **Crystal structures of some A^{II}B^{IV}VO₄ vanadates: crystal structure determination from powder diffraction and phase transitions**
Gwilherm Nénert, Malvern Panalytical B. V., The Netherlands
- 10:45–11:30 **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**

Afternoon session:

Chairpersons: Daniela Kovacheva, Petar Georgiev

- 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**
Predrag Vulic, ROFA Laboratory & Process Analyzers
- 16:15–19:15 **Poster session 2** (All posters should be placed in the poster area, but only posters with even numbers will be presented.)
- 19.15–22:00 **Conference dinner**

Friday 5 October 2018

Morning session:

Chairpersons: Daniela Karashanova, Thomas Kerestedjian

- 9:30–10:10 **Quantum rotation of dihydrogen ligands proton exchange dynamics in the prototypic hydrogen storage compound $\text{RuH}_2(\text{H}_2)_2(\text{PR}_3)_2$, $\text{R}=\text{Cp}$, Cy , tBu : DFT and Neutron Scattering Studies (Keynote lecture)**
Petar Georgiev, Faculty of Physics, Sofia University “St. Kliment Ohridski”
- 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**
- 11:15–11:55 **Structure and magnetic properties of ferromagnetic systems (Keynote lecture)**
Hristo Kolev, Institute of Catalysis, Bulgarian Academy of Sciences
- 12:00–12:30 **New carbon materials with graphite microstructure (Thematic lecture)**
Boyko Tsyntsarski, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences
- 12:35–13:10 **Challenges at characterization of particulate matter (Thematic lecture)**
Zara Cherkezova-Zheleva, Institute of Catalysis, Bulgarian Academy of Sciences
- 13:10–14:00 **Lunch break**

Afternoon session:

Chairpersons: Petar Tzvetkov, Zara Cherkezova-Zheleva

- 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 **Geopolymers: an overview. Suitable raw materials located in Bulgaria**
Alexander Nikolov, Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences
- 15:20–16:00 **Coffee break**
- 16.00–16.30 **Award for the best poster contribution**
- 16.30–17.30 **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. Cincić – 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. Shopska, 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. Dyulgerov, 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. V. 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. Ibrev, 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 Iglika 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. Atanasova-Vladimirova – 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 $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$
- P_45. G. Patronov, I. Kostova, D. Tonchev – Investigation of rare earth doped zinc borophosphate glasses
- P_46. T.M. Petrova, N.I. Velinov, I.B. Ivanov, T.T. Tabakova, V.D. Idakiev, I.G. Mitov – Structural characterization of $\text{Au/Cu}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ catalysts
- P_47. N. Rangelova, L. Aleksandrov – Synthesis, structure and properties of hybrids doped with copper ions in the silica-hydroxypropyl cellulose system
- 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
- P_54. T. Tasheva, V. Dimitrov – 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
- P_55. M. Todorova, R. Bakalska, S. Zareva, T. Kolev – Crystal structure of a new stilbazolium tosylate with enlarge conjugated system
- P_56. T. Todorova – Comparison of [Al]ZSM-5 and [Ga]ZSM-5 zeolites – synthesis and catalytic applications
- P_57. D. Tsekova, G. Gencheva – Solid state structure of paramagnetic complexes of hemato porphyrin IX
- P_58. L. Tsvetanova, R. Nikolova, V. Kostov-Kytin, S. Ferdov – Framework elasticity of the Mn-ETS-4
- P_59. D. Vasilev, R. Titorenkova – The degree of structural disorder in apatite from tooth enamel
- P_60. V. Velcheva, G. Gencheva – 1, 3, 5-triamino-1, 3, 5-trideoxy-cis-inositol- characterization in solid state and in solution
- P_61. L. Vladislavova, R. Harizanova, I. Avramova, G. Avdeev, C. Rüssel – X-ray photoelectron spectroscopy and scanning electron microscopy investigation of strontium-substituted barium titanate obtained from oxide glasses
- P_62. S. Yaneva, Tz. Velinov – In situ immobilization of tyrosinase onto polymer thin films by quartz crystal microbalance technique
- P_63. A. Yordanova, R. Iordanova, I. Koseva, P. Tzvetkov, R. Kukeva, V. Nikolov – Structural and luminescence studies of chromium doped nanosized $\text{Sc}_{2-x}\text{In}_x(\text{WO}_4)_3$ solid solutions
- P_64. I. Zagranjarska, K. Kostova, R. Nikolova, B. Shivachev, V. Dimitrov – Study of the configuration of aminobenzyl naphthols by NMR and X-ray spectroscopy
- P_65. L. Tsvetanova, R. Nikolova, K. Kosev, N. Petrova – Crystalline adducts of urea with MgI_2
- P_66. K. Sezanova, D. Kovacheva, D. Rabadjieva, R. Gergulova – Mg and Zn modified calcium phosphate fine powders examined by Rietveld refinement
- P_67. G. Issa, I. Genova, T. Tsoncheva, J. Henych, M. Dimitrov, V. Štengl, D. Kovacheva – Nanosized mesoporous titania promoted with tin and zirconium oxides as catalysts for total oxidation of ethyl acetate and methanol decomposition
- P_68. L. Slavov, M. Iliev, R. Ilieva, R. Angelova, Ch. Ghelev, I. Grigorov, G. Kolarov, L. Gurdev, Z. Cherkezova-Zheleva, V. Grurdeva, D. Stoyanov, I. Nedkov – Characterization of in-situ sampling particulate matter of air pollution localized by lidar monitoring

ABSTRACTS

CONTENTS

The Mars Science Laboratory Experience	21
<i>D. Bish</i>	
CALIPSOPLUS – overview and targeted research possibilities	22
<i>B. Seidlhofer, A. Vollmer, A. Anselmo, B. Schramm, M. Grobosch, M. Helm</i>	
Halogen bond – a rival to hydrogen bond as interaction of choice in crystal Engineering	23
<i>V. Stilinović*</i>	
Investigation and development of new types of hybrid nanocomposites based on polyolefins and Azerbaijan natural minerals	24
<i>N. T. Kakhrmanov, R. V. Kurbanova, N. S. Koseva</i>	
Disordered structures & the fear to publish them	25
<i>A. Ugrinov</i>	
Size-dependent emergence of crystallinity in molecular clusters	26
<i>A. Proykova</i>	
Imaging and spectroscopic microanalysis using synchrotron soft X-ray radiation	27
<i>G. Tzvetkov</i>	
Synthesis and nano/microstructure of metal oxides: selected examples	28
<i>M. Ristic, S. Music</i>	
Structural characterization of silver and gold nanoparticles synthesised by recycling of <i>Rosa Damascena</i> waste from oil industry in Bulgaria	29
<i>R. Angelov, B. Georgieva, A. Slavov, I. Vasileva, T. Dodevska, D. Karashanova</i>	
TEM analysis of gold nanoparticles attached on the surface of organoclay and obtained by two different methods	30
<i>V. Angelov, E. Ivanov, R. Kotsilkova</i>	
CALIPSOplus – an integrating activity for advanced communities in Horizon 2020	31
<i>A. Anselmo, A. Vollmer, B. Seidlhofer, B. Schramm, M. Grobosch, M. Helm</i>	
Evaluation of CA-4 benzoxazolone derivative 19Z's biological activity against tumor cell lines	32
<i>G. Atanasov, R. Rusev, O. Petrov, B. Shivachev, M. D. Apostolova</i>	
Pyroxene composition: Evidence from the Vitosha pluton, Western Srednogorie Bulgaria	33
<i>S. Atanasova-Vladimirova, I. Piroeva</i>	
Sol-gel synthesis and properties of Sm modified TiO ₂ nanopowders	34
<i>A. Bachvarova-Nedelcheva, St. Yordanov, I. Stambolova, R. Iordanova, V. Blaskov</i>	
Phenol removal using ANA-type zeolite synthesized from fly ash	35
<i>B. Barbov</i>	
Halogen bonding in the systems of benzoyl-4-pyridoylmethane and perhalogenated hydrocarbons	36
<i>N. Bedeković, V. Martinez, V. Stilinović, D. Cinčić</i>	

Crystal chemistry of mixed $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4 \cdot \text{H}_2\text{O}$ dittrmarites used as highly efficient precursors for synthesis of electrochemically active $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ phospho-olivines.....	37
<i>T. Boyadzhieva, V. Koleva, R. Stoyanova</i>	
Quantum Design PPMS-9T: cryostat system for electric, magnetic and thermal experiments at high magnetic fields and temperature range 2–400 K.....	38
<i>K. Buchkov, B. Blagoev</i>	
Development of MSWI bottom ash based geopolymer	39
<i>B. Chen, A. Keulen, G. Ye</i>	
Challenges at characterization of particulate matter	40
<i>Z. Cherkezova-Zheleva, D. Paneva, B. Kunev, H. Kolev, M. Shopaska, I. Nedkov</i>	
Green synthesis of iron oxide magnetic nanoparticles using different plant aqueous extracts and their photocatalytic properties.....	41
<i>Z. Cherkezova-Zheleva, D. Paneva, M. Tsvetkov, E. Encheva, K. Strehina, N. Mirchev, M. Shopaska, J. Krstić, V. Radonjić</i>	
Thermal decomposition of new phase obtained at transformation of zinc hydroxysalt minerals	42
<i>Z. Delcheva, Ts. Stanimirova, N. Petrova</i>	
Synthesis of chiral aminoalcohol – configuration determination and catalytic application	43
<i>K. Dikova, M. Tavlinova-Kirilova, K. Kostova, A. Chimov, R. Nikolova, B. Shivachev, V. Dimitrov</i>	
Deposition of nanosized ZrO_2 sol gel films using different stabilizing agents and study of the effect on the morphology and optical properties.....	44
<i>O. Dimitrov, I. Stambolova, S. Vassilev, T. Babeva</i>	
Synthesis, crystal growth and some characterization of mixed crystals $\text{M}'_2\text{Mg}_{(1-x)}\text{M}_x''(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}' = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$, $\text{M}'' = \text{Co}, \text{Ni}, \text{Zn}$).....	45
<i>T. Dimitrova, V. Cvetkova, P. Marinova, P. Marinova, V. Karadjova</i>	
Comparative study of monocationic forms obtained by ion exchange of purified clinoptilolite tuff.....	46
<i>L. Dimowa, N. Petrova, I. Piroeva</i>	
Conformational polymorphism in (3-acetamidophenyl)boronic acid.....	47
<i>V. M. Dyulgerov, L. T. Dimowa, R. Rusev, N. L. Petrova, R. P. Nikolova, B. L. Shivachev</i>	
The halogen bonding proclivity of the aldehyde group in cocrystals of 2-hydroxy-1-naphthaldehyde and perfluorohalogenobenzenes	48
<i>L. Fotović, V. Nemeč, V. Stilinović, D. Cinčić</i>	
Complex study of phase transformations in wear-resistant cast alloys.....	49
<i>R. Vi. Gavrilova, V. K. Lazarova</i>	
Complexes of “Platinum Blues” with creatine, creatinine and allantoin – formation of Pt^{III} species with electrochemical oxidation.....	50
<i>B. Georgieva, G. Gencheva</i>	
Experimental and modeling study of Co-deposition of Ni-Cu alloys at low current densities	51
<i>D. Goranova, R. Rashkov, H. Popova, V. Tonchev</i>	

