Sixth National Crystallographic Symposium
with International Participation

PROGRAM and ABSTRACTS

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

Institute of Optical Materials and Technologies
“Acad. Jordan Malinovski” – BAS
Institute of Mineralogy and Crystallography – BAS
Institute of General and Inorganic Chemistry – BAS
Geological Institute – BAS
Institute of Catalysis – BAS

October 5–7, 2016, Sofia, Bulgaria
Bulgarian Academy of Sciences, Grand Hall, 15 Noemvri str. N1
ORGANIZING COMMITTEE

Chairpersons
Assoc. Prof. Daniela Karashanova, IOMT – BAS
Prof. Boris Shivachev, IMC – BAS

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Prof. Rositsa Nikolova, IMC – BAS
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Dr. Yana Tzvetanova, IMC – BAS
Hristina Sbirkova, IMC – BAS
Totka Todorova, IMC – BAS
Liliya Tzvetanova, IMC – BAS
Radoslav Angelov, IOMT – BAS
INVITED SPEAKERS

**Prof. Svetlana Mintova, ENSICAEN, France**
- Design of nanosized zeolites for advanced applications

**Prof. Krzysztof Wozniak, University of Warsaw, Poland**
- A century after the Braggs – crystallography beyond the independent atom model

**Prof. Srebri Petrov, Chemistry Department, University of Toronto, Canada**
- Application of Rietveld method in X-ray powder diffraction

**Prof. Boriana Mihailova, University Hamburg, Germany**
- Crystal chemistry and phonon states in hydrous silicates: Amphiboles and tourmalines

**Prof. Atul Khanna, Department of Physics, Guru Nanak Dev University, India**
- Structural studies of borate and tellurite glasses, anti-glass and crystalline phases

**Assoc. prof. Bogdan Ranguelov, IPC – BAS**
- In situ reflection electron microscopy – crystal growth modes and phase transitions

**Prof. Pavleta Shestakova, IOCCP – BAS**
- Solid state NMR characterization of zeolite Beta based drug formulations containing Ag and sulfadiazine

**Prof. Katharina Fromm, University of Fribourg Department of Chemistry**
- From mixed-metal coordination compounds towards nanomaterials

**Prof. Radostina Stoyanova IGIC – BAS**
- Polyanion compounds: From minerals to electrode materials for lithium and sodium ion batteries

**Assoc. prof. Yuri Kalvachev, IMC – BAS, Bulgaria**
- Seed-assisted synthesis, modification and application of zeolites

**Evdokiya Salamanova, Karolinska Institute, Department of Biosciences and Nutrition, Sweden**
- Effects of point mutations on the activity and propensity of helical formation of the τ1-transactivation domain of Glucocorticoid receptor

**Ivanina Sergeeva, IG – BAS**
- Crystal chemistry and structural characterisation of natural Cr-spinels

**Prof. Alexander Karamanov, IPC – BAS**
- Sinter-crystallization of glass-ceramics: Theory and application

**Prof. Tsonko Kolev, IMB-BAS**
- New Structural Motifs of Hydrogensquarates of Amino Acids and Amino Acid Derivatives and their Application in Organic Material Science

**Prof. Galina Gencheva, Sofia University**
- Transition metal coordination polymers constructed with organic linkers based on tertiary phosphine oxides – synthesis and structural diversity

**Prof. Abidin Kiliç, Anadolu University, Turkey**
- Calculate the rotation kinetic energy of the full symmetric molecules with Clifford algebra

**Liliya Vladislavova, Otto-Schott-Institut für Materialforschung, Friedrich-Schiller-Universität Jena, Germany**
- Surface and internal crystallization in glass ceramics with a low thermal expansion phase
The organizers of the VI-th National Crystallographic Symposium (NCS2016) express their thanks and appreciation to all those who are generously contributing to the success of this meeting.

Симпозиумът се организира със съдействието на Фонд „Научни изследвания“, по договор за съфинансиране ДПМНФ 01/13 от 27.09.2016 г.
Dear Colleagues and Friends, dear NCS2016 Participants,

On behalf of the Organizing committee as well as the Bulgarian Crystallographic Society (BCS), it is our pleasure to welcome you to Sofia at the VI-th National Crystallographic Symposium (NCS2016), 05–07 October 2016.

This is the eight event organized under the auspices of the BCS (Five symposia and two Schools) and is intended to popularize crystallographic techniques and methods and to connects scientists from all disciplines for which crystallography is important. The program of the Symposium features varied topics presented by excellent scientists. With a total of 22 lectures featuring 8 keynote speakers, a large number of hot topics from biology, chemistry, physics and mineralogy are to be covered. The social program, will allow you all to meet connect and exchange knowledge.

The NCS2016 will be hosted in the Main Building of the Bulgarian Academy of Sciences. It location in the old Sofia center, is closer to several tourist sites. Not to forget the friendly atmosphere and affable locals that promote for the good mood.

We thank also all the sponsors, exhibitors and Bulgarian science foundations for their support, all our volunteers and helpers the organizers of previous NCS events and especially Yana for the last minute work. Last but not least, we would like to thank YOU for your participation. We hope that you are going to enjoy the NCS symposia

NCS Organizers
**Poster Prizes** The NCS2016 Organizers are pleased to continue the publication of the NCS2016 works in the journal Bulgarian Chemical Communications.

**Poster Prizes**
A prize will be awarded to the best poster from a Young scientist (graduate or undergraduate student, and will consist of open voucher.

**NCS2016 Cocktail**
The official NCS2016 Cocktail will take place on Thursday 06 October 2016 from 17:30 onwards at the BAS restaurant.
SYMPOSIUM VENUE

1 Lecture Hall

2 Registration

3 Coffee breaks

4 Sponsors space

Main Entrance

"15 November" str.

bul. Tsar Osvoboditel"
Posters (approximate) number location, for all poster sessions
Wednesday 5 October 2016

9:00–11:30  Registration
11:30–11:45  Opening ceremony
   Welcome by Symposium cochairs D. Karashanova, B. Shivachev and Rositsa Nikolova – President of BCS
   Official Addresses from the authorities and hosts
   BCS recognizing of Prof. Kostadin Petrov for advancement of crystallography in Bulgaria (Rosica Nikolova and Ognyan Petrov)

Session I  Chairing: Prof. Ognyan Petrov, IMC – BAS
11:45–12:30  Keynote lecture
   A Century After the Braggs – Crystallography Beyond the Independent Atom Model
   Prof. Krzysztof Wozniak, University of Warsaw, Poland

12:30–14:00  Lunch Break

Session II  Chairing: Prof. Rositsa Nikolova, IMC – BAS
14:00–14:45  Keynote lecture
   Design of nanosized zeolites for advanced applications
   Prof. Svetlana Mintova, ENSICAEN, France

14:45–15:15  Lecture
   Seed-assisted synthesis, modification and application of zeolites
   Assoc. prof. Yuri Kalvachev, IMC-BAS, Bulgaria

15:15–15:45  Lecture
   Effects of point mutations on the activity and propensity of helical formation of the τ1-transactivation domain of glucocorticoid receptor
   Evdokiya Salamanova, Karolinska Institute, Department of Biosciences and Nutrition, Sweden

15:45–16:15  Commercial lecture, Aquachim
   From micro to nano: Microscopy innovations and solutions for materials research
   Anton Tonchev, Zeiss, Germany

16:30–17:30  Poster session 1 (PS1)
## Thursday 6 October 2016

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<td>10:15-10:45</td>
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<td>Bas ter Mull, Panalytical, Netherlands</td>
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<td>Liliya Vladislavova, Otto-Schott-Institut für Materialforschung, Friedrich-Schiller-Universität Jena, Germany</td>
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15:30–16:00  
*Commercial lecture, JEOL*

**Development of a New Generation Multi-Purpose Electron Microscope: JEOL F2**  
Guillaume Brunetti, PhD, JEOL (Europe) SAS, Croissy sur Seine, France

16:15–17:30  
**Poster session 2 (PS2)**

17:30  
**NCS’2016 cocktail**

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**Friday 7 October 2016**

**Session VI**  
*Chairing: Assoc. prof. Daniela Karashanova, IOMT – BAS*

- 9:00–9:45  
  *Keynote lecture*
  **In situ reflection electron microscopy – crystal growth modes and phase transitions**  
  Assoc. prof. Bogdan Rangelov, IPC–BAS

- 9:45–10:15  
  *Lecture*
  **New Structural Motifs of Hydrogensquarates of Amino Acids and Amino Acid Derivatives and their Application in Organic Material Science**  
  Prof. Tsonko Kolev, IMB–BAS

- 10:15–10:45  
  *Lecture*
  **Calculate the rotation kinetic energy of the full symmetric molecules with Clifford algebra**  
  Prof. Abidin Kiliç, Anadolu University, Turkey

- 10:45–11:15  
  **Coffee break**

**Session VII**  
*Chairing: Prof. Radostina Stoyanova, IGIC – BAS*

- 11:15–12:00  
  *Keynote lecture*
  **Solid state NMR characterization of zeolite Beta based drug formulations containing Ag and sulfadiazine**  
  Prof. Pavleta Shestakova, IOCCP – BAS

- 12:00–12:30  
  *Commercial lecture, Infolab – Bruker*
  **New developments in Bruker XRD systems**  
  Dipl.-Ing., MBA Ante Mrkonjic, Bruker, Germany

- 12:30–13:30  
  **Lunch Break**

**Session VIII**  
*Chairing: Prof. Lyudmil Antonov, IOCCP – BAS*

- 13:30–14:15  
  *Keynote lecture*
  **From mixed-metal coordination compounds towards nanomaterials**  
  Prof. Katharina Fromm, University of Fribourg Department of Chemistry
14:15–14:45  Lecture
Transition metal coordination polymers constructed with organic linkers based on tertiary phosphine oxides – synthesis and structural diversity
Prof. Galina Gencheva, Sofia University

14:45–15:15  Commercial lecture, Elta90
TA Instruments (Thermal analysis)

15:15  Best young scientist poster presentations prize and closing ceremony

**Poster session 1, Wednesday 5 October 2016**


P_2. R. I. Kostov, S. Dencheva – New data on the crystal morphology of brazilianite (Galiléia, Minas Gerais, Brazil)

P_3. Z. Delcheva, K. Ivanova, Ts. Stanimirova – Phase transitions during washing of ktenasite-like minerals


P_5. A. Bachvarova-Nedelcheva, R. Iordanova, R. Gegova, Y. Dimitriev – Crystallization of gels in the binary TiO$_2$ – M$_n$O$_m$ ($M_nO_m$ = TeO$_2$, SeO$_2$, B$_2$O$_3$, ZnO) systems

P_6. Sv. Ganev, S. Parvanov, S. Slavov, A. Bachvarova-Nedelcheva, R. Iordanova, Y. Dimitriev – Influence of TiO$_2$ on the thermal stability and crystallization of glasses within TeO$_2$-Bi$_2$O$_3$-Nb$_2$O$_5$-ZnO system

P_7. S. M. Gechev, O. E. Petrov, V. Y. Ganev, J. T. Mouhovski – X-ray powder diffraction of (Yb$_{0.007}$Na$_{0.05}$)Ca$_{0.72}$Sr$_{0.223}$F$_2$ and (Yb$_{0.006}$Na$_{0.04}$)Ca$_{0.917}$Sr$_{0.073}$F$_2$ crystals

P_8. S. M. Gechev, Y. P. Ivanova, J. T. Mouhovski – EPR and ultrasonics behaviour in (Yb, Na)-doped lasant alkaline-earth fluoride crystals


P_11. R. Ivanova, M. Dimitrov, D. Kovacheva – Influence of the hydrothermal treatment temperature on the properties of mixed ceria-zirconia catalysts for ethyl acetate combustion

P_12. N. Kaneva, A. Bojinova, K. Papazova, D. Dimitrov – Enhanced of structural and photocatalytic properties of ZnO films onto aluminum foil prepared at different temperatures

P_13. B. Georgiev, G. Gencheva – New “platinum blues” of alantoin and creatinine – a study on the impact of the formal redox potential on antiproliferative properties

P_15. I. Mihailova, L. Radev, D. Mehandjiev – Effect of calcination temperature on phase transformation and chemical durability of fayalite waste

P_16. A. Mileva, G. Issa, J. Henych, V. Štengl, D. Kovacheva, T. Tsoncheva – Ceria and titania oxides obtained by urea assisted homogeneous hydrolysates method as catalysts for environmental protection: Effect of Ce/Ti ratio


P_18. G. Patronov, I. Kostova, D. Tonchev – Synthesis and characterization of samarium doped zinc borophosphate glasses

P_19. A. Yordanova, R. Iordanova, P. Tzvetkov, V. Nikolov – Nanosized Cr^{3+} doped Sc_{2-x}In_{x}(WO_4)_3 solid solutions

P_20. T. Petrova, N. Velinov, I. Genova, I. Georgieva, T. Tsoncheva, D. Kovacheva, N. Petrov, I. Mitov – Synthesis and characterization of copper-manganese ferrites with the composition Cu_{1-x}Mn_xFe_2O_4 supported on activated carbon