Crystal and molecular structure, spectroscopic properties and <i>in vitro</i> antiproliferative effects of new Au ^{III} complexes with dipyrin-2-ylamine	52
<i>P. Gorolomova, B. Krebs, R. Nikolova, B. Shivachev, S. Simova, G. Momekov, G. Gencheva</i>	
Synthesis and characterization of willemite ceramic pigments in the system xCoO. (2-x)ZnO. SiO ₂	53
<i>Ts. Ibrevva, Ts. Dimitrov, R. Titorenkova, I. Markovska, E. Tacheva, O. Petrov</i>	
Catalytic oxidation of ethyl acetate by copper modified Ce-Mn and Ce-Ti mesoporous nanostructured oxides	54
<i>R. Ivanova, G. Issa, M. Dimitrov, J. Henych, M. Kormunda, D. Kovacheva, V. Štengl, T. Tsoncheva</i>	
Synthesis and X-ray crystallographic studies of ferrocenylmethylidene and arylidene substituted camphane based compounds	55
<i>M. Kamenova-Nacheva, I. Slavchev, V. Dimitrov, R. Nikolova, B. Shivachev, G. M. Dobrikov</i>	
Heterogeneous photocatalytic degradation of reactive Black 5 in aqueous suspension by La-modified ZnO powders	56
<i>N. Kaneva, A. Bojinova, K. Papazova, D. Dimitrov</i>	
Comparison of the properties of reduced graphene oxide obtained by different mild reducing agents.....	57
<i>D. Kichukova, D. Kovacheva, A. Staneva</i>	
Structure and magnetic properties of ferromagnetic systems	58
<i>H. Kolev</i>	
Rare Earth doped silicate glass-ceramics for LED application.....	59
<i>I. Koseva, P. Tzvetkov, P. Ivanov, A. Yordanova, V. Nikolov</i>	
Influence of gas mediums on the thermal decomposition of thaumasite from Igljika deposit, Bulgaria.....	60
<i>B. Kostova, V. Petkova, Y. Tzvetanova, E. Serafimova</i>	
XRD study on the structural evolution of Zn-exchanged titanosilicate ETS-4 during thermal treatment.....	61
<i>V. Kostov-Kytin, R. Nikolova, G. Avdeev</i>	
Powder X-ray diffraction microstructural analysis of synthetic apatite subjected to thermal treatment and high energy dry milling	62
<i>V. Kostov-Kytin</i>	
Polydentate ligands combining pirlindole and piperazine fragments.....	63
<i>V. Kurteva, B. Shivachev, R. Nikolova</i>	
A new phase obtained by oxidation of nanosized spinel MnFe ₂ O ₄	64
<i>Ts. Lazarova, D. Kovacheva</i>	
Mechanism of Sr ²⁺ uptake by clinoptilolite – kinetics and structural control	65
<i>N. Lihareva, L. Dimowa, O. Petrov, Y. Tzvetanova, S. Atanasova-Vladimirova</i>	
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	66
<i>D. Marinova, Tsv. Bancheva, M. Georgiev, D. Stoilova</i>	

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	67
<i>D. Marinova, V. Kostov-Kytin, R. Nikolova, R. Kukeva, E. Zhecheva, R. Stoyanova</i>	
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 blöditite type structure	68
<i>D. Marinova, M. Wildner, Tsv. Bancheva, M. Georgiev, D. Stoilova</i>	
TEM characterization of Mg_2NiH_4 based material prepared at low temperature	69
<i>P. Markov, E. Grigorova, D. Nihtianova</i>	
Akermanite based bioactive ceramics: physicochemical and in-vitro bioactivity characterization	70
<i>I. Mihailova, L. Radev</i>	
Thermoanalytical behavior of doped ZrW_2O_8 at elevated temperatures from 20 °C up to 800 °C	71
<i>N. Mirchev, M. Tsvetkov, G. Avdeev, K. Avramova, M. Gancheva</i>	
The influence of the modifying Eu(III) on the $\alpha \rightarrow \beta$ phase transition temperature of zirconium tungstate	72
<i>M. Nedyalkov, E. Encheva, M. Tsvetkov, M. Milanova</i>	
Crystal structures of some $\text{AB}^{\text{IV}}\text{VO}_4$ vanadates: crystal structure determination from powder diffraction and phase transitions	73
<i>G. Néner, P. O'Meara, T. Degen</i>	
Characterization of a novel acid-activated geopolymers based on fayalite slag from local copper industry	74
<i>A. Nikolov, R. Titorenkova, N. Velinov, Z. Delcheva, B. Chen</i>	
Synthesis of geopolymers using natural zeolite and sodium aluminate	75
<i>A. Nikolov, H. Nugteren, I. Rostovsky, Z. Delcheva</i>	
Preparation and antimicrobial properties of silver nanoparticles supported by natural zeolite clinoptilolite	76
<i>M. Panayotova, N. Mintcheva, O. Gemishev, G. Tyuliev, G. Gicheva, L. Djerahov</i>	
Investigation on crystallization and transformation processes in amorphous alloy $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$	77
<i>D. Paneva, Z. Cherkezova-Zheleva, V. Petkova, B. Kostova, H. Kolev, G. Avdeev, G. Stefanov</i>	
Investigation of rare earth doped zinc borophosphate glasses	78
<i>G. Patronov, I. Kostova, D. Tonchev</i>	
Structural characterization of $\text{Au}/\text{Cu}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ catalysts	79
<i>T.M. Petrova, N.I. Velinov, I.B. Ivanov, T.T. Tabakova, V.D. Idakiev, I.G. Mitov</i>	
Synthesis, structure and properties of hybrids doped with copper ions in the silica-hydroxypropyl cellulose system	80
<i>N. Rangelova, L. Aleksandrov</i>	
Synthesis and structure solution of novel quaternary ammonium salts of quinoline and 4,4'-bipyridine	81
<i>R.I. Rusev, V.B. Kurteva, L.T. Dimova, B.L. Shivachev</i>	

New phenylboronic acid azo dye – structure determination and sugar sensing properties	82
<i>R.I. Rusev, B.L. Shivachev</i>	
Crystallization and crystal structure of lysozyme with nanosized titanium oxide	83
<i>H.I. Shirkova-Dimitrova, V. Ganev, B.L. Shivachev</i>	
Spectroscopic analysis of sulphuric acid treated biodegradable waste	84
<i>E. Serafimova, V. Petkova</i>	
Spectroscopic analysis of sewage sludge and fly ash from the biomass for land recultivation	85
<i>V. Stefanova, E. Serafimova</i>	
Physicochemical characterization on clinically retrieved Tritanium orthodontic archwires.....	86
<i>A. Stoyanova-Ivanova, I. Ilievska, V. Petrova, M. Gueorgieva, V. Petrov, L. Andreeva, A. Zaleski, V. Mikli</i>	
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.....	87
<i>T. Tasheva, V. Dimitrov</i>	
Crystal structure of a new stilbazolium tosylate with enlarge conjugated system	88
<i>M. Todorova, R. Bakalska, S. Zareva, T. Kolev</i>	
Comparison of [Al]ZSM-5 and [Ga]ZSM-5 zeolites – synthesis and catalytic applications	89
<i>T. Todorova</i>	
Solid state structure of paramagnetic complexes of hematoporphyrin IX	90
<i>D. Tsekova, G. Gencheva</i>	
New carbon materials with graphite microstructure	91
<i>B. Tsyntsarski, M. Todorova, G. Georgiev, A. Bahova, N. Petrov, T. Budinova, B. Petrova, I. Stoycheva, U. Szeluga, S. Pusz, B. Kumaneck, B. Trzebicka</i>	
Framework elasticity of the Mn-ETS-4	92
<i>L. Tsvetanova, R. Nikolova, V. Kostov-Kytin, S. Ferdov</i>	
The degree of structural disorder in apatite from tooth enamel.....	93
<i>D. Vasilev, R. Titorenkova</i>	
1, 3, 5-triamino-1, 3, 5-trideoxy-cis-inositol- characterization in solid state and in solution.....	94
<i>V. Velcheva, G. Gencheva</i>	
X-ray photoelectron spectroscopy and scanning electron microscopy investigation of strontium-substituted barium titanate obtained from oxide glasses.....	95
<i>L. Vladislavova, R. Harizanova, I. Avramova, G. Avdeev, C. Rüssel</i>	
<i>In situ</i> immobilization of tyrosinase onto polymer thin films by quartz crystal microbalance technique.....	96
<i>S. Yaneva, Tz. Velinov</i>	
Structural and luminescence studies of chromium doped nanosized $\text{Sc}_{2-x}\text{In}_x(\text{WO}_4)_3$ solid solutions	97
<i>A. Yordanova, R. Iordanova, I. Koseva, P. Tzvetkov, R. Kukeva, V. Nikolov</i>	
Study of the configuration of aminobenzyl-naphthols by NMR and X-ray spectroscopy	98
<i>I. Zagranjarska, K. Kostova, R. Nikolova, B. Shivachev, V. Dimitrov</i>	
Crystalline adducts of urea with MgI_2	99
<i>L. Tsvetanova, R. Nikolova, K. Koseva, N. Petrova</i>	

Mg and Zn modified calcium phosphate fine powders examined by Rietveld refinement.....	100
<i>K. Sezanova, D. Kovacheva, D. Rabadjieva, R. Gergulova</i>	
Nanosized mesoporous titania promoted with tin and zirconium oxides as catalysts for total oxidation of ethyl acetate and methanol decomposition.....	101
<i>G. Issa, I. Genova, T. Tsoncheva, J. Henych, M. Dimitrov, V. Štengl, D. Kovacheva</i>	
Characterization of in-situ sampling particulate matter of air pollution localized by lidar monitoring.....	102
<i>L. Slavov, M. Iliev, R. Ilieva, R. Angelova, Ch. Ghelev, I. Grigorov, G. Kolarov, L. Gurdev, Z. Cherkezova-Zheleva, V. Grurdeva, D. Stoyanov, I. Nedkov</i>	

THE MARS SCIENCE LABORATORY EXPERIENCE

D. Bish

Department of Earth and Atmospheric Sciences, Indiana University, USA

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

B. Seidhofer^{1*}, A. Vollmer¹, A. Anselmo¹, B. Schramm², M. Grobosch², M. Helm²

¹ Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str.
15 12489 Berlin, Germany

² Helmholtz-Zentrum Dresden-Rossendorf e.V., Bautzner Landstrasse 400,
01328 Dresden, Germany

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.



* E-mail: beatrix-kamelia.seidhofer@helmholtz-berlin.de

Keywords: synchrotron radiation, transnational access, european commission.

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

V. Stilinović*

Department of Chemistry, Faculty of Science, University of Zagreb, Croatia

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]

[1] Stilinović, V., Horvat, G., Hrenar, T., Nemeč, V., Cinčić, D. (2017). *Chem. Eur. J.* 23, 5244–5257.

[2] Eraković, M., Nemeč, V., Lež, T., Porupski, I., Stilinović, V., Cinčić, D. (2018) *Cryst. Growth Des.* 18, 1182–1190.

[3] Zbačnik, M., Pajski, M., Stilinović, V., Vitković, M., Cinčić, D. (2017) *CrystEngComm.* 19, 5576–5582.

[4] Bedeković, N., Stilinović, V., Friščić, T., Cinčić, D. (2018) *New J. Chem.*, DOI: 10.1039/C8NJ01368C.

* E-mail: vstilinovic@chem.pmf.hr

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

N. T. Kakhramanov^{1,*}, R. V. Kurbanova¹, N. S. Koseva²

¹ *Institute of Polymer Materials, National Academy of Sciences of Azerbaijan,
124 Samed Vurgun Str., AZ 5004 Sumgait, Azerbaijan*

² *Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev Str, Bl. 103A,
1113 Sofia, Bulgaria*

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.

* E-mail: najaf1946@rambler.ru

Keywords: hybrid nanocomposites, natural mineral, composite structure.

DISORDERED STRUCTURES & THE FEAR TO PUBLISH THEM

A. Ugrinov

North Dakota State University, Fargo ND, USA

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.

* E-mail: Angel.Ugrinov@ndsu.edu

Keywords: single crystals, disordered structures.

SIZE-DEPENDENT EMERGENCE OF CRYSTALLINITY IN MOLECULAR CLUSTERS

A. Proykova

Sofia University, 5 James Bourchier Blvd., Sofia-1164, Bulgaria

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.

Acknowledgement: The author acknowledges a computational support from the project UNITE BG05M2OP001-1.001-0004/28.02.2018 (2018-2023) and the contract D-055-2018/20.06.2018 with the Research & Development & Innovation Consortium of the Sofia Tech Park for using the cluster NESTUM.

* E-mail: anap@phys.uni-sofia.bg

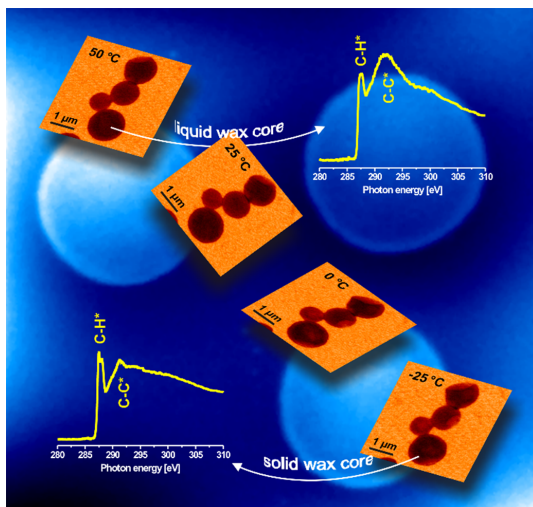
Keywords: phase transformation and phase coexistence in solid clusters, Molecular Dynamics, Monte Carlo, Density functional theory.

IMAGING AND SPECTROSCOPIC MICROANALYSIS USING SYNCHROTRON SOFT X-RAY RADIATION

G. Tzvetkov

Faculty of Chemistry and Pharmacy, University of Sofia, J. Bourchier 1, 1164 Sofia, Bulgaria

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.



* E-mail: george.tzvetkov@gmail.com

Keywords: STXM, NEXAFS, nanomaterials, microanalysis.

SYNTHESIS AND NANO/MICROSTRUCTURE OF METAL OXIDES: SELECTED EXAMPLES

M. Ristic*, S. Music

Rudjer Boskovic Institute, Bijenicka cesta 54, P.O. Box 180, 10002 Zagreb, Croatia

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.

Croatian Science Foundation, project No. IP-2016-06-8254, is gratefully acknowledged for funding support

- [1] M. Ristic, M. Marcijuš, Z. Petrovic, M. Ivanda, S. Music, *Croat. Chem. Acta* 87 (2014) 315.
- [2] Z. Petrovic, M. Ristic, M. Marcijus, M. Ivanda, S. Music, *Mat. Lett.*, 176 (2016) 278.
- [3] M. Ristic, M. Marcijus, Z. Petrovic, M. Ivanda, S. Music, *Mater. Lett.*, 156 (2015) 142.
- [4] M. Ristic, M. Marcijus, Ž. Petrovic, S. Music, *Ceram. Int.*, 40 (2014) 10119.
- [5] M. Ristic, E. Kuzmann, Z. Homonnay, S. Musić, J. Alloys, Comp., 767 (2018) 504.
- [6] M. Ristic, A. Kremenovic, M. Reissner, Ž. Petrovic, S. Music, manuscript in preparation.

* E-mail: ristic@irb.hr

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

R. Angelov¹, B. Georgieva¹, A. Slavov², I. Vasileva², T. Dodevska², D. Karashanova^{1,*}

¹ *Institute of Optical Materials and Technologies “Acad. J. Malinowski”, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria*

² *Department of Organic Chemistry and Inorganic Chemistry, Technological Faculty, University of Food Technologies, 26 Maritza Blvd., Plovdiv 4002, Bulgaria*

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”.

[1] Agro statistics, Ministry of Agriculture, Food and Forestry, December 2016, 315.

[2] A. Slavov et al., J. Ind. Crops Prod. 100 (2017a) 85–94.

* E-mail: dkarashanova@yahoo.com

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

V. Angelov*, E. Ivanov, R. Kotsilkova

*Open Laboratory for Experimental Mechanics of Micro and Nanomaterials (OLEM),
Institute of Mechanics, Bulgarian Academy of Sciences,
Acad. G. Bonchev St., bl.4, 1113 Sofia, Bulgaria*

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.

* E-mail: v.angelov@imbm.bas.bg

Keywords: organoclay, gold nanoparticles.

CALIPSOplus – AN INTEGRATING ACTIVITY FOR ADVANCED COMMUNITIES IN HORIZON 2020

A. Anselmo^{1,*}, A. Vollmer¹, B. Seidlhofer¹, B. Schramm², M. Grobosch², M. Helm²

¹ Helmholtz-Zentrum Berlin für Materialien und Energie GmbH,
Albert-Einstein-Str. 15, 12489 Berlin, Germany

² Helmholtz-Zentrum Dresden-Rossendorf e.V., Bautzner Landstr. 400,
01328 Dresden, Germany

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/>

* E-mail: ana.anselmo@helmholtz-berlin.de

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

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

G. Atanasov^{1,*}, R. Rusev², O. Petrov³, B. Shivachev², M. D. Apostolova¹

¹ *Institute of Molecular Biology "Roumen Tsanev", Sofia, Bulgaria*

² *Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Sofia, Bulgaria*

³ *Faculty of Chemistry and Pharmacy – Sofia University "St. Kliment Ohridski",
Sofia, Bulgaria*

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].

[1] Gerova M. S. et al., Combretastatin A-4 analogues with benzoxazolone scaffold: Synthesis, structure and biological activity, *Eur. J. Med. Chem* (2016) 120, 121–133.

* E-mail: atanasovg@bio21.bas.bg

Keywords: combretastatin A-4, benzoxazolone, cytotoxicity.

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

S. Atanasova-Vladimirova*, I. Piroeva

*Institute of Physical Chemistry "Rostislav Kaischew", Bulgarian Academy of Sciences,
Akad. G. Bonchev Str., bl. 11, Sofia 1113, Bulgaria*

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.

Acknowledgement: 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.

[1] M. Morimoto, *Mineralogical Magazine*, 52, (1988) 535–550.

[2] K.D. Putirka, *Reviews in Mineralogy*, 69 (2008) 61–120.

* E-mail: statanasova@ipc.bas.bg

Keywords: clinopyroxene, diopsite, augite, Vitoshka pluton.

SOL-GEL SYNTHESIS AND PROPERTIES OF Sm MODIFIED TiO₂ NANOPOWDERS

A. Bachvarova-Nedelcheva^{1,*}, St. Yordanov², I. Stambolova¹,
R. Iordanova¹, V. Blaskov¹

¹ *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
“Acad. G. Bonchev” str., bld. 11, 1113 Sofia, Bulgaria*

² *Institute of Metal Science, equipment, and technologies “Acad. A. Balevski” with Center
for Hydro- and Aerodynamics at the Bulgarian Academy of Sciences,
67 “Shipchenski prohod” str., 1574 Sofia, Bulgaria*

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.

Acknowledgements: The authors are grateful to the financial support of Bulgarian National Science Fund at the Ministry of Education and Science, Contract No DN07/2 14.12.2016.

* E-mail: albenadb@svr.igic.bas.bg

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

PHENOL REMOVAL USING ANA-TYPE ZEOLITE SYNTESIZED FROM FLY ASH

B. Barbov*

*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev St., bl. 107, 1113 Sofia, Bulgaria*

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.

Acknowledgements: The author acknowledge financial support by the “Program for career development of young scientists, Bulgarian Academy of Sciences’2017” (Contract No. DFNP 17-7/24.07.2017).

* E-mail: barbov@imc.bas.bg

Keywords: synthesis, zeolites, fly ash, phenol.

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

N. Bedeković*, V. Martinez, V. Stilinović, D. Cinčić

*Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a,
10 000 Zagreb, Croatia*

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.

[1] G. R. Desiraju., P. Shing Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure and Applied Chemistry*, **85** (2013), 1711–1713.

[2] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, **116** (2016), 2478–2601

[3] J. J. Brown, A. J. Brock, M. C. Pfrunder, J. P. Sarju, A. Z. Perry, A. C. Whitwood, D. W. Bruce, J. C. McMurtrie and J. K. Clegg *Aust. J. Chem.*, **70** (2017), 594–600.

* E-mail: nbedekovic@chem.pmf.hr

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

T. Boyadzhieva*, V. Koleva, R. Stoyanova

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bldg. 11, Sofia 1113, Bulgaria*

Dittmarite-type compounds, $\text{NH}_4\text{MPO}_4\cdot\text{H}_2\text{O}$ ($\text{M}^{2+} = \text{Mn, Fe, Co, Ni}$), 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.

Acknowledgments: The authors are grateful to the financial support from the National Science Fund of Bulgaria (Project DN09/13).

* E-mail: tanya_jb@svr.igic.bas.bg

Keywords: Solid solutions; *Cation substitution*; Dittmarites; Phospho-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

K. Buchkov*, B. Blagoev

*Georgy Nadjakov, Institute of Solid State Physics, Bulgarian Academy of Sciences,
72 TzarigradskoChaussee Blvd., 1784 Sofia, Bulgaria*

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.

* E-mail: buchkov@issp.bas.bg

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

DEVELOPMENT OF MSWI BOTTOM ASH BASED GEOPOLYMER

B. Chen^{1,*}, A. Keulen², G. Ye¹

¹ *Microlab, Section Materials and Environment, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands*

² *Mineralz (part of Renewi), Eindhoven, The Netherlands*

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.

Acknowledgement: The presentation of this study is supported by the National Science Fund of Bulgaria under contract No. DM17/3 from 12.12.2017.

* E-mail: B.Chen-4@tudelft.nl

Keywords: MSWI bottom ash, geopolymer, metallic Al.

CHALLENGES AT CHARACTERIZATION OF PARTICULATE MATTER

Z. Cherkezova-Zheleva^{1,*}, D. Paneva¹, B. Kunev¹, H. Kolev¹,
M. Shopska¹, I. Nedkov²

¹ *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bld.11,
1113 Sofia, Bulgaria*

² *Acad. Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences,
Tzarigradsko chaussee Blvd., 1784 Sofia, Bulgaria*

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.

Acknowledgments: Authors gratefully acknowledge the financial support of the Bulgarian National Science Fund - Project DN 18/16/ 2017.

* E-mail: zzhel@ic.bas.bg

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

Z. Cherkezova-Zheleva^{1,*}, D. Paneva¹, M. Tsvetkov², E. Encheva¹, K. Strehina¹, N. Mirchev³, M. Shopska¹, J. Krstić⁴, V. Radonjić⁴

¹ *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bld.11, 1113 Sofia, Bulgaria*

² *University of Sofia, Faculty of Chemistry, 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria*

³ *Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bld.11, 1113 Sofia, Bulgaria*

⁴ *University of Belgrade, Institute of Chemistry, Technology & Metallurgy, Department of Catalysis & Chemical Engineering, 12 Njegoseva, 11000 Belgrade, Serbia*

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.

Acknowledgements: Authors gratefully acknowledge the financial support of the Bulgarian National Science Fund – Project DN 18/16/ 2017 and to the Ministry of Education, Science, and Technological Development (Project III 45001).

* E-mail: zzhel@ic.bas.bg

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

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

Z. Delcheva^{1,*}, Ts. Stanimirova², N. Petrova¹

¹ *Institute of Mineralogy and Crystallography - Bulgarian Academy of Sciences,
107 Acad. G. Bonchev Str., Sofia, Bulgaria*

² *Faculty of Geology and Geography, Department of Mineralogy, Petrology and Economic Geology,
University of Sofia "St. Kliment Ohridski", 15 Tzar Osvoboditel Blvd., 1000 Sofia, Bulgaria*

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.

* E-mail: zlatka.delcheva.1989@gmail.com

SYNTHESIS OF CHIRAL AMINOALCOHOL – CONFIGURATION DETERMINATION AND CATALYTIC APPLICATION

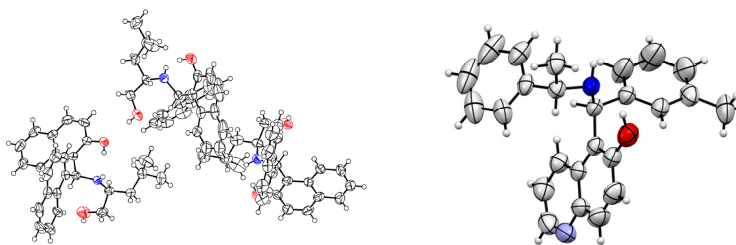
K. Dikova^{1,*}, M. Tavlinova-Kirilova¹, K. Kostova¹, A. Chimov¹, R. Nikolova²,
B. Shivachev², V. Dimitrov¹

¹ *Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev 9, Sofia 1113, Bulgaria*

² *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev 107, Sofia 1113, Bulgaria*

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

Acknowledgements: Bulgarian National Science Fund (Projects UNA-17/2005, DRNF-02/1/2009).

* E-mail: petkova@orgchm.bas.bg

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

O. Dimitrov^{1,*}, I. Stambolova², S. Vassilev¹, T. Babeva³

¹ *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad G. Bonchev St, bl 10, Sofia 1113, Bulgaria*

² *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad G. Bonchev St, bl 11, Sofia 1113, Bulgaria*

³ *Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad G. Bonchev St, bl 109, Sofia 1113, Bulgaria*

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.

* E-mail: ognian.dimitrov@iees.bas.bg

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

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

T. Dimitrova*, V. Cvetkova, P. Marinova, P. Marinova, V. Karadjova

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

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.