P_22. I. Tomov, S. Vassilev, G. Avdeev – Examination of the secondary extinction by converting XRD data from step scan into continuous scan

P_23. D. Tsanova-Tosheva, E. Radeva, D. Dechev, R. Bezdušnyi, P. Petrov – Crystallographic structure of biocompatible nanocoatings deposited on Co-Cr substrate

P_24. L. Tsvetanova, R. Nikolova – Deformations of ETS-4 Ti-Si framework after ion exchange and temperature lowering


P_27. D. Vasilev, G. Jegova, M. Rashkova, R. Titorenkova – Compositional and structural differences of apatite from enamel and dentine

P_28. A. Krasteva, F. Krzyżewski, M. Zaluska-Kotur, H. Popova, V. Tonchev – Step bunching and macrostep formation in 1D atomic scale model of unstable vicinal crystal motion

P_29. H. Popova, V. Tonchev – Simultaneous deposition of particles with different functionality: models, based on cellular automata


P_31. L. Dimitrov, O. Petrov, N. Lihareva – Transformation of Australian perlite in phillipsite and its possible use as ion-exchanger

P_32. V. Kostov-Kytin, V. Petkova, T. Kaljuvee – Powder XRD microstructural analysis of thermally treated synthetic fluor-hydroxylapatite
**Poster session 2, Thursday 6 October 2016**

**P_1.** T. Boyadzhieva, V. Koleva, R. Stoyanova, E. Zhecheva – Preparation, structure and spectroscopic analysis of Mg-substituted NaMnPO₄ and LiMnPO₄ phospho-olivines

**P_2.** V. Angelov, E. Ivanov, R. Kotsilkova – The structure of three phase epoxy/organoclay/gold nanocomposites and the size distribution of gold nanoparticles over organoclay

**P_3.** S. Chakarova, G. Gencheva – Novel paramagnetic platinum-based complexes with bidentate n,n-donor ligands – pyridine-2-amine and pyridine-4-amine

**P_4.** V. B. Delchev, K. B. Gavazov – Using quantum mechanics for crystal structure solutions: 4-(2-pyridylazo)resorcinol

**P_5.** O. Petrov, L. Dimitrov – Synthesis of microporous products from waste amorphous silica

**P_6.** L. Dimowa, O. Petrov, M. Kadiyski, M. Tarassov – Structural study of Tl-exchanged clinoptilolite using Rietveld refinement

**P_7.** S. M. Gechev – UV-VIS-NIR structural study of (Yb, Na)-co-doped calcium-(strontium) fluoride single crystals

**P_8.** P. Gorolomova, V. Velcheva, G. Gencheva – Experimental and theoretical study on the molecular and electronic structure, spectroscopic properties and coordination behaviour of the ligand 2,2’-dipyridylamine

**P_9.** K. Hegetschweiler, V. Velcheva, G. Gencheva – New PtIV complexes of N,O-containing ligand 1,3,5-triamino-1,3,5-trideoxy-cis-inositol with potential antitumor activity

**P_10.** M. Kalapsazova, E. Zhecheva, R. Stoyanova – Diffraction methods for analysis of layered NaₓNi₀.₅Mn₀.₅O₂ as cathode materials

**P_11.** N. G. Kostova, M. Balaz, P. Balaz – Photocatalytic properties of mechanochemically synthesized copper sulfides

**P_12.** V. Kurteva, B. Shivachev, R. Nikolova, S. Simova, L. Antonov – First example of three stable desmotropes

**P_13.** Ts. Lazarova, D. Kovacheva – Study of the structural characteristics of nanosized Mn-Fe₂O₄ obtained combustion synthesis. Influence of the type of fuel

**P_14.** Y. Manolova, A. Crochet, K. M. Fromm, L. Antonov – Molecular wires: Design of new tautomeric ligands

**P_15.** D. Marinova, M. Wildner, D. Stoilova – Crystal structures and infrared spectra of the Tutton compounds Rb(Cs)₂Mg(CrO₄)₂·6H₂O and Rb₂Mg(SO₄)₂·6H₂O, and of solid solutions Rb₂Mg(Cr₁₋ₓSₓO₄)₂·6H₂O

**P_16.** M. Markova, M. Vrazhilova, G. Gencheva – Paramagnetic polynuclear platinum complexes of 5-fluorouracil. II. Determination of the number, stoichiometry and stability constants of platinum complex species formed during the interaction

**P_17.** P. H. Nagaraj, R. Ettrich – Structural studies of the type I restriction-modification system EcoR124I complex and its methyltransferase subunit using X-ray crystallography and cryo-EM hybrid approach
P_18. M. Ormanova, D. Dechev, R. Bezdushnyi, P. Petrov – Crystallographic structure of multilayer system TiN/CrN deposited by DC magnetron sputtering

P_19. J. Romanova, M. R. Ranga Prabhath, Y. Sadik, P. D. Jarowski – The role of substituent effects in tuning metallophilic interactions and emission energy of bis-4-(2-pyridyl)-1,2,3-triazolato platinum(II) complexes


P_21. S. Elagoz, Y. Ergun, A. Kilic – The expansion of the low-growth InGaAs layer and characterization

P_22. D. Stanisheva, M. Gerova, B. Shivachev, O. Petrov – Synthesis and crystal structure of benzo[bl]imidazo[1,5-d][1,4]-oxazepines

P_23. S. Todorova, V. Kurteva, S. Simova, B. Shivachev, R. Petrova – Unsymmetrical NH-ureas attached to dihydro-2h-benzo[1,3]oxazin-2-one scaffold

P_24. M. Vakarelska-Popovska, I. Madjarov, M. Stevchova, V. Karadjova, Zh. Velkov – Vibrational and structural analysis of copper (II) complex with 3-hydroxy flavone


P_28. Y. Ergun, M. Hostut, S. Elagoz, A. Kilic – The growth of InGaAs / InAlAs superlattices and characterization for product quantum cascade laser


P_30. H. I. Sbirkova, B. L. Shivachev – Comparison of the crystal structures of DNA sequence d(CGTAATTCACG) with and without DAPI


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Crystal chemistry and structural characterization of natural Cr-spinels
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Borates and tellurites are technologically important materials, which produce variety of glassy and crystalline phases. $\text{B}_2\text{O}_3$ is the best oxide glass former; its melt never crystallizes at ambient pressure even at very slow cooling rates [1]. Pure $\text{TeO}_2$ forms glass under the condition of very high melt-quenching rates; while binary and ternary tellurite systems containing alkali, alkaline-earth, rare-earth, transition and heavy metal oxides form glasses rather easily at normal quenching rates, and have wide glass-formation range. Like borates, tellurite glasses have a dual Te-O coordination ($\text{N}_{\text{Te-O}}$) of 3 and 4 with oxygen. $\text{N}_{\text{Te-O}}$ can be determined by Raman spectroscopy and neutron diffraction studies, and it decreases on incorporating metal oxides such as $\text{ZnO}$, $\text{Al}_2\text{O}_3$, $\text{PbO}$, $\text{WO}_3$, $\text{Nb}_2\text{O}_5$, $\text{Eu}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$ and $\text{MoO}_3$ into the tellurite and borotel-lurite network [2–6]. Borotellurite glasses that contain two glass formers i.e. $\text{B}_2\text{O}_3$ and $\text{TeO}_2$ form transparent glasses over a limited $\text{B}_2\text{O}_3$ concentration of 5 to 25 mol%. $^{11}\text{B}$ Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) and infrared spectroscopy studies confirm that the boron-oxygen co-ordination ($\text{N}_{\text{B-O}}$) decreases with increase in $\text{B}_2\text{O}_3$ mol% in borotellurite glasses. Pure borotellurite glasses are hygroscopic and absorb atmospheric water vapors to form crystalline precipitates of $\alpha$-$\text{TeO}_2$ in an amorphous matrix [3]. On adding $\text{Al}_2\text{O}_3$ into borotellurites to form alumino-borotellurite glasses, the chemical durability enhances but the glass formation range deteriorates due to decrease in $\text{N}_{\text{B-O}}$ [3]. Alumino-borotellurite glasses show crystalline-amorphous phase separation at high alumina concentration. $^{27}\text{Al}$ MAS-NMR studies show that alumino-borotellurite glasses contain $\text{AlO}_4$, $\text{AlO}_5$ and $\text{AlO}_6$ structural units and the concentration of penta and hexa units is in the range of 50 to 60%. Heavy metal oxides when mixed with $\text{TeO}_2$ forms anti-glass phases, which have atomic order, like crystalline materials but exhibit vibration disorder [7]. In this talk an overview of structure-property correlations in heavy metal oxide borate and tellurite systems is presented.


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TRANSITION METAL COORDINATION POLYMERS CONSTRUCTED WITH ORGANIC LINKERS BASED ON TERTIARY PHOSPHINE OXIDES – SYNTHESIS AND STRUCTURAL DIVERSITY

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The coordination polymers are comparatively new class of polymeric materials created on the boundary of coordination chemistry and material science. In recent years particular attention is paid to control on their synthesis that allows the designing of specific structures with promising applications in different fields of the practice. The synthetic routes can be modulated by external factors such as solvents, pH value, temperature, etc. Among the other factors, the choice of appropriate organic ligands has proven to be one of the most effective ways to manipulate versatile structures, where the length, the flexibility or rigidity, functional donor groups and substituents, modes of coordination can bring to significant effects on the final structures. The selection of metal ions in respect to nature, oxidation state, coordination polyhedron provides the obtaining polymer compounds with desired properties.

The presented study concerns the synthesis, single-crystal structure and physicochemical properties of series of $\text{Zn}^{2+}$, $\text{Cu}^{2+}$ and $\text{Mn}^{2+}$ coordination polymers obtained by bi- and tridentate ligands, such as bis-(dimethylphosphinylmethylenoxy)-benzenes (o-I, m-I and p-I), 1,3,5-tris(dimethylphosphinylmethylenoxy)benzene (tris-I) and bis((dimethylphosphinyl)methylene)amine (bis-NL). These ligands coordinate through the phosphoryl oxygen donors from the tertiary phosphine oxide-substituents. The characteristics of the ligands used such as nucleophilicity of the donors, bond angles, molecular length, bulkness, etc., determine the formation of different 1D, 2D or 3D polymeric structures. The flexible ligands can adopt different conformations to form complexes with varied structures depending on the mutual position of the donor functional groups and the nature of metal ions. The different size and coordination ability of the counterions have also a decisive impact on the spatial structure of the compounds.

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Keywords: coordination polymers, transition metal complexes, tertiary phosphine oxides.
SINTER-CRYSTALLIZATION OF GLASS-CERAMICS: THEORY AND APPLICATION

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The sinter-crystallization is an alternative method for production of glass-ceramics, which expands the application range of these materials. During its production cycle the densification and the phase formation of used glass powders or grains carry out in the same temperature range. As a result, the sintering strongly depends by the crystallization trend and sometimes its prediction is complicated. At the same time, the crystallization process and the final morphology of samples depend from the heating rate, the fraction size and several other parameters. In some cases, the phenomenon of crystallization induced porosity is also observed, which additionally compromises the evaluation of reached degree of sintering. As a consequence, a definite theory which explains all cases of sinter-crystallization is not created.

The lecture is based on the author’s experience within various types of sintered glass-ceramics and his analysis of the existing theoretical models for sinter-crystallization. By using complex dilatometric, DTA, XRD and SEM results it is highlighted that these materials formally can be divided into three main groups:

- Compositions with low crystallization ability in which the densification completes before the formation of notable amount of crystal phase and sintered samples can be obtained at low temperature and extended crystallization step.

- Compositions with moderate crystallization ability in which the sintering is partially inhibited by the phase formation and well sintered glass-ceramics can be manufactured at high heating rates and short crystallization step.

- Compositions with high crystallization ability in which the sintering is inhibited by the phase formation and secondary densification, near the liquids temperatures, can be used.

Finally, modification of used at the moment Frenkel – Muller equation for the sinter-crystallization is proposed. The relationship between the sintering ability and the tendency for formation of crystallization induced porosity is also made.

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Keywords: sintering, crystallization, glass-ceramics.
NEW STRUCTURAL MOTIFS OF HYDROGENSQUARATES OF AMINO ACIDS AND AMINO ACID DERIVATIVES AND THEIR APPLICATION IN ORGANIC MATERIAL SCIENCE

Ts. M. Kolev


Search of new materials with electrooptical (EO) and nonlinear optical (NLO) properties in the bulk requires a strategy for obtaining non-centrosymmetric crystals and the employment of chiral agents (e.g. chiral counter ions) is a powerful technique for obtaining such crystals. Considerable progress has been made in recent years by controlling the assembly of individual molecules in solids, using hydrogen bonding as a powerful non-covalent force for organizing organic molecules. Squaric acid (H$_2$Sq) provides a very useful template for generating strong hydrogen bonded self-assemblies from polarizable cations in general and amino acids in particular. In the last 20 years series of noncentrosymmetric crystals have been synthesized, isolated spectroscopically and structural elucidated by means of the single crystal X-ray diffractions study. The possibility of this strong acid to stabilize both hydrogen squarate anion (HSq$^-$) and squarate dianion (Sq$^{2-}$) allows controlling its self assembly in the crystals and tuning their spectroscopic, optical electrooptical and non-linear-optical properties. On the other side formation of squaric acid amides and diamides is another possibility to generate new organic materials with non-linear-optical application. In this contribution are presented the structures of hydrogensquarates of the most proteinogenic amino acids. The structures of the HSq studied suggest the same anion can serve as very sensitive indicator for amino acid and their derivatives.
CRYSTAL CHEMISTRY AND PHONON STATES
IN HYDROUS SILICATES:
AMPHIBOLES AND TOURMALINES

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Tourmalines (XY₃Z₆[T₆O₁₈][BO₃]₃⊥V₃W) and amphiboles (AB₂C₅T₈O₂₂W₂) are two mineral supergroups that have been challenging geoscientists for a long time due to their extensive compositional variations at the non-tetrahedral crystallographic sites. Known in the pass mainly as “garbage-can minerals”, nowadays tourmalines and amphiboles are gaining continuously growing interest not only for geosciences as “geological DVDs” but also for materials and environmental science as well as when studying cultural-heritage artefacts. However, the presence of light elements hinders the proper application of electron microprobe analysis (EMPA) to determine the chemical composition, which calls for alternative analytical methods. Raman spectroscopy has the great potential to be used for crystallochemical studies because: (i) Raman-active phonon modes obey strict symmetry-related selection rules, i.e. the structure type can immediately be fingerprinted, (ii) the phonon wavenumbers depend on the atomic masses and interatomic force constants, while relative integrated peak intensities are indicative of the concentration of specific chemical species, which allows for distinguishing between different mineral species; (iii) when calibration curves are available, one can determine the site occupancy with a certain degree of preciseness; (iv) Raman spectroscopy is non-destructive, easy-to-be-handle method that can be applied to micron-size grains in crude rocks and even to standard glass-covered thin sections.

In this contribution, a model for crystal-chemistry determination of TAl-free amphiboles [1] and tourmalines [2] via the Raman scattering arising from OH-stretching phonon modes is presented. The study of tourmalines is further extended to framework vibrations, demonstrating the ability of Raman spectroscopy to determine trivalent iron [3]. It is also shown that Raman spectroscopy is as good as EMPA to determine the host-rock type, when using petrological models based on the amounts of major and minor elements in tourmaline [4].


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Keywords: Raman spectroscopy, amphibole, tourmaline, phonon.
APPLICATION OF RIEtveld METHOD IN X-RAY POWDER DIFFRACTION

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Recently the Rietveld method applies widely in x-ray powder diffraction technique due to valuable compositional, structural and quantitative information that it can provide for analyzed materials. Some examples of its application on various synthetic, natural and pharmaceutical samples are included in this presentation. The disclosed examples comprise Rietveld analyses on powders, thin films and metals. The subsequent stages of the whole diffraction analysis are considered including: phase identification, verification, preparation of the input data and carrying out the Rietveld profile fitting procedure. Some specific details in the refinement procedure are explained.

Other practical approaches based on whole-pattern decomposition procedure are also shown such as: determination of the mean particles size, checking out the purity of the analyzed sample, inspection of the indexing and determination of the space group of unknown and quantification of the amorphous content in the analyzed material. All analyses are carried out using Bruker AXS data processing software Eva v.12. The Rietveld refinement was done by Bruker AXS structural software Topas v. 3.0.

The examples presented here could be useful for colleagues working in the field of X-ray powder diffraction as well as for those involved in research of various solid state technological and synthetic products.
IN SITU REFLECTION ELECTRON MICROSCOPY – CRYSTAL GROWTH MODES AND PHASE TRANSITIONS

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Visualization of the most basic features of the crystal growth process and phase transitions on surfaces plays a key role in understanding of these nanoscale phenomena in condensed matter physics. The ultimate experimental technique for observation of in situ crystal surface dynamics is the reflection electron microscopy. Specially designed holder is used to manipulate precisely the thermodynamic conditions (under saturation / super saturation or equilibrium) around the investigated sample. The basic mechanisms of homoepitaxy are demonstrated by meaning of deposition flux of adatoms impinging on Si(111) vicinal crystal surface at different temperatures – step flow growth mode, layer by layer mode growth, normal growth mode, as well as spiral growth mode and the famous step bunching transition [1, 2]. Switching between these modes of crystal growth is shown, depending on the surface geometry – when the width of a terrace on a vicinal surface exceeds certain critical value, the step flow mode is switched to 2D island growth, which is a precursor for appearing of periodic patterns of pyramids (wedding cakes) onto the surface.


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Keywords: electron microscopy, crystal growth, nucleation.
EFFECTS OF POINT MUTATIONS ON THE ACTIVITY AND PROPENSITY OF HELICAL FORMATION OF THE $\tau_1$-TRANSACTIVATION DOMAIN OF GLUCOCORTICOID RECEPTOR

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The intrinsically disordered proteins (IDPs) hold important functions at cellular level, such as regulation of transcription and translation, signalling, storage of small molecules and self-assembly of macromolecular units in active complexes. The lack of compact 3D-structure or folding upon binding to their targets is related to the specific role of the unstructured regions. The Glucocorticoid receptor (GR) belongs to a family of ligand-inducible nuclear receptors and two of its domains ($\tau_1$ and $\tau_2$) have shown a conserved activity after they have been removed from the receptor entity [1]. The disordered core region of the $\tau_1$-domain consists of 58-amino-acids. It carries most of the activity and has shown a helical propensity in hydrophobic solvents. We have investigated the process of mutagenesis of the $\tau_1$-core transactivation domain in GR and the importance of the amino acid residues to its transactivation activity. In silico, we have used a model system to correlate the experimental activities to helical propensity of series of mutated peptides. For our goal we used CHARMM simulation package [2] with Charmm36ff to perform Molecular Dynamics simulations at different temperature regimes.


Solid state NMR ($^1$H, $^{13}$C, $^{27}$Si, $^{27}$Al and $^1$H-$^{29}$Si CP-HETCOR) was applied for characterization of zeolite Beta-based (HB) dual drug formulations with antibacterial properties, containing Ag, sulfadiazine (SD) and silver sulfadiazine (AgSD) [1]. A mechanism for transformation of octahedral defect framework Al sites and encapsulation of the extraframework Al (EFAI) present in the parent Beta material into framework tetrahedral species as a result of the drug loading procedure is proposed. The nature of the drug-carrier interactions and the location of the drug molecules inside the pores and/or on the crystallite surface are discussed.

The $^{27}$Al NMR spectra showed that the loading of SD, Ag or AgSD resulted in a reinsertion of the EFAI into the zeolite matrix of the parent HB carrier. $^1$H spectra suggested that the mechanism of EFAI inclusion involves exchange between the zeolite protons and $\text{H}^+$ or $\text{Ag}^+$ cations, originating from SD and AgSD respectively, that play a role of charge compensating species. The comparison of onepulse and CP $^{29}$Si spectra in combination with $^1$H spectra, suggested that the loaded drug (SD, AgSD) is predominantly localized in the vicinity of Si(0Al) groups and a larger amount of it is most probably embedded within the zeolite pores. The amount of the SD drug confined into the pores of HB zeolite is higher than that included into the Ag modified carrier. $^1$H-$^{29}$Si HETCOR spectra of SD/AgB and AgSD/HB samples show similar correlation patterns, evidencing the analogous localization of the drug into the zeolites. Comparison of $T_1$ and $T_2$ relaxation times of pure drugs and drug loaded formulations indicate that the drug incorporated into the pores of the zeolite matrix is in amorphous form.

Search for low-cost energy storage systems, sodium ion batteries have been designed as an alternative to the present-day lithium ion batteries. Both lithium and sodium ion batteries operate via the same mechanism, involving a reversible solid state transfer of Li$^+$ or Na$^+$ between anodes and cathodes. There are three types of solid state reactions that can ensure a reversible transfer of alkaline ions: intercalation, conversion (or displacement) and alloying. When the electrochemical process is based on intercalation reactions, electrode materials having specific structural and redox properties are needed. Among several groups of substances, polyanion compounds provide a diversity of structures all of which are able to intercalate lithium and sodium ions quickly and reversibly. From the first report on electrochemical properties of lithium iron phospho-olivine LiFePO$_4$ in 1997 till now, there is a challenging research competition aimed at defining the most suitable polyanion-structure matrix for reversible and fast lithium and sodium intercalation.

This presentation aims to underline how the knowledge on minerals and their structures can contribute to the identification of new class of electrode materials for lithium and sodium ion batteries. We demonstrate this by our recent studies on sodium manganese phosphates and sulfates: NaMnPO$_4$ with a triphylite and maricite-type of structures, Na$_{2+\delta}$Mn$_{2-\delta/2}$(SO$_4$)$_3$ with an alluadite-type of structures. Inspired from the mineral world, specific precursors such as KMnPO$_4$.H$_2$O with a dittmarite-type of structure and Na$_3$Mn(SO$_4$)$_3$.2H$_2$O with a kröhnkite-type of structure are used in order to obtain pure NaMnPO$_4$ and Na$_{2+\delta}$Mn$_{2-\delta/2}$(SO$_4$)$_3$ with desired structures [1–3]. Finally, the role of the alluadite- and olivine-type of structures as open structural matrices ensuring fast alkaline ion mobility is emphasized [1,3].


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Keywords: polyanion compounds, intercalation, sodium ion batteries, lithium ion batteries.
SEED-ASSISTED SYNTHESIS, MODIFICATION 
AND APPLICATION OF ZEOLITES

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As a well-established family of nanoporous materials, zeolites are of vital importance for the chemical, petrochemical and many other industries. Zeolites are widely used in industry because of their high adsorption capacity, strong acid sites and shape/size selectivity combined with high thermal and acid stability. The pore size often is a drawback when on zeolites must perform transformations of molecules with larger dimensions or the resulting products are of a large size. One way to overcome this disadvantage and to provide improved diffusion of molecules is a synthesis of zeolite crystals with smaller size. Several techniques for the preparation of zeolites with nanosized crystals are known – synthesis from clear solutions; synthesis with space limiting agents, and seed-assisted synthesis. In seed-induced synthesis, the addition of seed crystals introduces crystallites into the system which play role as nuclei. Over them crystal growth takes place. The higher is the number of crystallites in the initial gel, the smaller is the size of particles obtained. The synthesis in the presence of seeds has other advantages namely - directing the synthesis towards the desired product and increase the speed of crystallization.

In this contribution, seed-assisted synthesis of Beta zeolite in fluoride media [1] and its catalytic activity in the reaction of m-xylene transformation is presented. The study of seed-assisted synthesis is further extended to preparation of mordenite, without using of organic template [2] and post synthetic modification of obtained zeolite in order to improve its catalytic performance [3]. Synthesis in the presence of seed is applied also during preparation of zeolite X from coal combustion fly ash from Bulgarian Thermal Power Plant [4]. Process of CO\(_2\) adsorption on thus obtained zeolite X was carried out and adsorption capacity was determined [5]. This process is very important and can provide a promising solution for lowering of the CO\(_2\) emissions from power plants.

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Keywords: zeolite, hydrothermal synthesis, seed, mordenite, fly ash, zeolite X.
ELECTRON BACKSCATTER DIFFRACTION OF REE-Th-U MINERALS IN SEM – FROM SAMPLE PREPARATION TO INTERPRETATION OF RESULTS

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A systematic survey of pitfalls and challenges in application of electron backscatter diffraction (EBSD) for examination of REE-Th-U containing minerals as zircon (ZrSiO₄), monazite (LREEPO₄), xenotime (YPO₄), rhabdophane (LREEPO₄.H₂O) and others from the Igralishte granite pluton (Bulgaria) were carried out in the present work. Polishing conditions for samples, thickness of conductive coating, vacuum parameters and acceleration voltage in SEM were surveyed with the view of minimization of factors disturbing the quality of EBSD patterns and masking the real structural state of the studied phases. It was found that the polishing protocol preceding EBSD study recommended in the literature [1] is good enough but a special attention should be done to the final stage of preparation – to the chemical mechanical polishing by colloidal silica. Despite of the apparent attractiveness of low vacuum conditions in SEM (variable pressure regime, VP) allowing examinations of dielectric samples without additional coating with conductive substance, this vacuum regime was found to be unsuitable for investigations of REE-Th-U minerals. The reason for this is essential worsening of the spatial resolution and problems with focusing that is critical in view of the inherent small size of the considered minerals (below 200 μm) and their micrometric and sub-micrometric inhomogeneity. It was shown that high-vacuum conditions and a 20 kV acceleration voltage in SEM as well as a 10 nm thickness of conductive carbon coat for the samples give high-quality EBSD patterns and allow one to perform reliable comparison of the structural state and structural variations in the considered minerals. During the present research, an original approach was developed for accurate and reproducible carbon coating of samples with required thickness.