* E-mail: e-mail: vkar@mail.bg

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

L. Dimova^{1,*}, N. Petrova¹, I. Piroeva²

¹ *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Bl. 107 Acad. G. Bonchev Str., Sofia, Bulgaria*

² *Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. Georgi Bonchev Str., Bl. 11, Sofia, Bulgaria*

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.

[1] L. T. Dimova et al., *Clay Minerals*. 50 (2015) 41.

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

* E-mail: louiza.dimova@gmail.com

Keywords: ion exchange, structural refinement, clinoptilolite.

CONFORMATIONAL POLYMORPHISM IN (3-ACETAMIDOPHENYL) BORONIC ACID

V. M. Dyulgerov*, L. T. Dimowa, R. Rusew, N. L. Petrova,
R. P. Nikolova, B. L. Shivachev

Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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

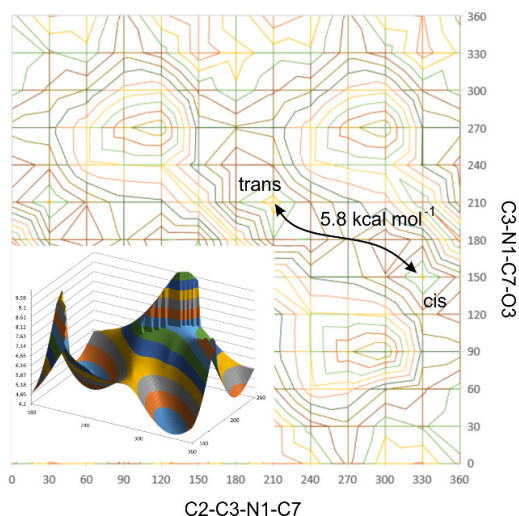


Fig. 1. Potential energy surface showing the barrier between *trans*/*cis* conformers.

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.

* E-mail: silver_84@mail.bg

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

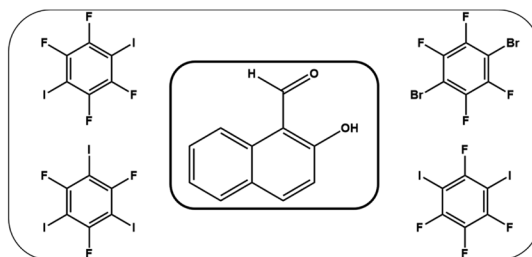
THE HALOGEN BONDING PROCLIVITY OF THE ALDEHYDE GROUP IN COCRYSTALS OF 2-HYDROXY-1-NAPHTHALDEHYDE AND PERFLUOROHALOGENOBENZENES

L. Fotović*, V. Nemeč, V. Stilić, D. Cinčić

*Department of Chemistry, Faculty of Science, University of Zagreb,
Horvatovac 102a, 10000 Zagreb, Croatia*

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.

* E-mail: lfotovic@stud.biol.pmf.hr

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

COMPLEX STUDY OF PHASE TRANSFORMATIONS IN WEAR-RESISTANT CAST ALLOYS

R. VI. Gavrilova, V. K. Lazarova*

*University of Chemical Technology and Metallurgy – Sofia, Faculty of Metallurgy
and Material Science 1756 Sofia, blvd. Kl. Ochridski 8, Bulgaria*

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.

* E-mail: r.gavrilova@abv.bg

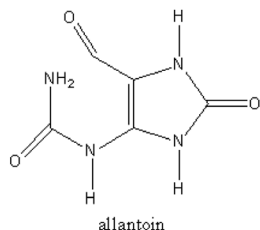
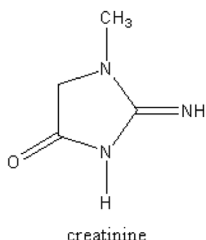
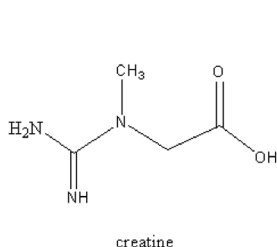
Keywords: wear-resistant cast alloys, heat treatment, structure transformations.

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

B. Georgieva*, G. Gencheva

Sofia University, Faculty of Chemistry and Pharmacy 1164 Sofia, 1 J. Bourchier Blvd, Bulgaria

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.

* E-mail: bisanora7@abv.bg

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

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

D. Goranova^{1,*}, R. Rashkov¹, H. Popova¹, V. Tonchev²

¹ *Institute of Physical Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Acad. G. Bonchev Str., bl. 11, Bulgaria*

² *Faculty of Physics, Sofia University, 1164 Sofia, 5 James Bourchier Blvd., Bulgaria*

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.

[1] D. Goranova, G. Avdeev, R. Rashkov, Surf. Coat. Technol. 240 (2014) 204–210.

* E-mail: desislavagoranova@gmail.com

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

P. Gorolomova^{1,*}, B. Krebs², R. Nikolova, B. Shivachev³, S. Simova⁴,
G. Momekov⁵, G. Gencheva¹

¹ Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski", 1164 Sofia,
1 J. Bourchier Blvd., Bulgaria

² Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, Germany

³ Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences,
Acad. G. Bonchev str., bl. 107, 1113 Sofia, Bulgaria

⁴ Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria

⁵ Faculty of Pharmacy, Medical University-Sofia 2 Dunav Str., 1000 Sofia, Bulgaria

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.

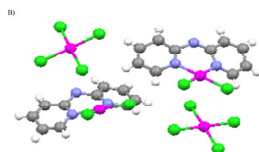


Fig. 1. Crystal structures of Au^{III} – complexes of dpa:
A) *Au1a* and B) *Au1b*.

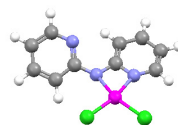


Fig. 2. Molecular structure of *Au2*, optimized at RB3LYP DFT functional.

* E-mail: poli_j_g@abv.bg

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

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

Ts. Ibrevva^{1,*}, Ts. Dimitrov², R. Titorenkova³, I. Markovska¹, E. Tacheva³, O. Petrov³

¹ "Assen Zlatarov" University, Department of Silicate Technology, Prof. Yakimov Str. 1,
8010 Bourgas, Bulgaria

² University "Angel Kanchev" Ruse, Branch Razgrad, bul. "Aprilsko Vastanie" 47, p.b. 110,
7200 Razgrad, Bulgaria

³ Institute of Mineralogy and Crystallography "Acad. I. Kostov", Bulgarian Academy of Sciences,
Acad. G. Bontchev Str., Bl. 107, Sofia 1113, Bulgaria

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 determined 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.

* E-mails: rosititorenkova@dir.bg; cvetila@abv.bg

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

R. Ivanova^{1,*}, G. Issa¹, M. Dimitrov¹, J. Henych², M. Kormunda³,
D. Kovacheva⁴, V. Štengl², T. Tsoncheva¹

¹ *Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Bulgaria*

² *Institute of Inorganic Chemistry of the Czech Academy of Sciences, 25068 Řež, Czech Republic*

³ *Faculty of Sciences, University of Jan Evangelista Purkyně, Ceske Mladeze 8,
400 96 Usti nad Labem, Czech Republic*

⁴ *Institute of General and Inorganic Chemistry, BAS, Sofia, Bulgaria*

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.

[1] G. R. Rao, et al., Bull. Catal. Soc. India, 2 (2003) 122.

* E-mail: radostinaiv@abv.bg

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

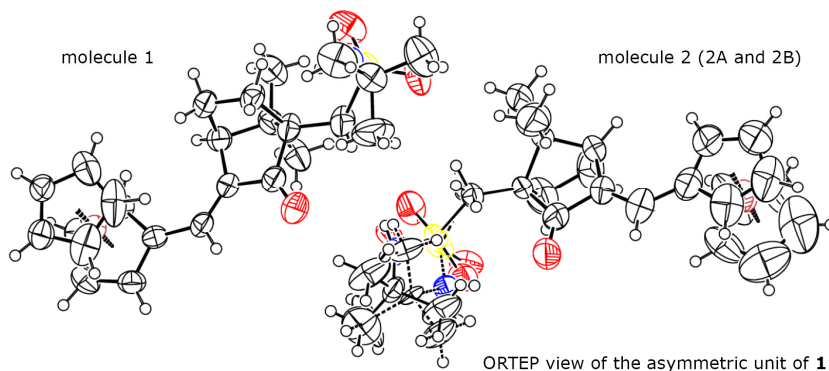
SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STUDIES OF FERROCENYLMETHYLIDENE AND ARYLIDENE SUBSTITUTED CAMPHANE BASED COMPOUNDS

M. Kamenova-Nacheva^{1,*}, I. Slavchev¹, V. Dimitrov¹, R. Nikolova²,
B. Shivachev², G. M. Dobrikov¹

¹ Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,
bl. 9, Acad. G. Bonchev Str., Sofia 1113, Bulgaria

² Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences,
bl. 107, Acad. G. Bonchev str., Sofia 1113, Bulgaria

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.

[1] N. L. Reddy et al., *Bioorg. Med. Chem. Lett.* 14 (2004) 5645–5649.

[2] M. Kamenova-Nacheva et al., *New J. Chem.* 41 (2017) 9103–9112.

* E-mail: anmari@orgchm.bas.bg

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

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

N. Kaneva*, A. Bojinova, K. Papazova, D. Dimitrov

*Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry,
Faculty of Chemistry and Pharmacy, University of Sofia, Sofia 1164, Bulgaria*

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”.

* E-mail: nina_k@abv.bg

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

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

D. Kichukova^{1,*}, D. Kovacheva¹, A. Staneva²

¹ *Institute of General and Inorganic Chemistry – Bulgarian Academy of Sciences,
1113 Sofia, Acad. Georgi Bonchev Blvd. bl.11, Bulgaria*

² *University of Chemical Technology and Metallurgy, 1756 Sofia,
8 Kliment Ohridski, Blvd., Bulgaria*

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.

* E-mail: diana123georgieva@gmail.com

Keywords: reduced graphene oxide, mild reducing agents.

STRUCTURE AND MAGNETIC PROPERTIES OF FERROMAGNETIC SYSTEMS

H. Kolev

*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St.,
Bldg. 11, Sofia 1113, Bulgaria*

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 $\text{Cu}(001)$ 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.

[1] Dittschar et al., J. Magn. Magn. Mat. **212**, (2000) 307.

[2] Hyungdon Kang., (2000), PhD thesis, Universität Bayreuth.

* E-mail: hgkolev@ic.bas.bg

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

RARE EARTH DOPED SILICATE GLASS-CERAMICS FOR LED APPLICATION

I. Koseva¹, P. Tzvetkov¹, P. Ivanov², A. Yordanova¹, V. Nikolov¹

¹ *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria*

² *Institute of Optical Materials and Technology, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria*

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

B. Kostova^{1,*}, V. Petkova^{1,2}, Y. Tzvetanova², E. Serafimova³

¹ *New Bulgarian University, Department of Nature Sciences, 21 Montevideo str., 1618 Sofia, Bulgaria*

² *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria*

³ *University of Chemical Technology and Metallurgy, 8, Kliment Ohridski, Blvd., 1756 Sofia, Bulgaria*

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.

[1] I. Kostov et al. The minerals of Bulgaria. Sofia (1964) 243.

[2] V. Ivanova-Panayotova, M. Kanazirski. *Geochem., Mineral. and Petrol.* 30 (1995) 79–90.

[3] H. Hiritsch, K. Klima. *Mitt. Naturwiss. Ver. Steiermark.* 118 (1988) 89–94.

[4] G. N. Kirov, *Mineral. Mag.* 36, 283 (1698) 1003–1011.

* E-mail: bkostova@nbu.bg

Keywords: thaumasite, thermal decomposition, thermal analysis.

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

V. Kostov-Kytin^{1,*}, R. Nikolova¹, G. Avdeev²

¹ *Bulgarian Academy of Sciences, Institute of Mineralogy and Crystallography "Acad. Ivan Kostov",
1113 Sofia, Acad. Georgi Bonchev Str., Bl. 107, Bulgaria*

² *Bulgarian Academy of Sciences, Institute of Physical Chemistry "Rostislav Kaischew",
1113 Sofia, Akad. G. Bonchev Str., bl. 11, Bulgaria*

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.

[1] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS). Report LAUR 86-748, Los Alamos National Laboratory, (2000).