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Keywords: EBSD, REE-Th-U minerals, preparation, carbon coating.
THE STRUCTURE OF THREE PHASE EPOXY\ORGANOCLAY\GOLD NANOCOMPOSITES AND THE SIZE DISTRIBUTION OF GOLD NANOPARTICLES OVER ORGANOCLAY

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The aim of this study is to investigate the structure of the Epoxy/Organoclay/Gold nanocomposites and the size distribution of gold nanoparticles over organoclay. Gold nanoparticles are synthesized from precursor HAuCl₄ in aqueous solution and they are with different size and shape. The nanocomposites are prepared by “in-situ” polymerization method.

XRD measurements are performed on the clay powder and the epoxy based nanocomposites. The X-Ray diffractograms are obtained using Bruker D8 Advance diffractometer. The crystalline phases are identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files. The mean particle size (L) of gold nanoparticles is determined from the line broadening reflections, using the Scherer equation. The calculations are done using FIT computer program [1].

Transmission electron microscope JEOL JEM 2100 is used for characterization of the structure at micro- and nano-scale of the samples.

The size and the shape of the gold nanoparticles shown in the TEM image are further analyzed using PEBBLES software – a user-friendly software which implements an accurate, unbiased, reproducible, and fast method to measure the morphological parameters of a population of nanoparticles (NPs) from TEM micrographs. In this software, the morphological parameters of the projected NP shape are obtained by fitting intensity models to the TEM micrograph [2].

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Keywords: XRD, TEM, organoclay, nanocomposites.
CRYSTALLIZATION OF GELS IN THE BINARY
TiO$_2$ – $M_nO_m$ (M$_nO_m$ = TeO$_2$, SeO$_2$, B$_2$O$_3$, ZnO) SYSTEMS

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The present investigation deals with the sol-gel synthesis and phase characterization of binary TiO$_2$ – $M_nO_m$ (M$_nO_m$ = TeO$_2$, SeO$_2$, B$_2$O$_3$, ZnO) powders with nominal composition 80TiO$_2$.20$M_nO_m$. The competitive influence of different components on the phase formation was verified. Several oxides were selected as a second component: a classical network former (B$_2$O$_3$), conditional network formers (TeO$_2$, SeO$_2$) and an intermediate oxide (ZnO). The TiO$_2$ is very successfully used to produce amorphous and crystalline titanate materials via sol-gel process. Titanium alkoxides are extremely reactive toward hydrolysis and many investigations have been performed concerning the modification of titanium precursors to control their reactivity. Titanium butoxide was used as a main precursor, while the other components were introduced as telluric (VI) acid (H$_6$TeO$_6$), selenous acid (H$_2$SeO$_3$), boric acid (H$_3$BO$_3$) and zinc acetate [Zn(O$_2$CCH$_3$)$_2$.2H$_2$O]. According to XRD analysis the heat treated up to 300°C gels exhibit a predominantly amorphous phase and metallic tellurium or TiO$_2$ (anatase). The amount of amorphous phase gradually decreases with increasing the temperature but it is still found up to 500°C. Further increasing of the temperature (700°C) result in a obtaining of polyphase products containing several crystalline phases simultaneously (rutile, anatase, TiTe$_3$O$_8$ and ZnTiO$_3$). The average crystallite size of TiO$_2$ (anatase) (calculated using Sherrer’s equation) in the powdered samples heat treated at 400°C is about 10 nm. It is observed that the addition of H$_2$SeO$_3$ or H$_3$BO$_3$ stimulates the earlier TiO$_2$ (anatase) crystallization about 300°C while at presence of Zn acetate or H$_6$TeO$_6$ it appears at higher temperatures 400 and 500°C, respectively. For comparison, at heating of pure Ti butoxide anatase crystallizes about 400°C.

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Keywords: sol–gel, powders, X-ray diffraction.
PREPARATION, STRUCTURE AND SPECTROSCOPIC ANALYSIS OF Mg-SUBSTITUTED NaMnPO₄ AND LiMnPO₄ PHOSPHO-OLIVINES

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Owing to high energy density, high safety and long-term durability, LiMPO₄ (M = Fe, Mn, Co, Ni) phopsho-olivine materials have received a great deal of attention as promising electrode materials in powerful batteries. To meet the current requirements for cheaper “green” batteries the recent research is focused to the sodium analogues of phospho-olivines, NaMPO₄, and particularly to NaMnPO₄.

Mg-doping in LiMnPO₄ is found to be an effective approach to improve its rate capability. With the expectation of a similar effect, here, we have examined the Mg substitution for Mn ions in the olivine-type structure of NaMnPO₄. The replacement of Mn ions with small amounts of Mg ions (up to 15 at.% in respect to Mn) ensures: (i) Dilution and reduction in the crystal lattice of the Mn³⁺ ions that are responsible for the structure instability of the desodiated phase MnPO₄ (ii) Reduction of interfacial strain related to the large volume change in the phase boundary NaMnPO₄/MnPO₄ during the electrochemical cycling.

To prepare NaMn₁₋ₓMgxPO₄ phospho-olivines we have designed a special synthesis route based on ion-exchange reactions at low temperature using Mg-substituted dittmarite-type precursors KMn₁₋ₓMgxPO₄.H₂O as structure-directing templates. For comparison the corresponding lithium analogues LiMn₁₋ₓMgxPO₄ have been also synthesized by the same method. The structure, spectroscopic characteristics and morphology of the target MMn₁₋ₓMgxPO₄ (M = Na, Li) phospho-olivines and initial dittmarite precursors KMn₁₋ₓMgxPO₄.H₂O are studied by Rietveld method, IR spectroscopy and SEM.

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Keywords: phospho-olivines, Mg doping, NaMnPO₄, LiMnPO₄.
NOVEL PARAMAGNETIC PLATINUM-BASED COMPLEXES WITH BIDENTATE N,N-DONOR LIGANDS – PYRIDINE-2-AMINE AND PYRIDINE-4-AMINE

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This work is a part of our project focused on the synthesis and characterization of new anticancer platinum-based polynuclear complexes from the “Platinum Blue” type with N,N-containing heterocyclic amines – pyridine-2-amine (2-AP) and pyridine-4-amine (4-AP). The high effect of pharmacological activity among the organic compounds from this class stimulates many research efforts to synthesize their metal complexes with expected properties as drugs. In this study, the intensively-colored paramagnetic high oxidation platinum compounds were obtained with bidentate chelating ligands containing pyridine-N and exocyclic NH₂-donor groups instead of classical open and cyclic amides and imides. The aim of the research was to find out the impact of the position of the amino group towards the pyridine N-atom on the structure of the “Platinum Blue” complexes.

Two platinum paramagnetic complexes, respectively the trinuclear Complex I \( \text{C}_{20}\text{H}_{30}\text{Cl}_5\text{N}_8\text{O}_3\text{Pt}_3 \), green) and the tetranuclear Complex II \( \text{C}_{25}\text{H}_{34}\text{Cl}_4\text{N}_{10}\text{O}_2\text{Pt}_4 \), blue), have been synthesized during the interaction of \( \text{PtCl}_4^{2-} \) and 2-AP (M:L=1:1) in mixed solvent \( \text{C}_2\text{H}_5\text{OH/H}_2\text{O} (1:1) \). The pH value of the systems was adjusted using KOH solution. The achieve the tetranuclear structure of the second complex, the reaction system was diluted with more 20 mL \( \text{C}_2\text{H}_5\text{OH/H}_2\text{O} (1:1) \) after 3 days. The dinuclear Pt(III) Complex III \( \text{C}_{10}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_3\text{Pt}_2 \), yellow) have been obtained in aqueous solution using 4-AP (M:L=1:1).

The reactions were monitored by potentiometric and UV-Vis spectroscopy methods. The solid-state and solution structure of the complexes were characterized by UV-Vis, IR, EPR and NMR spectroscopy.

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Keywords: pyridine-2-amine, pyridine-4-amine, platinum complexes.
USING QUANTUM MECHANICS FOR CRYSTAL STRUCTURE SOLUTIONS: 4-(2-PYRIDYLAZORESORCINOL

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We performed a quantum mechanical study of two stable planar tautomeric forms of 4-(2-pyridylazo)resorcinol (PAR) at the MP2/cc-pVDZ level of theory (see Fig. 1).

As expected the OH tautomer of the compound has about 15 kJ.mol\(^{-1}\) lower energy than the NH tautomer (in the gas phase). The powder X-ray diffraction pattern of PAR was recorded and used for Rietveld refinement and the crystal structure elucidation using the two tautomers as rigid bodies within the EXPO2014 software. The attempts to use the NH tautomer in order to fit the experimental and the calculated curve led to a bad conversion of the structural parameters. When the movable atom H\(_{20}\) was set to relax in the course of simulation annealing, it led to the OH tautomer of PAR. The same result was obtained when the N\(_9\)N\(_{10}\)C\(_{11}\)C\(_{12}\) angle is left to relax in the course of a simulation annealing. Obviously, the planar OH tautomer is the only present one in the solid state.

The final factors after the structure elucidation simulation annealing procedure are: Rwp = 16.607 and Rp = 11.225; the G factor is 1.129317 (with respect to the OH tautomer). The final unit cell parameters in the P 21/n space group (monoclinic) are: a = 13.6870 Å, b = 18.9889 Å, c = 3.7720 Å, β = 95.875°. The FWHM parameters are: U = 3.4835, V = –0.4230, and W = 0.0527.

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PHASE TRANSITIONS DURING WASHING OF KTENASITE-LIKE MINERALS

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The copper hydroxy-sulfate minerals are an important part of the oxidation zone of copper sulfide deposits. Due to their specific conditions of formation, narrow limits of stability, they are very informative about the conditions of hypergene alteration processes. Instead of co-precipitation, some of them (brochantite, langite, posnjakite) could be obtained by water treatment of high alkaline (pH = 6.5-7.5) copper hydroxy sulfate minerals with ktenasite type structure and general formula \( \text{Cu}_4(\text{OH})_6(\text{SO}_4)M^{2+}(\text{SO}_4)\cdot n\text{H}_2\text{O} \) (\( M^{2+} = \text{Zn, Cu, Ca, Cd, Mn} \); \( n = 3, 4, 6 \)) [1].

The current study presents the results of laboratory testing of phase formation from copper hydroxy-sulfate minerals with ktenasite type structure. The results of experimental research reveal that water treatment of ktenasite-like minerals causes formation of different hydrated copper sulfate hydroxy mineral phases depending on the speed of removal of the ion pair \( M^{2+}\text{–SO}_4^{2–} \). It was found that the release rate of the pair can be controlled by: the mineral/water amount ratio and/or the method of treatment – in dynamic or static mode. The rate of the ion pair releasing in static conditions depends only on the rate of diffusion equalization of the concentrations between the two environments: the interlayer spacing and the washing distilled water. In a static mode a large amount of washing water provides greater difference in concentrations and reduces the boundary layer around ktenasite particles, wherein the concentration of the ion pair increases. In dynamic mode, due to continuous supply of clean water, constant maximum difference in concentrations is kept which causes removal of the ion pair with some water.

In both modes the treatment with a greater quantity of water leads to formation of phases with lower water content, as a result of release rate of the ion pair. At high rate the anhydrate brochantite \( \text{Cu}_4(\text{OH})_6(\text{SO}_4) \) is formed. In the smooth exit (slower rate) of the ion pair \( M^{2+}\text{–SO}_4^{2–} \) causes a gradual hydration of the hydroxide layer surface with water molecules, forming hydrated minerals posnjakite \( \text{Cu}_4(\text{OH})_6(\text{SO}_4)\cdot \text{H}_2\text{O} \) and langite \( \text{Cu}_4(\text{OH})_6(\text{SO}_4)\cdot 2\text{H}_2\text{O} \) will remain stable at further washing.


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Keywords: brochantite, langite, posnjakite, water treatment.
TRANSFORMATION OF AUSTRALIAN PERLITE IN PHILLIPSITE AND ITS POSSIBLE USE AS ION-EXCHANGER

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A supplementary method was elaborated to nano-sized zeolite EMT preparation, which utilizes the waste mother waters from this synthesis for transformation of natural perlite into phillipsite. The method is reproducible and cheap and was applied to perlite sample from Australian field deposit. One of the obtained phillipsite samples was tested as ion-exchanger with solutions containing K⁺, Cs⁺ and Sr²⁺ for simulated radioactive fixation of these ions. It was found that the fixation of these ions with time is better fitted, applying pseudo-second-order kinetic model.

Cation-exchange effectiveness for Cs⁺ and Sr²⁺ of the obtained phillipsite sample was also tested in conditions of solutions, contaminated with nonionic surfactant Pluronic 123. The obtained distributions coefficients for K⁺, Cs⁺ and Sr²⁺ ions for the phillipsite sample, prepared from Blue Pacific field are comparable or better than the ones, reported in the literature for synthetic titanium octahedral molecular sieve.

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Keywords: perlite, synthesis, phillipsite, cation-exchange.
Nanostructured semiconductor oxide films have wide applications in different electronic, optical and sensing devices as well as in photocatalytic purification of waste waters.