[2] B.H. Toby, J. Appl. Crystallogr. 34 (2001) 210–213.

* E-mail: vkytin@abv.bg

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

V. Kostov-Kytin*

Bulgarian Academy of Sciences, Institute of Mineralogy and Crystallography, 1113 Sofia, Acad. Georgi Bonchev Str., Bl. 107, Bulgaria

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.

[1] J.R. Carvajal, Physica B, 192, 55, (1993).

* E-mail: vkytin@abv.bg

Keywords: apatite, Rietveld refinement, microstructural analysis.

POLYDENTATE LIGANDS COMBINING PIRLINDOLE AND PIPERAZINE FRAGMENTS

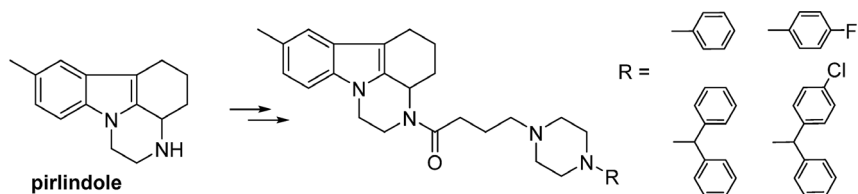
V. Kurteva^{1,*}, B. Shivachev², R. Nikolova²

¹ Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev street, bl. 9, 1113 Sofia, Bulgaria

² Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences, Acad. G. Bonchev street, bl. 107, 1113 Sofia, Bulgaria

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.

[1] a) P.A. Martorana et al., in *Psychiatry the State of the Art*, Vol. 8 (P. Pichot, P. Berner, R. Wolf, K. Thau, Eds.), Plenum Press: New York, 1985, pp. 195–198; b) R.Ulferts et al., *Antimicrob. Agents Chemother.* 60 (2016) 2627.

[2] a) R.V. Patel, S.W. Park, *Mini Rev. Med. Chem.* 13 (2013) 1579; b) A.K. Rathi et al., *Expert Opin. Ther. Pat.* 26 (2016) 777; c) S. Verma, S. Kumar, *Med. Chem. (Los Angeles)* 7 (2017) 750.

* E-mail: vkurteva@orgchm.bas.bg

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

A NEW PHASE OBTAINED BY OXIDATION OF NANOSIZED SPINEL MnFe_2O_4

Ts. Lazarova*, D. Kovacheva

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev str., Bl 11, Sofia 1113, Bulgaria*

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 MnFe_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, $\text{Co}_{8.5}\text{As}_3\text{O}_{16}$ (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).

Acknowledgements: The authors are thankful for the financial support by the National Science Fund of Bulgaria under the contract DN08/4/2016.

* E-mail: cveti_ura@abv.bg

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

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

N. Lihareva^{1,*}, L. Dimowa¹, O. Petrov¹, Y. Tzvetanova¹, S. Atanasova-Vladimirova²

¹ *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 107, 1113 Sofia, Bulgaria*

² *Institute of Physical Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria*

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).

* E-mail: nlihareva@abv.bg

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

D. Marinova¹, Tsv. Bancheva^{2,*}, M. Georgiev², D. Stoilova¹

¹ *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

² *Department of Inorganic Chemistry, UCTM, 1756 Sofia, Bulgaria*

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 $\text{Na}_2\text{Mn}(\text{SO}_4)_2$.

* E-mail: cvetelinabancheva@abv.bg

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

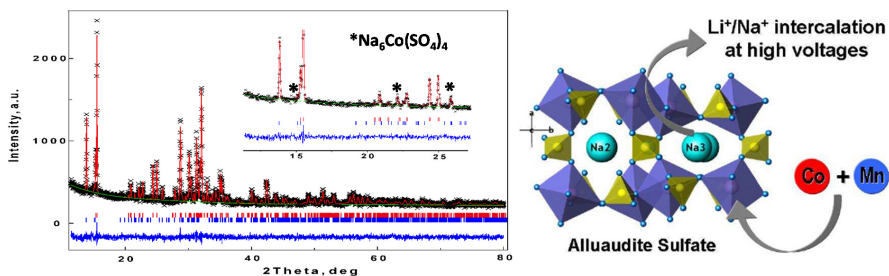
CRYSTAL STRUCTURE AND REDOX PROPERTIES OF ALLUAUDITE $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$ AS HIGH-VOLTAGE ELECTRODES FOR RECHARGEABLE BATTERIES

D. Marinova^{1,*}, V. Kostov-Kytin², R. Nikolova², R. Kukeva¹, E. Zhecheva¹, R. Stoyanova¹

¹ *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

² *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

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 $\text{Na}_6\text{Co}(\text{SO}_4)_4$ (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.

* E-mail: d.manasieva@gmail.com

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

D. Marinova¹, M. Wildner², Tsv. Bancheva³, M. Georgieva^{3,*}, D. Stoilova¹

¹ *Institute of General and Inorganic Chemistry, BAS, 1113 Sofia, Bulgaria*

² *Institut für Mineralogie und Kristallographie, Universität Wien, A-1090 Wien, Austria*

³ *Department of Inorganic Chemistry, UCTM, 1756 Sofia, Bulgaria*

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.

* E-mail: uctm.lector@uctm.edu

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 Mg_2NiH_4 BASED MATERIAL PREPARED AT LOW TEMPERATURE

P. Markov^{1,*}, E. Grigorova¹, D. Nihtianova^{1,2}

¹ *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria*

² *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria*

Mg_2Ni 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 Mg_2NiH_4 at milder temperature and for shorter period of time. A mixture of MgH_2 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 MgH_2 :Ni does not indicate a presence of MgO. The MgH_2 contents some traces of Mg and the main phase is tetragonal MgH_2 . The detected phases in ball milled sample are MgH_2 , 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 MgH_2 and monoclinic Mg_2NiH_4 , 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 Mg_2NiH_4 , orthorhombic Mg_2NiH_4 , tetragonal MgH_2 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 MgH_2 :Ni indicated average particles size of 7 nm. The formation at such low temperature of mainly monoclinic phase, but also some orthorhombic Mg_2NiH_4 during cycling has great effect on hydrogen sorption properties of magnesium. The most of the methods of Mg_2NiH_4 synthesis published in the literature are done at higher temperatures and more complicated procedures.

[1] M. Polanski et al., Int. J. Hydrogen Energy 38 (2013) 4003.

* E-mail: pvlmarkov@svr.igic.bas.bg

Keywords: TEM analysis; structure Mg_2NiH_4 ; hydrogen storage.

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

I. Mihailova*, L. Radev

*University of Chemical Technology and Metallurgy, 8 "St. Kliment Ohridski" Blvd.,
Sofia 1756, Bulgaria*

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 °C for 2 hours and then at 1000, 1100, 1300 °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 °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 °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).

* E-mail: irena@uctm.edu

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

N. Mirchev², M. Tsvetkov¹, G. Avdeev^{2,*}, K. Avramova², M. Gancheva³

¹ Sofia University "St. Kliment Ohridski", Department of Inorganic Chemistry, Bulgaria

² Institute of Physical Chemistry, "Rostislav Kaishev", Bulgarian Academy of Sciences, Bulgaria

³ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Bulgaria

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.

* E-mail: g_avdeev@abv.bg

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

M. Nedyalkov*, E. Encheva, M. Tsvetkov, M. Milanova

*Department of Inorganic Chemistry, Faculty of Chemistry and Pharmacy, Sofia University
"St. Kliment Ohridsky", J. Bourchier, 1, 1164 Sofia, Bulgaria*

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.

[1] J. Evans et al., Chemistry of Materials 8 (1996) 2809.

[2] Y. Yamamura et al., Physical Review B 70 (2004) 104107:1.

* E-mail: martin_nedyalkov_rze@abv.bg

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

G. Nénert¹, P. O'Meara², T. Degen¹

¹ Malvern Panalytical B. V., Lelyweg 1, 7602 EA, Almelo, The Netherlands

² Malvern Panalytical Ltd., 7310 Ground Floor, Beach Drive, Waterbeach, Cambridge, CB25 9AY, UK

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].

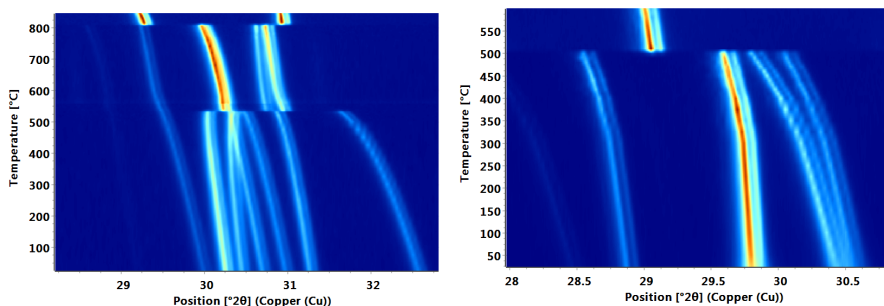


Fig. 1. Phase transitions in NaSrVO₄ (left, [4]) and AgPbVO₄ (right, [6])

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].

[1] Isupov V. A., Phase Transitions in Anhydrous Phosphates, Vanadates and Arsenates of Monovalent and Bivalent Elements, *Ferroelectrics*, 274, 1 (2002), pp 203–283.

[2] Choi S., Yun Y. J., Kim S. J., Jung H.-K. Thermally stable white-emitting single composition Na(Sr,Ba)PO₄:Eu²⁺, Mn²⁺ phosphor for near-ultraviolet-pumped light-emitting diodes, *Optical Letters*, (2013) 38, pp 1346–1348.

[3] Drai S., Olazcuaga R., Le Flem G., Etude cristallographique du vanadate NaSrVO₄ et de son homologue NaSrCrO₄, *Journal of Solid State Chemistry*, 10, (1974) pp 95–101.

[4] G. Nénert, P. O'Meara, T. Degen, Crystal structure and polymorphism of NaSrVO₄: the first A'B^{II}XVO₄ larnite-related structure from X-ray powder diffraction data, *Phys. Chem. Minerals* (2017) 44: 455–463.

[5] G. Nénert, Synthesis and crystal structure of the new vanadate AgCaVO₄: Comparison with the arcanite structure. *Z. Kristallogr.* 2017; 232(10): 669–674.

[6] G. Nénert, in preparation.

* E-mail: gwilherm.nenert@malvernpanalytical.com

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

A. Nikolov^{1,*}, R. Titorenkova¹, N. Velinov², Z. Delcheva¹, B. Chen³

¹ *Institute of Mineralogy and Crystallography, Bulgarian Academy of Science, Sofia 1113,
Acad. Georgi Bonchev Str., Bulgaria*

² *Institute of Catalysis, Bulgarian Academy of Science, Sofia 1113,
Acad. Georgi Bonchev Str., Bulgaria*

³ *Microlab, Section Materials and Environment, Faculty of Civil Engineering
and Geosciences, Delft University of Technology, Stevinweg 1,
2628 CN Delft, The Netherlands*

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.

Acknowledgement: The results in this work has been achieved in fulfillment of a project financed by the National Science Fund of Bulgaria under contract No. DM17/3 from 12.12.2017.

* E-mail: drsashko@imc.bas.bg

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

SYNTHESIS OF GEOPOLYMERS USING NATURAL ZEOLITE AND SODIUM ALUMINATE

A. Nikolov^{1,*}, H. Nugteren², I. Rostovsky³, Z. Delcheva¹

¹ *Institute of Mineralogy and Crystallography, Bulgarian Academy of Science, Sofia 1113,
Acad. Georgi Bonchev Str., Bulgaria*

² *Department of Chemical Engineering, University of Technology, Delft, The Netherlands*

³ *Department of Building Materials and Insulations, UACEG, Sofia, Bulgaria*

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.

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.

* E-mail: drsashko@imc.bas.bg

Keywords: geopolymer, metazeolite, sodium aluminate, clinoptilolite.

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

M. Panayotova^{1,*}, N. Mintcheva¹, O. Gemishev², G. Tyuliev³,
G. Gicheva¹, L. Djerahov¹

¹ *Department of Chemistry, University of Mining and Geology, Sofia, Bulgaria*

² *Faculty of Biology "St. Kl. Ohridski" University, Sofia, Bulgaria*

³ *Institute of Catalysis of Bulgarian academy of sciences, Sofia, Bulgaria*

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.