Thin Oxide films (CeO$_2$, TiO$_2$) are coated on glass substrates by ultrasonic spray pyrolysis technique using metal salts in alcohol/water solution as a source material. The films were obtained at different substrate temperatures and deposition time.

The properties of nano-composite films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), ultraviolet–visible absorption spectroscopy (UV–vis) as a function of the deposition parameters.

The XRD patterns revealed that all films are nanostructured. The TiO$_2$ precursor resulted in the exclusive formation of Ti$_4$O$_7$ Magneli type phase. No additional crystallographic phase were detected on the X-ray diffractograms.

The obtained thin films have potential application as electrodes for oxygen reduction or photocatalysts.

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Keywords: oxide thin films, spray pyrolysis, semiconductors, surface morphology.
This study presents successful exchange of thallium cations in the clinoptilolite channels. Used material is clinoptilolite tuff from Beli Plast deposit, Bulgaria. Fully exchanged thallium forms of HEU–type zeolites have not been reported so far. Detailed description of thallium positions is reported for ZSM5 [1].

Here, the ion exchange procedure was performed at 90°C with 1N solution of TlNO$_3$ for 3 days. EDS analysis detected major thallium content and small amounts of Ca and K. Structural details obtained by PXRD Rietveld refinement reveal thallium positions in the three channels of clinoptilolite microporous structure. Thus, Tl$^+$ cations are located in three sites: Tl1, (Tl2 and Tl2′ – close to each other), and Tl3 in the channels A, B and C respectively (Fig. 1). Site Tl1 is located in the 10-member ring channel A. This position is shifted towards the centre in comparison with original sodium position in clinoptilolite. Site Tl1 is not fully occupied and identical position Tl1′ (distance Tl1 – Tl1′ 2.58 Å) is allowed. Site Tl2 is in the centre of the 8-member ring channel B, where H$_2$O molecule usually stays. A small amount of Tl cations are located in site Tl2′ close to Tl2 (distance – 2.42 Å). Site Tl3 is located in the 8-member ring channel C near to the original potassium position.


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**Keywords**: clinoptilolite, Tl exchange, Rietveld refinement.
THE EXPANSION OF THE LOW-GROWTH InGaAs LAYER AND CHARACTERIZATION

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InGaAs and InAlAs monolayer compound can grow with the MOCVD. However, the real challenge is to grow these structures with the conventional high magnifications MOCVD. Because the compounds of semiconductor’s thickness is smaller than 5nm in the active area of typical quantum cascade laser structure.

Therefore, firstly the growth rate is reduced and the thickness of the required parameter changes made to control precisely. In this study examined changes in thickness depending on these parameters.
THE GROWTH OF InGaAs / InAlAs SUPERLATTICES AND CHARACTERIZATION FOR PRODUCT QUANTUM CASCADE LASER

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The effects of various growth parameters were understood by detailed study on the material properties of InGaAs and InAlAs. The overall optimization of one layer InGaAs and InAlAs growth made, when separately optimized structures are grown together in a more precise thickness obtained by XRD scans.

Many superlattice layers in order to find potential problems that may occur during growth is enlarged. In this work, difficulties may be encountered is discussed in detail.
INFLUENCE OF TiO$_2$ ON THE THERMAL STABILITY AND CRYSTALLIZATION OF GLASSES WITHIN TeO$_2$-Bi$_2$O$_3$-Nb$_2$O$_5$-ZnO SYSTEM

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Currently intensive search is going onto find dielectric materials for Low Temperature Cofired Ceramics (LTCC) technology, that are applicable in wireless communication and broadcasting industry. In the last years as a preferred method for preparation was used melt quenching and crystallization from glasses (glass-ceramics). The tellurite glass materials as a matrix are very suitable due to low melting temperature, chemical resistance, good dielectric properties and good solubility of heavy metal ions. In this study we selected the TeO$_2$ – based glasses containing Nb$_2$O$_5$ and Bi$_2$O$_3$ up to 10 mol %, ZnO from 5–10 mol %, while the TiO$_2$ varies from 5–50 mol %. The batches of about 10 gr. were melted in silica crucibles at temperature between 800–1100°C. The obtained glasses were transparent and yellow colored (TiO$_2$ up to 20 mol %). The thermal stability of the samples was determined by DTA using the difference $\Delta T$ between exothermic peak of crystallization ($T_x$) and data for glass transition temperature $T_g$ ($\Delta T = T_x - T_g$). The crystallization behaviour of not vitrified quenching samples was investigated by X-ray diffraction analysis. Several crystalline phases were identified, between them more important are ZnTeO$_3$ and TiTe$_3$O$_8$ (in compositions above 20 mol % TiO$_2$) due to their good dielectric properties. The analysis of spectra shows that network of glasses consist TeO$_4$ (TBP) units, TeO$_{4,1}$ or more complicated units Te$_2$O$_5$, Te$_3$O$_8$ as well NbO$_6$ octahedra and ZnO$_4$ groups. This combination of structural units contributes for better kinetical stability of the amorphous phases. A comparison was made for thermal stability of melt quenched and prepared compositions by sol-gel method. It was proved that the selected compositions possess advantages that could be used for the synthesis of glass-ceramics containing TiTe$_3$O$_8$ and ZnTeO$_3$ with specific properties.

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Keywords: glass – ceramics, thermal stability, structure, properties.
X-RAY POWDER DIFFRACTION OF
(Yb$_{0.007}$Na$_{0.05}$)Ca$_{0.72}$Sr$_{0.223}$F$_2$ AND (Yb$_{0.006}$Na$_{0.04}$)Ca$_{0.917}$Sr$_{0.073}$F$_2$

CRYSTALS

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The object of study are determination of the unit cell parameters changes of preliminary constituted, co-doped Ca$_{1-x}$Sr$_x$F$_2$ fluoride crystals and the influence of Ca$^{2+} \rightarrow$ Sr$^{2+}$ replacement to the crystal lattice. The indexing of the XRD pattern is performed by the PDI software package [1]. The crystal system (Yb$_{0.007}$Na$_{0.05}$)Ca$_{0.72}$Sr$_{0.223}$F$_2$ was determined as cubic with space group $Fm\bar{3}m$, $a = 5.53795(22)$ Å, $D_x = 0.050$, $F_{14} = 116.87(.009, 14)$.

Both crystals are grown from repeatedly purified fluorspar and synthetics of SrF$_2$, YbF$_3$ and NaF. The main and trace elements chemical composition of the crystals were obtained by ICP-OES and LA-ICP-MS measurements. The trace elements content were determined about a ppm for Ce, Sm, Eu, Er and Pb (used as scavenger in the growing procedure) and ~10 ppm for Y.

The unit cell parameters increase with the Sr content augmentation. Such behavior would be quite slightly affected by the negligible doped concentrations of Yb and Na.


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Keywords: lasant fluorite crystals, element traces, powder XRD, unit cell parameters.
UV-VIS-NIR STRUCTURAL STUDY OF (Yb, Na)-CO-DOPED CALCIUM-(STRONTIUM) FLUORIDE SINGLE CRYSTALS

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The Yb-doped optical fluoride crystals are promising about femtosecond lasing issues. By Bridgman-Stockbarger method, there were grown such crystals (Fig. 1).

In NIR range are observable absorptions assigned to Yb$^{3+}$. Actually, the growth conditions by Bridgman methods are firmly reductive and the heterovalent isomorphism of 2 Ca$^{2+}$ (2 Sr$^{2+}$) substituted for Yb$^{3+}$ and Na$^+$ leads to structural changes. With the Yb$^{3+}$ concentration rising, the possible variety of Yb$^{3+}$ sited positions in the fluoride lattice also rises. The last resulted in strong Yb-clustering processes about the crystal system 1.8%(YbF$_3$),2.5%(NaF):CaF$_2$, which is not expressed about the system 1.8%(YbF$_3$),2.5%(NaF):Ca$_{0.67}$Sr$_{0.33}$F$_2$.

The MIR range reveals the existence of residual concentrations of O$^{2-}$, OH$^-$ groups, as well as CO$_2$ and CO, and traces of REE and TM impurities in ~ few ppm.

The UV-VIS spectral range again exhibits the characteristic high level of transmittance and low absorption and total reflection, typical about cutting-edge optical materials as the crystal fluorides. Exceptional are two intervals, respectively between 380–340 nm and 274–190 nm, possessing quite high absorption (almost 97%). About the first absorption interval, they should be responsible optically active centers of Yb$^{2+}$ and N$^+$, otherwise, about the second one interval the impact is upon O$^{2-}$ and OH$^-$ groups, as well as oxides and halides of traced REEs and TMs [1].


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Keywords: heterovalent isomorphic structural lattice changes, ytterbium clustering.
EPR AND ULTRASONICS BEHAVIOUR IN (Yb, Na)-DOPED LASANT ALKALINE-EARTH FLUORIDE CRYSTALS

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EPR analyses (9.23 GHz) about the co-doped lasant crystals 1.8%(YbF3),2.5%(NaF):Ca0.67Sr0.33F2 and 1.8%(YbF3),2.5%(NaF):CaF2 reveal that more dopants (Yb3+ and Na+) are incorporated in the second crystal structure as far as the used EPR technique is not sensitive to coupled electrons. The Bridgman growth conditions are firmly reductive, thus Yb3+ dominates at least of an order to Yb2+. The bigger Sr2+ radius prevents fluent doping in the Ca0.67Sr0.33F2 crystal matrix.

Performed ultrasonics study reveals that both crystal systems possess different longitudinal propagation wave velocities, around 6000 m/s vs. 6600 m/s for the co-doped mixed and single fluoride matrixes. Finished lasant windows from both crystal systems exhibit that although the various dopants incorporation levels, the attenuation coefficient is less in the lowest grown boules thirds and rises to the middle thirds, but finally about the highest crystal boules’ thirds, it undergoes further decreasing almost to initial values. The last briefly expresses the overall successive crystal growth stage conditions history. In the initial stage, residual tensions disrupt the normal crystal growth criterion mechanism due to trapped impurities existence or/and several nucleation centers. In the middle stage, the crystals should grow exclusively pure, and during the last growing stage, there are again residual tensions and edging effects, where the dopants stoichiometry is deviated away from the constituted one due to their species exhausted ions.

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Keywords: lasant fluoride crystals, EPR, ultrasonics, normal crystal growth criterion.
NEW “PLATINUM BLUES” OF ALANTOIN AND CREATININE – A STUDY ON THE IMPACT OF THE FORMAL REDOX POTENTIAL ON ANTIPROLIFERATIVE PROPERTIES

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The metal complexes that can be activated in the reducing environment of cancer cells, thus serving as prodrugs are of great interest. 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 alantoin and creatinine. It was found that processes of chemical and electrochemical oxidation lead to formation of platinum oligonuclear species with different chain lengths and formal Pt\(^{II}/Pt^{III}\) ratio. The properly selected conditions of the electrochemical experiment are a prerequisite for directed synthesis of polynuclear complexes with controlled chain length and the formal oxidation state of the platinum ions, and hence a desired value of the formal redox potential. The determined values of the formal redox potentials are in the range: – 0,2V to 0,5V. 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 structure of the newly synthesized complexes was studied by IR, UV/Vis and electrochemical methods for analysis.

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COORDINATION OF BIS((DIMETHYLPHOSPHINYL)METHYL) AMINE. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A MONONUCLEAR OCTAHEDRAL COPPER(II) COMPLEX

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The polydentate ligand bis((dimethylphosphinyl)methyl)amine (L) coordinates by the formation of five-membered N,O-chelate rings in mononuclear complexes or as a bridge O,O-linking between metal ions in polynuclear structures. It was established that the mode of coordination depends on the nature of the metal ions used and the reaction conditions. Here we present the synthesis, single-crystal structure and spectroscopic characterization of its mononuclear copper(II) complex with composition [CuL2]Cl2·2H2O. The compound crystallizes in monoclinic Cc space group with cell parameters a = 13.077(12) Å, b = 19.074(17) Å, c = 12.612(15) Å, β = 121.04(2)° and Z = 4. Its molecular structure consists of discrete six-coordinate copper(II) cations, two chloride anions and two water molecules. The two ligands are coordinated in an O,N,O-tridentate mode. Cu2+ ions in the CuO4N2-chromophores exhibit tetragonally compressed octahedral coordination.

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Keywords: octahedral copper(II) complex, amino-functionalized phosphine oxides, single-crystal structure.
EXPERIMENTAL AND THEORETICAL STUDY ON THE MOLECULAR AND ELECTRONIC STRUCTURE, SPECTROSCOPIC PROPERTIES AND COORDINATION BEHAVIOUR OF THE LIGAND 2,2’-DIPYRIDYLAMINE

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The nature of the ligands at the construction of “nonclassical” chemotherapeutic agents is very important because they are able to control the reactivity of the metal ions. Therefore, the study on the nature and coordination behaviour of the ligands is of crucial meaning to achieve cytotoxic properties.

Here we present a combined theoretical and experimental study of the molecular and electronic structure of 2,2’-dipyridylamine (dpa). This investigation have been carried out in order to predict the mode of its coordination at different reaction conditions and solvents. The molecular geometry parameters were calculated in gas phase using three different methods RHF/6-31G(d), B3LYP/6-31G(d) and MP2/6-31G(d), and the theoretical data were compared with single-crystal analysis data obtained in respect to the mutual location of donor functional groups. The conformational analyses (B3LYP/6-31G(d)) performed in gas phase and implicit aqueous and carbon tetrachloride solutions with neutral dpa, its protonated “acid”, the deprotonated “conjugated base” and zwitterion forms have shown the most stable conformers. The vibrational frequencies of the fundamental modes of the compound and its conjugated forms have been precisely assigned and analysed and the theoretical results were compared with the experimental vibrations. The best coincidence of the calculated and experimental IR spectra was found for the theoretical structures obtained with geometry optimization (B3LYP/6-311+G(d,p)) using the Z-matrix from the X-ray diffraction analysis. The comparison of the calculated IR parameters with the experimental spectroscopic data reveals the conformational preference in solid state and solution. Molecular electrostatic potential maps have been constructed and used to display the charge localization and to evaluate reactive sites for nucleophilic attack of the molecular systems in solution.

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Keywords: 2,2’-dipyridylamine, chrystal structure, quantum-chemical calculations, IR analysis, coordination behaviour.
NEW Pt<sup>IV</sup> COMPLEXES OF N,O-CONTAINING LIGAND 1,3,5-TRIAMINO-1,3,5-TRIDEOXY-CIS-INOSITOL WITH POTENTIAL ANTITUMOR ACTIVITY

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Transition metal complexes offer many advantages over the organic-based drugs, such as a wide range of coordination numbers and geometries, accessible different redox states, ‘tuneability’ of the thermodynamic behavior and kinetics of ligand substitution and a structural diversity. Nowadays, the design of innovative metal-based anticancer drugs aims to achieve a different mode of antitumor action and better targeting strategies. In this respect, the kinetic inertness and the two additional coordination sites of the octahedral platinum (IV) complexes are a prerequisite for overcoming the cisplatin’ drawbacks. The proper choice of the ligands in the outer and inner coordination sphere of Pt<sup>IV</sup> could model coordination compounds with ‘slow’ metal-ligand exchange rates comparable to those of the cell division processes, good water solubility and thermodynamic stability of Pt-D bonds.

This study deals with the structural characterization of new Pt<sup>IV</sup> complexes with 1,3,5-triamino-1,3,5-trideoxy-cis-inositol (taci) in solid state and in solution using single crystal X-ray diffraction and NMR spectroscopy. The ligand possesses six donor functional groups, three NH<sub>2</sub>- and three OH-groups alternating in axial or equatorial positions, respectively, which give four different modes of coordination. By changing the acidity of the medium, the molar ratio M:L and the counterions, three new complexes were obtained. In the complex [Pt(taci)<sub>3</sub>]<sub>3</sub>2DMF (1) (M:L=1), platinum has octahedral Pt(N<sub>3</sub>) coordination of three iodides and three taci-amino-nitrogens.

In the complex [Pt(taci)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub> (2) (M:L=2), the octahedral coordination of Pt<sup>4+</sup> is constructed with six axial amino-nitrogens from two taci molecules (PtN<sub>6</sub>) and four NO<sub>3</sub>– ions are disposed in the outer coordination sphere. A complex with composition [Pt(taci)(taci<sub>4H</sub>CO<sub>3</sub>)]<sub>2</sub>H<sub>2</sub>O (3) and asymmetric coordination of one taci ligand through two axial deprotonated OH-groups and one equatorial NH<sub>2</sub>-group and symmetric N<sub>3</sub>-coordination of the second taci was obtained. The complexes (1) and (2) crystallize in monoclinic P2<sub>1</sub>/n space group and the complex (3) in orthorhombic Pnma space group.

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Keywords: Pt<sup>IV</sup>-complexes, nonclassical antitumor agents, structural characterization.
STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF HEAT ACTIVATED NICKEL-TITANIUM ARCHWIRES

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Heat activated nickel-titanium (NiTi) archwires are widely used in the initial stages of orthodontic treatment. These alloys have the ability to exhibit a shape memory effect which can be related to displacive (martensitic) transformation, which can be induced by temperature variation or mechanical influence (stress).

The aim of this work is to study the effect of regular usage of archwires on their microstructure, chemical composition and phase transition temperature. For this purpose, two types of dental archwires with dimensions 0.016 × 0.022 inches were chosen: as-received and used heat-activated NiTi wires, produced by the company 3M Unitek, Monrovia, CA, USA. The analyses were carried out by the following techniques: X-ray diffraction analysis (XRD), Scanning Electronic Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Differential Scanning Calorimetry (DSC).

The room temperature XRD patterns show typical picks for NiTi alloy with austenite type structure. The phase transition was studied by means of DSC measurements in the temperature range from –50 to +50°C. It was shown that for NiTi archwires, besides the austenite to martensite transition, there is a presence of a rhombohedral intermediate phase (R phase). The results from EDS demonstrate that there is not remarkable change of the chemical composition of the surface of the investigated orthodontic archwires. SEM results show changes of the morphology of the wires after usage.

The results obtained within this study contribute to the establishment of some peculiarities of thermal behavior and the shape-memory effect of the archwires.

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INFLUENCE OF THE STRUCTURE AND MORPHOLOGY OF MnO₂ ON THE ELECTROCHEMICAL PERFORMANCE OF SUPERCAPACITORS SYSTEMS

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Manganese oxide is a promising electrode material for high energy supercapacitors because their high specific capacitance, low cost, natural abundance, and environmental benignity.

In the present work the effect of structure and morphology of nanosized manganese oxide is studied by physicochemical analysis (X-Ray diffraction, Transmission electron microscopy and Scanning electron microscopy) and electrochemical tests (charge/discharge galvanostatic cycling).

The supercapacitor cell is composed by a positive electrode – a composite with teflonized acetylene black(XC-35) and 50% MnO₂, negative electrode of activated carbon (Cabot CGP Super, 1800 m²g⁻¹) with addition of PTFE and carbon black (Cabot SC2) and alkaline electrolyte (7MKOH with addition of 35 gl⁻¹ LiOH). The cells thus assembled are subjected to electrochemical investigation at different current loads (30–420 mAg⁻¹) and prolong cycling (up to 1000 cycles) using Arbin BT2000 apparatus.

The results from the electrochemical investigations show that the structure and morphology of MnO₂ play a significant role on the supercapacitor performances. The highest discharge capacity (150–200 Fg⁻¹) and most stable cycle ability at prolong cycling (above 1400 cycles at 60 mAg⁻¹) are observed for pyrolusite phase of pure MnO₂ with crystalline size 5 nm.

Acknowledgement: The financial support of the BNSF under project DFNP-42/21.04.2016 and DFNI E02/18-2014 are gratefully acknowledged.
CeO$_2$-ZrO$_2$ system is one of the most studied mixed metal oxides in the literature due to its important role in the operation of automotive catalysts [1]. To enhance the redox properties and thermal stability of pure ceria, zirconia is often mixed as an additive to form solid solutions [2]. In this study, a series of nanosized ceria-zirconia mixed oxides were prepared using template-assisted precipitation with urea followed by a hydrothermal treatment step at two different temperatures (373 K or 413 K). The obtained materials were characterized by X-ray diffraction, nitrogen physisorption, UV-Vis spectroscopy, temperature-programmed reduction (TPR) with hydrogen and their potential application in catalysis was tested in ethyl acetate combustion as a model reaction for total oxidation of volatile organic compounds.

The results show that the addition of zirconia to ceria leads to improved ability for oxygen absorption/release observed with the mixed ceria-zirconia samples during the conducted TPR measurements resulting in enhancement of their redox properties in comparison with pure ceria. The mixed oxide samples prepared using higher hydrothermal treatment temperature (413 K instead of 373 K) possess more finely dispersed tetragonal zirconia particles and significantly higher total pore volumes due to larger pore sizes, while the BET specific surface areas remains similar. Thus improved textural characteristics favour the higher catalytic activity found with the mixed ceria-zirconia samples synthesized by using higher hydrothermal treatment temperature.


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Keywords: CeO$_2$-ZrO$_2$ nanocomposites, precipitation with urea, ethyl acetate combustion.
DIFFRACTION METHODS FOR ANALYSIS OF LAYERED 
\( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) AS CATHODE MATERIALS

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The demand for searching cheaper electrode materials increases continuously during the last years. Since lithium ion batteries are still expensive, sodium ion batteries have been advanced as alternative sources. Recently, we have proposed sodium deficient transition meta oxides as low-cost electrode materials. The idea is to develop hybrid alkaline batteries where sodium nickel-manganese oxides are directly used as electrode materials in lithium ion batteries instead of expensive lithium analogues [1, 2].

In this contribution we demonstrate the advantages of the diffraction methods (such as XRD and TEM analyses) for studying structural changes during reversible electrochemical intercalation of lithium and sodium into layered \( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) oxides with \( P3 \)-type structure. The alkaline intercalation into \( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) is carried out in model two-electrode cells of the type \( \text{A|APF}_6(\text{EC:DMC/DEC})|\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) (\( \text{A} = \text{Li}^{+}, \text{Na}^{+} \)). The cells are cycled at different rates in a broad potential ranges. The results show that the \( P3 \)-type \( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) is able to intercalate lithium reversibility in high amount, as a result of which a reversible capacity of about 120 mAh g\(^{-1}\) at the potential range of 2.5–4.5 V and C/30 rate is achieved. The ex-situ XRD and TEM analyses reveal a transformation of the initial \( P3 \)-type of structure into \( O3 \)-type one during lithium cycling. In contrast, \( P3\)-\( \text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) remind unchanged after sodium intercalation. This study shows the possible application of sodium deficient nickel-manganese oxides with \( P3 \)-type structure as cathodes in both hybrid alkaline ion batteries and sodium ion batteries.

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_Keywords:_ sodium deficient nickel-manganese oxides, layered structure, lithium-ion batteries, sodium-ion batteries.
ENHANCED OF STRUCTURAL AND PHOTOCATALYTIC PROPERTIES OF ZnO FILMS ONTO ALUMINUM FOIL PREPARED AT DIFFERENT TEMPERATURES

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Nanostructured thin films are deposited on commercial aluminum foil via sol-gel method and dip coating technique from zinc acetate complex solutions. The films annealed at different temperatures (100, 300 and 500 °C) are characterized by Scanning Electron Microscopy, X-ray diffraction and UV-vis analysis. It is established that the different temperatures cause changes in the morphology, composition and structure of ZnO films. The rise of annealing temperature leads to more pronounced ganglia-like surface. The ZnO crystalline structure is hexagonal wurtzite. The size of nanocrystallites varies from 30 to 88 nm in dependence on the annealing temperature. Furthermore, the ZnO films are tested with respect to Malachite Green (MG) photodegradation in aqueous solutions upon UV-light and without any illumination. ZnO photocatalytic action is investigated at various initial dye concentrations (3, 5 or 10 ppm). The decolorization kinetics of MG in water is studied as a model system for contaminated wastewaters. Photocatalytic efficiency depends on the surface roughness. Nanostructured films, annealed at 500 °C show the highest efficiency, due to their greatest surface roughness. The obtained results are promising for optimization of zinc oxide sol–gel synthesis and its application for degradation and complete mineralization of organic pollutants from wastewaters.

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Keywords: ZnO sol-gel films, aluminum foil, annealing temperature, photocatalysis.
CALCULATE THE ROTATION KINETIC ENERGY OF THE FULL SYMMETRIC MOLECULES WITH CLIFFORD ALGEBRA

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The geometric algebra produces the new fields of view in the modern mathematical physics and molecular physics definition of bodies and rearranging for equations of mathematics and physics. The new mathematical approaches play an important role in the progress of physics. The exponential form of complex numbers is useful in the theory of rotational motions. The quaternion algebra, which was defined by Sir W. R. Hamilton, was generalized for the three dimensional complex numbers.

After presenting Clifford algebra and platonic solids, the rotating energy of platonic solids’s with Clifford algebra are defined. This calculation is applied to a Platonic solids, which are called as tetrahedron, cube, octahedron, ikosahedron and dodecahedron. Also, the vertices of Platonic solids presented in the Cartesian coordinates are calculated.

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Keywords: Clifford Algebra, rotating energy of platonic solids, platonic solids.
QUANTUM CASCADE LASER MODELLING
VIA NEXTNANO.MSB

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The infrared long wavelength quantum cascade laser system’s design and fabrication performed with compatible AlInAs/InGaAs structures knitted composition generally.