* E-mail: marichim@mgu.bg

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

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

D. Paneva^{1,*}, Z. Cherkezova-Zheleva¹, V. Petkova^{2,3}, B. Kostova²,
H. Kolev¹, G. Avdeev⁴, G. Stefanov⁴

¹ Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St.,
Bld. 11, 1113 Sofia, Bulgaria

² New Bulgarian University, Department of Natural Sciences, 21 Montevideo Str.,
1618 Sofia, Bulgaria

³ Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
bl. 107, Acad. G. Bonchev Str., 1113 Sofia, Bulgaria

⁴ Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St.,
Bld. 11, 1113 Sofia, Bulgaria

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.

Acknowledgments: Authors gratefully acknowledge the financial support of the Bulgarian National Science Fund at the Ministry of Education and Science – Project № DCOST 01/22/ 2017.

* E-mail: daniela@ic.bas.bg

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

INVESTIGATION OF RARE EARTH DOPED ZINC BOROPHOSPHATE GLASSES

G. Patronov*, I. Kostova, D. Tonchev

Dept. Chem. Technology, University of Plovdiv "Paisii Hilendarski", 4000 Plovdiv, Bulgaria

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.

[1] S.V. Eliseeva et al., *New J. Chem.* 35 (2011) 1165.

[2] C.M. Reddy et al., *Renewable and Sustainable Energy Review* 51 (2015), 566.

* E-mail: patron@uni-plovdiv.bg

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

STRUCTURAL CHARACTERIZATION OF $\text{Au/Cu}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ CATALYSTS

T.M. Petrova*, N.I. Velinov, I.B. Ivanov, T.T. Tabakova, V.D. Idakiev, I.G. Mitov

Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

The spinel ferrites are known that have many important properties as magnetic, optical, catalytic etc., which provokes the scientific interest. The magnetite (Fe_3O_4) 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 $\text{Au/Cu}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) 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 $\text{Au/CuFe}_2\text{O}_4$ 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: $\text{Au/Cu}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4 \geq \text{Au/Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4 > \text{Au/Cu}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4 > \text{Au/CuFe}_2\text{O}_4 \geq \text{Au/MnFe}_2\text{O}_4$. 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.

Acknowledgement: T. Petrova and N. Velinov acknowledge financial support by the Bulgarian National Science Fund, Project DCOST 01/22/2017. I. Ivanov, T. Tabakova and V. Idakiev acknowledge financial support by the Bulgarian National Science Fund, Contract ДН 09/5/2016.

* E-mail: silberbarren@abv.bg

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

N. Rangelova^{1,*}, L. Aleksandrov²

¹ *University of Chemical Technology and Metallurgy, Department of Fundamentals of Chemical Technology, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

² *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str. bl. 11, 1113 Sofia, Bulgaria*

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.

* E-mail: rangelovang@gmail.com

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

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

R.I. Rusev^{1,3,*}, V.B. Kurteva², L.T. Dimowa¹, B.L. Shivachev¹

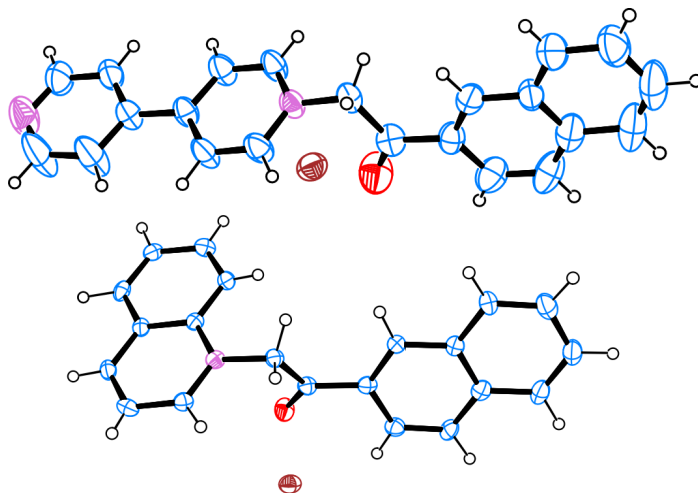
¹ Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 107, 1113 Sofia, Bulgaria

² Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria

³ University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd. 1756 Sofia, Bulgaria

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.



Acknowledgement: The financial support by The Bulgarian Science Fund, DRNF-02/01 and T02/14 is gratefully acknowledged.

* E-mail: r.rusev93@gmail.com

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

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

R.I. Rusew, B.L. Shivachev*

*Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences,
Acad. G. Bonchev str., bl. 107, 1113 Sofia, Bulgaria,*

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.

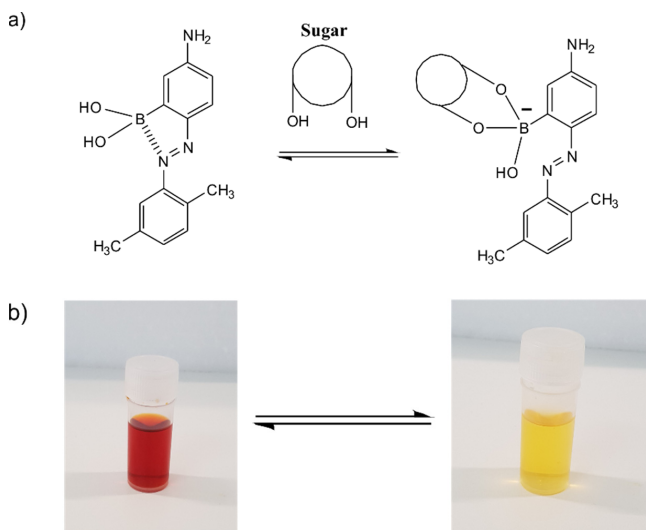


Fig. 1. Proposed mechanism of the sugar induced spectral change [3] (a) and visible representation of the color change (b)

[1] C. J. Ward, P. Patel, T. D. James, *Journal of the Chemical Society, Perkin Transactions 1*, 462 (2002).

[2] N. DiCesare, J. R. Lakowicz, *Organic letters* **3**, 3891 (2001).

[3] Y. Egawa, R. Gotoh, S. Niina, J.-i. Anzai, *Bioorganic & medicinal chemistry letters* **17**, 3789 (2007).

CRYSTALLIZATION AND CRYSTAL STRUCTURE OF LYSOZYME WITH NANOSIZED TITANIUM OXIDE

H.I. Sbirkova-Dimitrova*, V. Ganev, B.L. Shivachev

*Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria*

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

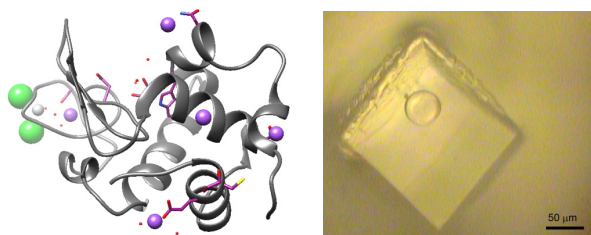


Fig. 1. a) Crystal structure of **6G5C** and b) Crystals after Laser ablation (LA-ICP-MS).

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.

[1] Callewaert, L., Aertsen, A., Deckers, D., Vanoirbeek, K. G., Vanderkelen, L., Van Herreweghe, J. M., ... & Michiels, C. W. (2008). PLoS pathogens, 4(3), e1000019.

[2] Luckarift, H. R., Dickerson, M. B., Sandhage, K. H., & Spain, J. C. (2006). Small, 2(5), 640–643.

* E-mail: sbirkova@mail.bg

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

SPECTROSCOPIC ANALYSIS OF SULPHURIC ACID TREATED BIODEGRADABLE WASTE

E. Serafimova^{1,*}, V. Petkova²

¹ *University of Chemical Technology and Metallurgy – Sofia, 8 “St. Kliment Ohridski” Bul., Sofia 1756, Bulgaria*

² *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., Bldg. 107, 1113 Sofia, Bulgaria*

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.

[1] Abelha P, I. Gulyurtlu, D. Boavida, J. Seabra Barros, I. Cabrita, J. Leahy, B. Kelleher, M. Leahy. Combustion of poultry litter in a fluidised bed combustor. *Fuel*, 82, (2003) 687–92.

[2] Abu-Zahra R. and Tahboub A.B. Effect of Organic Matter Sources on Chemical Properties of the Soil and Yield of Strawberry under Organic Farming Conditions. *World Applied Sciences Journal*, 5 (3), (2008) 383–388.

[3] Koukouzas N, Hamalainen J, Papanikolaou D, Tourunen A, Jantti T. Mineralogical and elemental composition of fly ash from pilot scale fluidised bed combustion of lignite, bituminous coal, wood chips and their blends. *Fuel*, 86, (2007) 2186–93.

[4] Petkova V., E. Serafimova, B. Kostova. Thermal behaviour of nitric-acid-treated biomass and chicken litter mixtures. *J. Therm. Anal. Cal.*, 126 (1), (2016) 149–160.

* E-mail: ekaterina_sr@abv.bg

Keywords: biodegradable waste, IR, XRD, SEM.

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

V. Stefanova^{1,*}, E. Serafimova²

¹ *University of Forestry- Sofia, 10 "St. Kliment Ohridski" Bul., Sofia 1756, Bulgaria*

² *University of Chemical Technology and Metallurgy – Sofia, 8 "St. Kliment Ohridski" Bul.,
Sofia 1756, Bulgaria*

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.

[1] Ningyu I., Bin, G., Yongzhen, D. Effects of Double Harvesting on Heavy Metal Uptake by Six Forage Species and the Potential for Phytoextraction in Field. *Pedosphere*, 26(5), (2016) 717–724.

[2] Singh, A., Agrawal, M. The role of organic vs. inorganic fertilizers in reducing phytoavailability of heavy metals in a wastewater-irrigated area. *Ecological Engineering*, 36, (2010)1733–1740

[3] Mahar, A., Wang, P., Li, R. Immobilization of Lead and Cadmium in Contaminated Soil. *Pedosphere*, 25(4), (2015) 555–568.

[4] Rossini-Oliva, S., Mingorance, M., Pena, A. Effect of two different composts on soil quality and on the growth of various plant species in a polymetallic acidic mine soil. *Chemosphere*, 168, (2017) 183–190.

* E-mail: venistefanova3@gmail.com

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

PHYSICOCHEMICAL CHARACTERIZATION ON CLINICALLY RETRIEVED TRITANIUM ORTHODONTIC ARCHWIRES

A. Stoyanova-Ivanova¹, I. Ilievska^{1,*}, V. Petrova¹, M. Gueorgieva², V. Petrov²,
L. Andreeva², A. Zaleski³, V. Mikli⁴

¹ *G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko
Chaussee, 1784 Sofia, Bulgaria*

² *Faculty of Dental Medicine, Medical University Sofia, St. G. Sofiiski Blvd., 1431 Sofia, Bulgaria*

³ *Institute of Low Temperatures and Structure Research, Polish Academy of Science, AS,
50-422 Wrocław, Poland*

⁴ *Institute of Materials and Environmental Technology, Tallinn University of Technology,
19086 Tallinn, Estonia*

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).

[1] www.medicalexpo.com/prod/american-orthodontics/product-115719783261.html

* E-mail: ivannyilievaska@gmail.com

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

T. Tasheva*, V. Dimitrov

*Department of Silicate Technology, University of Chemical Technology and Metallurgy,
8 Kl Ohridski Blvd., Sofia 1756, Bulgaria*

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.

* E-mail: tina.tasheva@gmail.bg

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

CRYSTAL STRUCTURE OF A NEW STILBAZIOLIUM TOSYLATE WITH ENLARGE CONJUGATED SYSTEM

M. Todorova^{1,*}, R. Bakalska², S. Zareva³, T. Kolev⁴

¹ University of Food Technology, Faculty of Technology, Dept. Organic Chemistry, 26 Maritsa Blvd., 4000 Plovdiv, Bulgaria

² Plovdiv University, Faculty of Chemistry, Dept. Organic Chemistry, 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria

³ Sofia University «St. Kliment Ohridski», Faculty of Chemistry and Pharmacy, 1164 Sofia, 1 James Bourchier Blvd., Bulgaria

⁴ Institute of Molecular Biology "Roumen Tsanev", Acad. G. Bonchev Str, bl. 21, 1113 Sofia, Bulgaria

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.