When the band-offset increased, increased difficulty with the disappearance of the formal compliance and consequent spontaneous radiation increasing the length, and hence the optical gain reduction. Another advantage of using the nextnano.msb version, the current–voltage characteristic can be obtained as output.
NEW DATA ON THE CRYSTAL MORPHOLOGY OF BRAZILIANITE  
(GALILÉIA, MINAS GERAIS, BRAZIL)

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Morphology of brazilianite NaAl₃(PO₄)₂(OH)₄ crystals from the Galiléia area, Minas Gerais, Brazil  
(part of the collection of DHC Ilia Deleff; Museum of Unique Crystals “Ilia Deleff”, University  
of Mining and Geology “St. Ivan Rilski”, Sofia) is studied by goniometric methods in order  
to determine the crystal forms. The Galiléia mine area includes also the original type mine  
for brazilianite Córrego Frio, where usually yellow-green crystals up to 10–12 cm have been  
reported [1–2]. On 29 crystal samples are described 25 crystallographic forms, among them  
14 new forms. The majority of brazilianite crystals are single terminated, spearhead shaped,  
elongated along the [001] zone, with observed dominant crystal forms for most of the studied  
crystals: i {210}, a {100}, w {201}, y {221}, q {121}, δ {223} and b {010}. In several cases are  
found the crystal faces x {101}, z {101}, θ {301}, μ {230}, g {111}, o {111}, ε {321}, r {253} and  
ρ {122}. Crystal forms found in single cases are: for sample N4 – ν {012}; for sample N10 –  
c {001}, ζ {332}, η {546}, κ {132} and λ {532}; for sample N26 – ξ {130} and n {011}; for sample  
N27 – π {223}. A new specific prismatic crystal habit of brazilianite is described, compared to  
the known crystal habits of brazilianite from Brazil and other countries worldwide [3–4] – spearhead  
shaped long-prismatic habit. Brazilianite has a 2a / (b + c) = 1.3 ratio, which is representative  
for the (I)a structural type, according to the crystal habit types of the paragenetic and chemical  
systematic of minerals [5]. In the case with the studied crystals, the dominant crystal habit can  
be denoted as (I)a[001].

Sofia (1999).

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Keywords: brazilianite, crystal, morphology, Brazil.
PHOTOCATALYTIC PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED COPPER SULFIDES

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Three copper sulfides (CuS, Cu\textsubscript{2}S and Cu\textsubscript{1.85}S) were synthesized using mechanochemical approach. The X-ray diffraction pattern and BET method were used to characterize the synthesized samples.

The photocatalytic degradation of representative organic dye pollutant, Methyl Orange (MO), was determined to evaluate the photoactivity of the mechanochemically synthesized CuS, Cu\textsubscript{2}S and Cu\textsubscript{1.85}S three copper sulfides. The control experiment shows that the MO is resistant to degradation during irradiation without photocatalyst. In case of MO which is an anionic dye, the intense peak at 463 nm was used to observe the overall photodegradation efficiency. It was observed that a blue shift was observed in the characteristic absorption peak. This might be due to demethylation of MO, which is most probably replaced with H atom. The three mechanochemically synthesized copper sulfides show the following photocatalytic trend for degradation of MO: Cu\textsubscript{2}S>Cu\textsubscript{1.85}S>CuS. The photodegradation of in the presence of mechanochemically copper sulfides was found to be a pseudo-first order kinetic process. The MO degradation rate constants of the samples were determined.

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Keywords: copper sulfides, mechanochemistry, photocatalysis.
POWDER XRD MICROSTRUCTURAL ANALYSIS OF THERMALLY TREATED SYNTHETIC FLUOR-HYDROXYLAPATITE

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Samples of nanosized synthetic Fluor-hydroxylapatite (SFHA) heated within the temperature range 400–910°C were studied by powder X-ray diffraction (PXRD) analysis. Description of the microstructural characteristics at different temperatures as well as their evolution during the thermal treatment were in the focus of investigations. The analysis of diffraction-line broadening was performed using Fullproff by the PseudoVoigt approximation and applying various size and strain models \([1]\). Williamson-Hall (WH) plot assuming Lorentzian profile broadening was used to evaluate the microstrain along some crystallographic directions. Certain consistencies of pattern in terms of domain sizes and microstrain appearance have emerged for the studied material upon heating and explanation for them is suggested.

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Keywords: apatite, Rietveld refinement, microstructural analysis.
STEP BUNCHING AND MACROSTEP FORMATION IN 1D ATOMISTIC SCALE MODEL OF UNSTABLE VICINAL CRYSTAL MOTION

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We introduced recently an atomistic scale model of irreversible vicinal crystal growth [1]. Important aspect of the model, since there is no step-step repulsion in it, is the formation of macrosteps but the step bunches retain a finite width and consist of both single and macrosteps. Thus, we obtained for two alternative sources of instability, biased diffusion and infinite Ehrlich-Schowebel barrier, the time-scaling of the quantities of interest – bunch size, bunch width and macrostep size in the two limiting regimes – of diffusion-limited (DL) and kinetics-limited (KL) growth [1].

Here we develop further this model allowing for the possibility for particle detachment from the steps and report results for unstable vicinal crystal evaporation. In this situation the instability sources, namely biased diffusion and SE, act differently and a number of models, both on atomic scale and of extended BCF-type is modelling sublimated systems. For our model we show that step bunching occurs with step-up diffusional bias when the adatom diffusion is fast (KL) and since we can change smoothly the number of diffusional steps $n_{DS}$ per growth-sublimation one, we are able to locate the onset of bunching with increasing $n_{DS}$. We analyse shape of the bunches, Fig. 1, and compare it to the growth case. We also show results for the time scaling of the bunch and macrostep size.

Fig. 1. Surface profile and the corresponding surface slope.

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Keywords: computer modelling; cellular automata; vicinal crystal growth; diffusion-limited vs. kinetics-limited.
The ability of a given compound to crystallize in more than one polymorph modification is among the most studied areas of modern solid state chemistry. Due to the different packing and/or molecular conformation the polymorph modifications differ in their physical and chemical properties, such as stability, solubility, density, melting point, dissolution rate, morphology, colour etc. The special case of polymorphism, closely related with tautomerism, is termed desmotropy. Based on numerous publications and definitions, it can be stated that if a compound can crystallize in more than one stable tautomeric form, it possess desmotropism. To the best of our knowledge, there are no examples in the literature on the isolation of more than two desmotrops of a given molecule.

The conformational behaviour of 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one was studied using a combination of X-ray diffraction, NMR spectroscopy in solution and solid state, and DFT calculations in gas phase. The compound can adopt four different tautomers, determined by the combination of the keto-enol tautomerism of pyrazolone and the attached 4-acyl carbonyl group.

The NMR analyses indicate that the keto-enol conformations with intramolecular H-bonding are preferred in solutions, which is in full agreement with the fact that all crystal phases were grown from yellow solutions. Potential energy surfaces simulations in gas phase show that each of the tautomeric forms has stable conformers, defined by energy minima, which could potentially be obtained in solid state. Crystallization trials produced five different crystal phases; three yellow and two colourless. The single crystal XRD and solid state NMR structural analyses revealed that three desmotrops are obtained, two of them as two different conformational polymorphs. So, that is the first record in the literature on the isolation of more than two desmotrops of a given compound.

The financial support by Swiss National Science Found (SupraMedChem@Balkans.Net, IZ74Z0_ 160515, SCOPES), Bulgarian Science Fund, projects UNA-17/2005, DRNF-02-13/2009, RNF-01/0110, and DRNF-02/01, and by EU, project FP7-REGPOT-2011-1/286205 “Beyond Everest”, is gratefully acknowledged.
STUDY OF THE STRUCTURAL CHARACTERISTICS OF NANOSIZED MnFe$_2$O$_4$ OBTAINED COMBUSTION SYNTHESIS. INFLUENCE OF THE TYPE OF FUEL

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Nanosized MnFe$_2$O$_4$ is partially inverse spinel with interesting properties and applications such as magnetic resonance imagine contrast agent, use to magnetic drug delivery for cancer treatment by hyperthermia. It is also use for the removing of heavy metals and toxic organic pollutants from waters. The manganese ferrite material is suitable as a catalyst and as an electrode material in asymmetric supercapacitors.

For the preparation of nanosized manganese ferrite the method of solution combustion synthesis is use which is based on the highly exothermic reaction between the starting reagents (oxidizer and fuel). In this work as a fuel is use a mixture of hydrocarbons and nitrogen containing fuels (glycine and glycerol) in various ratios aiming to follow the impact of the fuel on the structural characteristics of the obtained powders. The samples are thermally treated at various temperatures and in various atmosphere (air, argon).

The structural characteristics of the materials are studies by the methods of XRD diffraction, Infrared spectroscopy and Mössbauer spectroscopy.

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Keywords: MnFe$_2$O$_4$, XRD, Mössbauer spectroscopy, solution combustion synthesis.
The concept of molecular electronics, [1] based on the use of single molecules as building elements (wires, switches, rectifiers, etc.) and their further suitable assembly into working devices, has catalyzed intensive investigations in order to find such molecular level “hardware”. A synthesis of new tautomeric wires, based on hydroxypyridines, and investigation of their tautomeric and complexation properties in solution and solid state has been the aim of the study. The concept includes 2-hydroxypyridines linked via a π-electric bridge (double or triple bond). These ligands possess N-donor atoms at both ends, allowing in principle different metal ions to be coordinated at the individual Lewis basic sites, leading to formation of linear supramolecular polymers. Actually these linear polymers would play a role of molecular wire.

The structures of the ligands are as follow:

![B1](image1)

![B2](image2)

The compounds were synthesized using Hiyama-Heck reaction for obtaining their methoxy-derivatives and second reaction of demethylation leads to the target structures. Spectral investigations of stability of the target compound have shown some changes in spectra in solution by time. Different processes of crystallization were used to obtain a crystal structure of compounds B1 and B2 (solvent evaporation, slow cooling of the solution, vapour diffusion). The low solubility of the compounds play a significant role in this case, because only very few solvents can be used, mostly with high boiling points, which causes long evaporation times and thus crystallization processes.


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Keywords: molecular devices, tautomerism, supramolecular chemistry.
CRYSTAL STRUCTURES AND INFRARED SPECTRA
OF THE TUTTON COMPOUNDS Rb(Cs)₂Mg(CrO₄)₂·6H₂O
AND Rb₂Mg(SO₄)₂·6H₂O, AND OF SOLID SOLUTIONS
Rb₂Mg(Cr₁₋ₓSₓO₄)₂·6H₂O

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The crystal structures of Rb₂Mg(CrO₄)₂·6H₂O and Cs₂Mg(CrO₄)₂·6H₂O as well as those of solid solutions Rb₂Mg(Cr₁₋ₓSₓO₄)₂·6H₂O (0 > x < 1) were determined from single crystal X-ray diffraction data. They belongs to the group of Tutton salts, crystallizing isotypic to the respective sulfate and selenates in a monoclinic structure, which is characterized by isolated Mg(H₂O)₆ octahedra and CrO₄ tetrahedra, interlinked by hydrogen bonds and Rb⁺ and Cs⁺ cations.

Infrared spectra of the title Tutton compounds are discussed with respect to both the normal modes of the tetrahedral ions and the water molecules. The extent of energetic distortion of the isomorphously included sulfate ions as deduced from the values of Δν₃ (site group splitting) and Δν₃/νₛ (where νₛ is the centro-frequency value of the asymmetric stretches) is commented. The hydrogen bonds in the rubidium and cesium magnesium chromates are stronger than those in the respective selenates and sulfates as deduced from both the wavenumbers of ν₉D of matrix-isolated HDO molecules and the wavenumbers of νOH. On the basis of the spectroscopic experiments a conclusion was drawn that the chromate anions are stronger proton acceptors than the selenate and sulfate ions in the case of magnesium Tutton salts.

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PARAMAGNETIC POLYNUCLEAR PLATINUM COMPLEXES OF 5-FLUOROURACIL. II. DETERMINATION OF THE NUMBER, STOIHIOMETRY AND STABILITY CONSTANTS OF PLATINUM COMPLEX SPECIES FORMED DURING THE INTERACTION

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Since the discovery of the antitumor activity of cisplatin (by Rosenberg), its interactions with nucleotides and nucleobases have attracted attention in order to understand the mechanism of the antitumor activity at a molecular level. In the course of such investigations, dark blue platinum complexes called “platinum blues” were obtained. These reaction products themselves possess also antitumor activity. Despite the intensive efforts of many chemists to elucidate the identity of these compounds, their formulas and structure long remain unclear as the compounds were always obtained as mixtures and isolation of single compound is difficult. The several examples of the single-crystal structural determination of the representatives of this class show the mixed-valent paramagnetic polynuclear nature with Pt-Pt bond formation. In general, the amorphous nature of these compounds and their unreproducible composition restrict the understanding of the question such as metal-metal separation, delocalization of spins due to the presence of Pt$^{III}$-centers in a Pt chain and high antitumor activity.

This study aims to accumulate experimental data referring to the conditions for reproducible “platinum blues” formation on the basis of the interaction between K$_2$PtCl$_4$ and 5-fluorouracil. The processes of complex-formation were studied with the UV-Vis spectroscopy. The impact of the reaction conditions such as concentration, acidity of the medium, time, molar ratio, etc. were investigated. The number of complex species obtained during the interactions are identified computationally, and their composition was determined by the classical methods known as “molar ratios” and “isomolar series”. The stoichiometry of some platinum species formed in solution was proved using method of “corresponding solutions” and their stability constants were determined by computational methods.