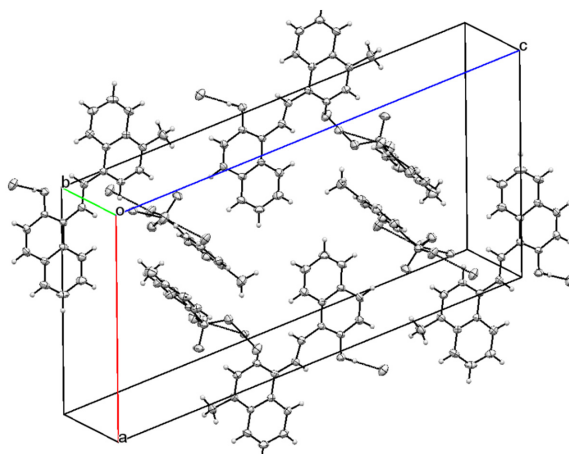


Fig. 1. Three-dimensional arrangement of the molecules in the crystals of the dye.

* E-mail: mtodorova@uni-plovdiv.bg

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

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

T. Todorova*

*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev St., bl. 107, 1113 Sofia, Bulgaria*

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.

Acknowledgements: The author acknowledge the financial support by “Program for career development of young scientists and PhD students at the Bulgarian Academy of Sciences – 2017 (Contract No. DFNP 17-87/28.07.2017).

* E-mail: todorova@imc.bas.bg

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

SOLID STATE STRUCTURE OF PARAMAGNETIC COMPLEXES OF HEMATOPORPHYRIN IX

D. Tsekova, G. Gencheva*

*Department of Analytical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University,
1 J. Bourchier Str., BG1164 Sofia, Bulgaria*

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.

* E-mail: ggencheva@chem.uni-sofia.bg

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

NEW CARBON MATERIALS WITH GRAPHITE MICROSTRUCTURE

B. Tsyntsarski^{1,*}, M. Todorova¹, G. Georgiev¹, A. Bahova¹, N. Petrov¹,
T. Budinova¹, B. Petrova¹, I. Stoycheva¹, U. Szeluga², S. Pusz²,
B. Kumanek², B. Trzebicka²

¹ *Institute of Organic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Acad. G. Bonchev str., Bulgaria*

² *Centre of Polymer and Carbon Materials, Zabrze, 41-819 Zabrze
ul. M. Curie-Skłodowskiej 34, Poland*

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.

Acknowledgements: The authors appreciate the funding by bilateral project between Polish Academy Sciences and Bulgarian Academy of Sciences, and by Horizon 2020 EIT RIS Blow-up project No 16320.

* E-mail: btsintsarski@orgch.bas.bg

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

FRAMEWORK ELASTICITY OF THE Mn-ETS-4

L. Tsvetanova^{1,*}, R. Nikolova¹, V. Kostov-Kytin¹, S. Ferdov²

¹ *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Sofia 1113, Bulgaria*

² *Department of Physics, University of Minho, 4800-058 Guimarães, Portugal*

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

D. Vasilev*, R. Titorenkova

*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 107, Sofia 1113, Bulgaria*

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.

* E-mail: rosititorenkova@dir.bg

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

V. Velcheva*, G. Gencheva

*Faculty of Chemistry and Pharmacy, Sofia University "St. Kl. Ohridski",
1 James Bouchier blvd., Sofia, Bulgaria*

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.

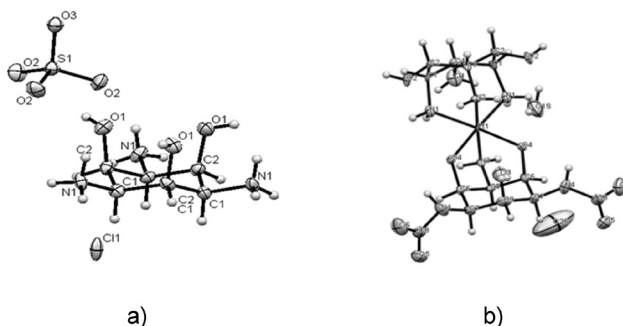


Fig. 1. Structure of a) $taci_{+3H}.SO_4.Cl.H_2O$ and b) $[Pt(taci)(taci-_{2H}(OH)(NHCO_2)_2].2H_2O$.

* E-mail: vyara.velcheva@gmail.com

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

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

L. Vladislavova^{1,2,*}, R. Harizanova¹, I. Avramova³, G. Avdeev⁴, C. Rüssel²

¹ *University of Chemical Technology and Metallurgy, Department of Physics,
8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

² *Otto Schott Institute, University of Jena, Fraunhoferstr. 6, 07743 Jena, Germany*

³ *Institute of General and Inorganic Chemistry, BAS, Bl. 11, Acad. G. Bonchev. Str.,
1113 Sofia, Bulgaria*

⁴ *Institute of Physical Chemistry, BAS, Bl. 11, Acad. G. Bonchev. Str.,
1113 Sofia, Bulgaria*

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.

Acknowledgement: This work is financially supported by contract UCTM-NIS/2018 and DAAD grant 91655716.

* E-mail: rharizanova@uctm.edu

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

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

S. Yaneva^{1,*}, Tz. Velinov²

¹ *University of Chemical Technology and Metallurgy, Department of Fundamentals
of Chemical Technology, Sofia 1756, Bulgaria*

² *Sofia University, Department of Solid State Physics and Microelectronics,
5 blvd. James Bourchier, 1164 Sofia, Bulgaria*

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.

* E-mail: sp_yaneva@uctm.edu

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

A. Yordanova*, R. Iordanova, I. Koseva, P. Tzvetkov, R. Kukeva, V. Nikolov

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Sofia, Bulgaria*

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.

* E-mail: a.yordanova@svr.igic.bas.bg

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

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

I. Zagranjarska^{1,*}, K. Kostova¹, R. Nikolova², B. Shivachev², V. Dimitrov¹

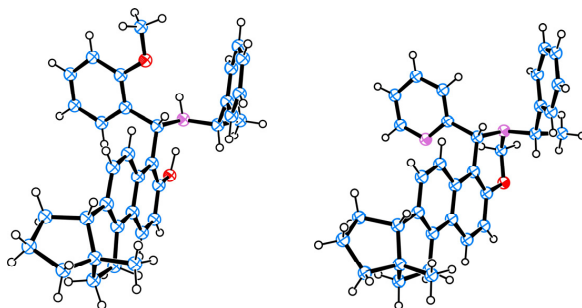
¹ Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev 9, Sofia 1113, Bulgaria

² Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev 107, Sofia 1113, Bulgaria

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).

* E-mail: irenash@orgchm.bas.bg

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

CRYSTALLINE ADDUCTS OF UREA WITH MgI_2

L. Tsvetanova, R. Nikolova*, K. Kosev, N. Petrova

*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str. 107, Sofia*

The simple magnesium salts form a large number of hydrates. Generally, they form crystals at room temperature but there are some water-rich ones which are stable only at temperatures below 273 K [1]. The partial substitution of the water molecules with other simple dipole molecule like Urea could make such compounds more stable. In view of above and in continuation of our previous investigations of magnesium salts [2], we determined the phases of the system Urea – MgI_2 – H_2O . Three crystalline Urea(CON_2H_4) adducts were obtained at room temperature and Urea: MgI_2 ratio varying between 1:1 and 1:10. X-ray analysis of single crystal samples of $MgI_2 \cdot 2U \cdot 4H_2O$ (tetraaquabis (urea-O) magnesium diiodide), $MgI_2 \cdot 4U \cdot 2H_2O$ (diaqua tetra (urea-O) magnesium diiodide) and $MgI_2 \cdot 8U$ (hexa(urea-O) magnesium diiodidetetraurate) show that in all three compounds the Mg^{2+} exhibits an octahedral coordination (MgX_6)²⁺X=Urea, H_2O). When possible the inclusion of Urea in the complex cations is preferred over water while the I⁻ anions is always kept (Fig. 1).

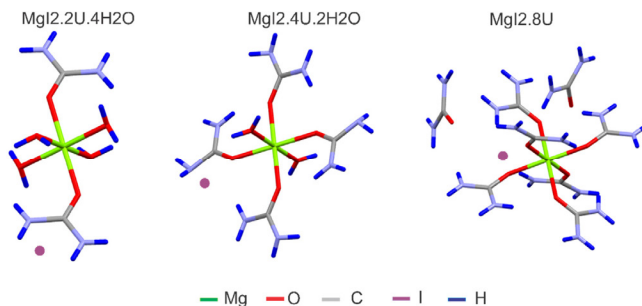


Fig. 1. Structural units of the studied compounds. Chemical elements are marked with different colors.

A complex network of hydrogen bonds supports the three dimensional packing of studied compounds. DTA-TG analyses indicate that the number and strength of hydrogen bonds influence the thermal stability of the crystal structure.

[1] E. Hennings et al., Crystal structures of hydrates of simple inorganic salts. I. Water-rich magnesium halide hydrates $MgCl_2 \cdot 8H_2O$, $MgCl_2 \cdot 12H_2O$, $MgBr_2 \cdot 6H_2O$, $MgBr_2 \cdot 9H_2O$, $MgI_2 \cdot 8H_2O$ and $MgI_2 \cdot 9H_2O$. *Acta Cryst.* C69 (2013), 1292–1300.

[2] R. Rusev et al., Ureates and hydrates of magnesium chloride, nitrate and tetrafluoroborate, *Bulgarian Chemical Communications*, 50 (2018), Sp. Iss. J, 79–89.

* E-mail: rosica.pn@clmc.bas.bg

Keywords: urea, magnesium iodide, adduct, crystal structure.

Mg AND Zn MODIFIED CALCIUM PHOSPHATE FINE POWDERS EXAMINED BY RIETVELD REFINEMENT

K. Sezanova*, D. Kovacheva, D. Rabadjieva, R. Gergulova

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl.11, 1113 Sofia, Bulgaria*

Ion modified calcium phosphate-based ceramics have been developed to simulate the composition of the mineral component of bone tissues and to strengthen some specific biologically important behaviors. It is expected that such ceramic will be prospective materials for bone reconstruction and remodeling. Mg and Zn are preferable among all the substitutes in the biological apatites as they are essential for the organisms. Most often, bioceramics based on hydroxyapatite (HA), tricalcium phosphate (α - or β -TCP) or bi-phase HA/ β -TCP are used due to their good osteoconductivity, physiological tolerance, biocompatibility and long-term stability

In this study fine powders of magnesium-modified as well as zinc-modified calcium phosphates with a $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Zn}^{2+})/\text{P}$ ratio of 1.3–1.4 and various $\text{Me}^{2+}/(\text{Me}^{2+} + \text{Ca}^{2+})$ ($\text{Me} = \text{Mg}, \text{Zn}$) molar ratios in the range from 0 to 0.10 were prepared by the method of continuous precipitation in biomimetic electrolyte systems of simulated body fluid, keeping pH 8 and with further maturation in mother liquid. The precipitates were step-wise calcined to 1000°C.

XRD studies of calcined powders showed that Zn^{2+} and Mg^{2+} ion substitution for Ca^{2+} ions stabilize the β -TCP structure and the effect was more pronounced in the case of Zn substitution. Mixtures of HA and β -TCP calcium phosphates were found in non-modified sample and in this one with low ion ratio $\text{Me}^{2+}/(\text{Ca}^{2+} + \text{Me}^{2+}) < 0.03$. Single-phase Zn- β -TCP and Mg- β -TCP were observed for all modified samples with $\text{Zn}^{2+}/(\text{Zn}^{2+} + \text{Ca}^{2+}) \geq 0.03$ and $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+}) = 0.05$.

Rietveld refinement of the XRD data was performed to find the positions and occupancy of Mg^{2+} and Zn^{2+} ions. The refinement confirms both Mg^{2+} and Zn^{2+} ions substitute the Ca^{2+} ions mainly in the octahedral Ca(5) sites of Mg/Zn- β -TCP. Ca(4) position with threefold coordination remains partially occupied, which is in line with cationic deficiency of the obtained powders. The unit cell parameters were calculated and relations with the type and degree of substitution were determined.

* E-mail: ksezanova@abv.bg

Keywords: Mg- β -TCP, Zn- β -TCP, Biomimetic synthesis, Rietveld refinement.

NANOSIZED MESOPOROUS TITANIA PROMOTED WITH TIN AND ZIRCONIUM OXIDES AS CATALYSTS FOR TOTAL OXIDATION OF ETHYL ACETATE AND METHANOL DECOMPOSITION

G. Issa^{1,*}, I. Genova¹, T. Tsoncheva¹, J. Henych², M. Dimitrov¹,
V. Štengl², D. Kovacheva³

¹ *Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Sofia, 1113, Bulgaria*

² *Materials Chemistry Department, Institute of Inorganic Chemistry AS CR*

³ *Institute of Inorganic Chemistry, BAS, Sofia, 111, Bulgaria*

The aim of current investigation is to develop novel nanosized mesoporous materials based on promoted with Sn and Zr titania systems and to test them as catalysts in various processes, which are important for environmental protection, such as total oxidation of ethyl acetate and methanol decomposition. The titania-zirconia and titania-tin oxide materials were synthesized by a template-assisted technique using CTAB as a template, hydrothermal treatment at 373 K and calcination at 773 K. The samples were denoted as xTiyZr and xTiySn, where x:y was the metal mol ratio, which for the bi-component samples was 1. The obtained materials were characterized by low temperature nitrogen physisorption, XRD, SEM, TEM, Raman, UV-Vis, FTIR and thermo-programmed reduction with hydrogen. The catalytic properties of the obtained materials were studied in oxidation of ethyl acetate and methanol decomposition. The template assisted hydrothermal technique insures preparation of materials with high crystallinity, high BET surface area and accessibility due to the development of mesoporous structure. The bi-component materials demonstrated higher dispersion and improved textural characteristics in comparison with the mono-component oxides and this was more pronounced when ZrO₂ was used as a dopant. XRD and spectroscopic study reveals formation of solid metal oxide solution in all bi-component systems. The addition of ZrO₂ or SnO₂ dopant into TiO₂ provokes strong intimate contact between the individual oxides results in the formation of different catalytic active sites and their role in catalytic reaction is in the focus of the study.

Acknowledgement: Financial support from project DM-09/4/2016 is acknowledged. Bilateral project between Bulgarian Academy of Sciences and Czech Academy of Sciences is also acknowledged.

* E-mail: Issa@abv.bg

Keywords: nanostructured metal oxides, ethyl acetate oxidation, methanol decomposition.

CHARACTERIZATION OF IN-SITU SAMPLING PARTICULATE MATTER OF AIR POLLUTION LOCALIZED BY LIDAR MONITORING

L. Slavov¹, M. Iliev², R. Ilieva², R. Angelova¹, Ch. Ghelev¹, I. Grigorov¹,
G. Kolarov¹, L. Gurdev¹, Z. Cherkezova-Zheleva³, V. Grurdeva²,
D. Stoyanov¹, I. Nedkov^{1,*}

¹ *Institute of Electronics, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee Blvd,
Sofia, Bulgaria*

² *Faculty of Biology, St. Kl. Ohridski University of Sofia, 8, Dragan Tsankov Blvd, Sofia, Bulgaria*

³ *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St.,
Bld.11, 1113 Sofia, Bulgaria*

The present work is part of comprehensive studies on particulate matter (PM) in atmospheric aerosol. The data presented pertains to the winter-spring tran period 2018 year. PM pollutions than 10 and 2.5 μm were under studied. It combines lidar monitoring over a densely populated urban area (city of Sofia, capital of Bulgaria) with on-the-spot sampling at sites with high concentration of dust products. Once the place of high PM concentration was localized by the lidar, samples were taken using a Hygitest 106 (Maimex) – a high-efficiency portable device for sampling and concentration determination of PM in atmospheric aerosol. X-ray diffraction and Mössbauer studies at room temperature of PM were used for investigation of the inorganic part of PM. The collected dust material was subjected to microbiological investigation. Standard procedure for isolation of pure microbial cultures was applied. The obtained bacterial and fungal isolates were identified on the basis of morphological, physiological and biochemical characteristics. Thus, we established that the surface of the micron-sized particles can adsorb both mechanical and microbial contaminants, while the liquid envelope, when the PM is dispersed as aerosols, may preserve this nano-world and, in some cases, create conditions favoring the occurrence of chemical and bio-processes. The lidar maps constructed can be further used for tracing the full air mass transport, carrying contamination from a number of pollution sources (chemical, biological, dust, etc.), distributed over the scanned region.

Acknowledgments: The work was financially supported in part by contract H18/26 “Complex studies of particulate matter in the atmosphere...” with the Bulgarian National Science Fund and included in the European Program of COST Action CA16202 „International network on encouraging the use of monitoring and forecasting dust products”.

* E-mail: nedkovivan@yahoo.co.uk

Keywords: lidar monitoring, particulate matter, bioaerosols, air quality.

AUTHOR INDEX

A

Aleksandrov, L. • 80
Andreeva, L. • 86
Angelova, R. • 20
Angelov, R. • 29
Angelov, V. • 30
Anselmo, A. • 22, 31
Apostolova, M. • 32
Atanasova-Vladimirova, S. • 33, 65
Atanasov, G. • 32
Avdeev, G. • 61, 71, 77, 95
Avramova, I. • 95
Avramova, K. • 71

B

Babeva, T. • 44
Bachvarova-Nedelcheva, A. • 34
Bahova, A. • 91
Bakalska, R. • 88
Bancheva, Tsv. • 66, 68
Barbov, B. • 35
Bedeković, N. • 36
Bish, D. • 21
Blagoev, B. • 38
Blaskov, V. • 34
Bojinova, A. • 56
Boyadzhieva, T. • 37
Buchkov, K. • 38
Budinova, T. • 91

C

Chen, B. • 39, 74
Cherkezova-Zheleva, Z. • 40, 41, 77, 102
Chimov, A. • 43
Cinčić, D. • 36, 48
Cvetkova, V. • 45

D

Degen, T. • 73
Delcheva, Z. • 42, 74, 75
Dikova, K. • 43
Dimitrova, T. • 45
Dimitrov, D. • 56
Dimitrov, M. • 54, 101
Dimitrov, O. • 44
Dimitrov, Ts. • 53
Dimitrov, V. • 43, 55, 87, 98
Dimowa, L. • 46, 47, 65, 81
Djerahov, L. • 76
Dobrikov, G. • 55
Dodevska, T. • 29
Dyulgerov, V. • 47

E

Encheva, E. • 41, 72

F

Ferdov, S. • 92
Fotović, L. • 48

G

Gancheva, M. • 71
Ganev, V. • 83
Gavrilova, R. • 49
Gemishev, O. • 76
Gencheva, G. • 50, 52, 90, 94
Genova, I. • 101
Georgieva, B. • 29, 50
Georgiev, G. • 91
Georgiev, M. • 66, 68
Gergulova, R. • 100
Ghelev, Ch. • 102
Gicheva, G. • 76
Goranova, D. • 51
Gorolomova, P. • 52
Grigорова, E. • 69
Grigorov, I. • 102
Grobosch, M. • 22, 31
Grurdeva, V. • 102
Gueorgieva, M. • 86
Gurdev, L. • 102

H

Harizanova, R. • 95
Helm, M. • 22, 31
Henyeh, J. • 54, 101

I

Ibrevia, Ts. • 53
Idakiev, V. • 79
Ilieva, R. • 102
Iliev, M. • 102
Ilievska, I. • 86
Iordanova, R. • 34, 97
Issa, G. • 54, 101
Ivanova, R. • 54
Ivanov, E. • 30
Ivanov, I. • 79
Ivanov, P. • 59

K

Kakhramanov, N. • 24
Kamenova-Nacheva, M. • 55
Kaneva, N. • 56
Karadjova, V. • 45
Karashanova, D. • 29
Keulen, A. • 39
Kichukova, D. • 57
Kolarov, G. • 102
Koleva, V. • 37
Kolev, H. • 40, 58, 77

Kolev, T. • 88
 Kormunda, M. • 54
 Koseva, I. • 59, 97
 Koseva, N. • 24
 Kosev, K. • 99
 Kostova, B. • 60, 77
 Kostova, I. • 78
 Kostova, K. • 43, 98
 Kostov-Kytin, V. • 61, 62, 67, 92
 Kotsilkova, R. • 30
 Kovacheva, D. • 54, 57, 64, 100, 101
 Krebs, B. • 52
 Krstić, J. • 41
 Kukeva, R. • 67, 97
 Kumanek, B. • 91
 Kunev, B. • 40
 Kurbanova, R. • 24
 Kurteva, V. • 63, 81

L

Lazarova, Ts. • 64
 Lazarova, V. • 49
 Lihareva, N. • 65

M

Marinova, D. • 66, 67, 68
 Marinova, P. • 45
 Markov, P. • 69
 Markovska, I. • 53
 Martinez, V. • 36
 Mihailova, I. • 70
 Mikli, V. • 86
 Milanova, M. • 72
 Mintcheva, N. • 76
 Mirchev, N. • 41, 71
 Mitov, I. • 79
 Momekov, G. • 52
 Music, S. • 28

N

Nedkov, I. • 40, 102
 Nedyalkov, M. • 72
 Nemeč, V. • 48
 Nénerť, G. • 73
 Nihtianova, D. • 69
 Nikolov, A. • 74, 75
 Nikolova, R. • 43, 47, 55, 61, 63, 67, 92, 98, 99
 Nikolov, V. • 59, 97
 Nugteren, H. • 75

O

O'Meara, P. • 73

P

Panayotova, M. • 76
 Paneva, D. • 40, 41, 77
 Papazova, K. • 56
 Patronov, G. • 78
 Petkova, V. • 60, 77, 84
 Petrova, B. • 91

Petrova, N. • 42, 46, 99
 Petrova, N. L. • 47
 Petrova, R. • 52
 Petrova, T. • 79
 Petrova, V. • 86
 Petrov, N. • 91
 Petrov, O. • 32
 Petrov, O. E. • 53, 65
 Petrov, V. • 86
 Piroeva, I. • 33, 46
 Popova, H. • 51
 Proykova, A. • 26
 Pusz, S. • 91

R

Rabadjjeva, D. • 100
 Radev, L. • 70
 Radonjić, V. • 41
 Rangelova, N. • 80
 Rashkov, R. • 51
 Ristic, M. • 28
 Rostovsky, I. • 75
 Rusew, R. • 32, 47, 81, 82
 Rüssel, C. • 95

S

Sbirkova-Dimitrova, H. • 83
 Schramm, B. • 22, 31
 Seidlhofer, B. • 22, 31
 Serafimova, E. • 60, 84, 85
 Sezanova, K. • 100
 Shivachev, B. • 32, 43, 47, 52, 55, 63, 81, 82, 83, 98
 Shopska, M. • 40, 41
 Simova, S. • 52
 Slavchev, I. • 55
 Slavov, A. • 29
 Slavov, L. • 102
 Stambolova, I. • 34, 44
 Staneva, A. • 57
 Stanimirova, Ts. • 42
 Stefanova, V. • 85
 Stefanov, G. • 77
 Štengl, V. • 54, 101
 Stilićnović, V. • 23, 36, 48
 Stoilova, D. • 66, 68
 Stoyanova-Ivanova, A. • 86
 Stoyanova, R. • 37, 67
 Stoyanov, D. • 102
 Stoycheva, I. • 91
 Strehina, K. • 41
 Szeluga, U. • 91

T

Tabakova, T. • 79
 Tacheva, E. • 53
 Tacheva, T. • 87
 Tavlinova-Kirilova, M. • 43
 Titorenkova, R. • 53, 74, 93
 Todorova, M. • 88, 91
 Todorova, T. • 89

Tonchev, D. • 78
Tonchev, V. • 51
Trzebicka, B. • 91
Tsekova, D. • 90
Tsoncheva, T. • 54, 101
Tsvetanova, L. • 92, 99
Tsvetkov, M. • 41, 71, 72
Tsyntsarski, B. • 91
Tyuliev, G. • 76
Tzvetanova, Y. • 60, 65
Tzvetkov, G. • 27
Tzvetkov, P. • 59, 97

U

Ugrinov, A. • 25

V

Vasileva, I. • 29
Vasilev, D. • 93
Vassilev, S. • 44

Velcheva, V. • 94
Velinov, N. • 74, 79
Velinov, Tz. • 96
Vladislavova, L. • 95
Vollmer, A. • 22, 31

W

Wildner, M. • 68

Y

Yaneva, S. • 96
Ye, G. • 39
Yordanova, A. • 59, 97
Yordanov, St. • 34

Z

Zagranyarska, I. • 98
Zaleski, A. • 86
Zareva, S. • 88
Zhecheva, E. • 67