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Keywords: “platinum blues”, 5-fluorouracile, stability constants, stoichiometry.
EFFECT OF CALCINATION TEMPERATURE
ON PHASE TRANSFORMATION AND CHEMICAL
DURABILITY OF FAYALITE WASTE

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The effect of calcination temperature on the phase evolution of an iron rich metallurgical
waste was studied in air. This waste remains after flotation of copper slag and contains
fayalite (copper silicate) as a main crystalline phase. Fayalite waste (FW) samples were
heated at 500, 700, 1000 and 1100° C for 3 hours. These temperatures were selected based
on simultaneous TG/DTA of FW. The changes of phase composition were investigated using
of XRD and FTIR analysis. Gradual up to complete transformation of initial minerals was
registered. The structure formed was observed by optical microscopy. The chemical durability
of FW and thermally treated samples were estimated by leaching test using ICP-AES.

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Keywords: structural phase transformation, copper slag, fayalite, chemical durability.
CERIA AND TITANIA OXIDES OBTAINED BY UREA ASSISTED HOMOGENEOUS HYDROLYSES METHOD AS CATALYSTS FOR ENVIRONMENTAL PROTECTION: EFFECT OF Ce/Ti RATIO

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Multi-component metal oxide materials reveal a great potential for a development of catalysts with desired design and tunable properties. Mesoporous metaloxide nanocomposites have been intensively studied in catalysis as simple approach for tuning the active sites by the formation of mixed oxides and/or supporting effects. In this study mesoporous titanium–cerium oxide materials with different composition were prepared by homogeneous precipitation with urea. The samples were characterized by XRD, UV–Vis, FTIR, Raman, temperature programmed reduction in hydrogen and their catalytic properties were studied in methanol decomposition and total oxidation of ethyl acetate as representative catalytic tests, supplying reduction and oxidation reaction atmosphere, respectively.

Both reactions have also essential impact solving the problems related to the environment protection as alternative fuel supplying hydrogen and VOCs elimination, respectively. Well crystallized materials with high surface area and pore volume were prepared. As compared to the monocomponent materials, bicomponent ones were characterized with higher dispersion, better textural parameters and improved redox properties. This affects the catalytic activity and selectivity of the samples in the methanol decomposition and ethyl acetate combustion, which could be successfully controlled by the Ce/Ti ratio.

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Keywords: nanostructured oxides, ethyl acetate combustion, methanol decomposition.
INVESTIGATION ON THE CRYSTALLIZATION BEHAVIOUR OF SODIUM-ALUMINOBOROSILICATE GLASSES WITH HIGH CONCENTRATIONS OF Ba AND Ti

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The efficient energy storage and energy consumption are some of the most acute and important problems nowadays. Thus, the synthesis and the investigation of the microstructure with respect to the physical properties of materials are of great importance. A substance well-known for a long time and with outstanding dielectric properties, as well as easy to prepare in the form of glass-ceramics, is barium titanate, \( \text{BaTiO}_3 \).

The present work reports the synthesis of \( \text{BaTiO}_3 \)-containing glass-ceramics by applying appropriate annealing programs and varying the ratio of \( \text{Na}_2\text{O} \) to \( \text{Al}_2\text{O}_3 \) from a compound sodium-aluminoborosilicate glass. The phase composition is studied by X-ray diffraction and additionally to the presence of \( \text{BaTiO}_3 \), also some silicate-based phases are detected. The microstructures of the obtained glass-ceramics are investigated by electron microscopy and depending on the ratio between \( \text{Na}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \), the presence of morphologically differing crystalline structures is concluded. Computed tomography is utilized to determine the volume fractions and size distributions of the barium titanate crystals in the glass ceramics and high degree of crystallization is observed.

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Keywords: barium titanate, crystallization, microstructure.
Type I restriction-modification enzymes in bacteria are multisubunit, multifunctional molecular machines that recognize specific, typically asymmetric, DNA target sequences of ~13 to 17 bp. Depending on the methylation status of adenine residues in the target sequence, three enzyme (1 Hsd S and 2 Hsd M) subunits either acting together as a typical methyltransferase or recruiting a pair of endonuclease motor subunits that enzymatically initiates translocation of DNA and eventually cleave non-specifically at apparently random sites. The type I RM system EcoR124I complex meets the sample standard required for cryo-EM procedures and the 3D reconstructions by single particle analysis. It has a molecular mass of about 400 kDa with low symmetry and highly flexible in its open conformation. One of our goals to understand each of the subunit interactions and with the DNA molecule during the cleavage activity and the potential role of EcoR124I pentameric complex in horizontal gene transfer mechanism.

While the first crystal structure of the motor (Hsd R) subunit was solved by our group, but no crystal structure of the methyltransferase (MTase) subunit has been reported. The available structural information is based either on poor resolution (~35 Å) model by a combination of negative staining cryo-EM and SAXS/SANS or computational modeling. The interdisciplinary approach of cryo-EM and X-ray crystallography caters perfectly to the objectives of the project. The aim is to solve atomic-scale structure of the trimeric MTase in complex with DNA using a combinatorial approach. The cryo-EM experimental data has been obtained for the EcoR124I pentamer in complex with a 30-mer dsDNA using FEI's Titan Krios. A preliminary model from the cryoEM data subset has been obtained and the in-house measurement of crystals of the HsdM subunit diffract to ~1.5 Å. The crystal structure and cryo-EM maps enable us to understand the structural transition between the native structure and in complex with dsDNA. The aim is directed towards understanding structural flexibility of the HsdS and HsdM subunits and the mechanism of MTase interaction with the motor subunit and conformational changes that occur upon DNA binding. Furthermore, we envisage to use computational methods to predict the trajectory of movements arising from the conformational transition and the rotations within the inter-domain hinges.

CRYSTALLOGRAPHIC STRUCTURE OF MULTILAYER SYSTEM
TiN/CrN DEPOSITED BY DC MAGNETRON SPUTTERING

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TiN/CrN multilayer coating system is a hard, wear resistant material which is widely used for cutting and forming tools and other components operating in an abrasive wear environment. This study offers a combined method of surface modification of tool steel including electron beam treatment (EBT), plasma nitriding (PN) and TiN/CrN multilayer deposition by DC (direct current) magnetron sputtering [1].

The crystallographic structure was investigated by XRD (X-ray diffraction) with Cu Kα characteristic radiation. The measurements were performed in symmetrical Bragg-Brentano (B-B) mode from 20° to 80° at 2θ scale. The step has been chosen 0.1° with counting time 10 sec. per step.

The microstructure of the obtained layers was investigated by Scanning Electron Microscopy (SEM), as backscattered electrons have been used. The accelerated voltage was 20 kV. The chemical composition was studied by Energy-Dispersive X-ray Spectroscopy (EDX).

The mechanical properties (i.e. hardness and Young’s modulus) were measured, as the experiments were performed using Nanomechanical tester (Brucker, USA). Prior to the indentation, the surface of the studied samples was polished.

The obtained results demonstrate the possibility of formation of hard and wear resistant multilayer coating of TiN/CrN. It was shown the opportunity of formation of surface coatings with good stoichiometry and great mechanical properties with the chosen technological parameters, applied during the deposition.


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Keywords: multilayer system TiN/CrN, magnetron sputtering, XRD.
SYNTHESIS AND CHARACTERIZATION OF SAMARIUM DOPED ZINC BOROPHOSPHATE GLASSES

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In recent years, zinc phosphate glasses doped with rare earths are actively investigated. The focus is to amendment of their optical, mechanical and thermal properties depending on the ratio of different components, with a view to their possible applications in optoelectronics, laser technology and solar energy.

The present research is directed to the synthesis and characterization of samarium doped ZnO-rich borophosphate glasses. The ratio of the main components – ZnO, B$_2$O$_3$, P$_2$O$_5$, the content of the dopant rare earth element Sm (as Sm$_2$O$_3$), and the conditions of synthesis and analysis are set on the basis of literature data and our previous studies. Two series samples are synthesized – no doped with a composition (68+x)ZnO – 18B$_2$O$_3$ – (14–x)P$_2$O$_5$ and doped – (67.5+x)ZnO – 18B$_2$O$_3$ – (14–x)P$_2$O$_5$ – 0.5Sm$_2$O$_3$, where x = 0, 2, 4, 6.

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 studied by powder X-ray diffraction, differential scanning calorimetry and infrared spectroscopy, and their optical properties – by photoluminescence analysis.

The obtained compositions are amorphous, homogeneous and transparent glasses except for the samples with the highest content of ZnO.

The synthesized zinc borophosphate glasses doped with samarium have potential for practical application in optical devices.

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Keywords: samarium doped zinc borophosphate glasses, x-ray powder diffraction, photoluminescence.
SYNTHESIS OF MICROPOROUS PRODUCTS FROM WASTE AMORPHOUS SILICA

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Unusual source of silica was applied for synthesis of microporous materials. During the recycling of spent lead car batteries, silica polymer composite is obtained. By thermal treatment the silica polymer composite is transferred to amorphous silica. Powder XRD investigation of the obtained pyrolytic silica confirms its amorphous character. This silica serves as a starting material for preparation of various types of microporous crystalline phases.

Using pyrolytic silica as a silica source and additionally applying appropriate chemical reagents, in hydrothermal conditions, various types of zeolites were prepared. Among them are zeolite P, faujasite and mordenite. From organic free gel, high silica zeolite ZSM-5 was also synthesized. The obtained microporous materials were characterized by powder XRD, Scanning electron microscopy (Fig. 1), Solid state MAS NMR and BET surface area analysis.

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Keywords: amorphous silica, synthesis, microporous products.
SYNTHESIS AND CHARACTERIZATION OF COPPER-MANGANESE FERRITES WITH THE COMPOSITION Cu$_{1-x}$Mn$_x$Fe$_2$O$_4$ SUPPORTED ON ACTIVATED CARBON

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Ferrite materials are attractive for the modern science due to their broad applications in electronics, catalysts, biology, medicine, etc. Depending on the location of the two-valent and three-valent ions in the crystal lattice of the spinel type ferrites can be classified as normal, inverse and partially inverse.

The present study addresses a synthesis of mixed copper-manganese ferrite catalysts with compositions Cu$_{1-x}$Mn$_x$Fe$_2$O$_4$, where x=0; 0.2; 0.4; 0.6; 0.8 and 1, supported on active carbon. Consequently, the focus is on the characterization of the catalyst structure and their performance in methanol decomposition to H$_2$ and CO.

The active carbon that was used for supports is based on waste material – peach stones. The deposition of the active phase was carried out by impregnation in an ultrasound bath of solutions containing nitrates of copper, manganese and iron.

The characterization of the samples was carried out by X-ray diffraction, Mössbauer spectroscopy and a catalytic test in a reaction for methanol decomposition. The results obtained reveal that the developed ferrite catalysts have cubic and partially inverse spinel structure. It was established that catalysts are unstable in the reduction medium and are changed substantially thus forming magnetite and carbide of Haag. Further, it was established that the presence of copper in the manganese ferrites improves the catalytic activity at the low-temperature and this tendency increases with increase of the copper content.

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Keywords: copper-manganese ferrites, activated carbon, Mössbauer spectroscopy, methanol decomposition.
SIMULTANEOUS DEPOSITION OF PARTICLES WITH DIFFERENT FUNCTIONALITY: MODELS, BASED ON CELLULAR AUTOMATA

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We develop the modelling approach reported in [1] developed in order to account for the possibility for co-deposition of two particles with different functionality. We present four variations of the model that circle around the theme “diffusion-limited vs. kinetics-limited” and identify the important parameters to be followed and eventually tuned during the quantitative stages of the study. The engine of our simulation is a Cellular Automaton that permits to make parallel growth updates and a diffusion module which is serial one. The simultaneous (parallel) growth update permits to keep track of the time measured in growth updates. The variation of the number of diffusional updates $n_{DS}$ that follow a growth one permits to switch smoothly between diffusion-limited ($n_{DS}=1$) and kinetics-limited ($n_{DS}>>1$) conditions of growth. When playing with two types of particles it is possible to have diffusion-limitations on the deposition of the one type and kinetic-limitations on the deposition of the other type. By varying the ways these two regimes interplay we build systematically our quantitative approach. A set of parameters to be followed is suggested, such as phase transformation ratio, coordination numbers, velocities of the process, etc. Brief discussion is provided on how to distinguish between the different variants of the model.

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Keywords: Computer modelling; Cellular Automata; Co-deposition; Diffusion-limited vs. kinetics-limited.
The role of substituent effects in tuning metalophilic interactions and emission energy of bis-4-(2-pyridyl)-1,2,3-triazolatoplatinum(II) complexes

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Four novel 5-subsituted-pyridyl-1,2,3-triazolato Pt(II) homoleptic complexes with intriguing photoluminescence properties were recently designed and synthetized in our laboratory [1–3]. Despite the broad range of the donor/acceptor strength of the substituents at 5-position, the series of complexes is characterized with weak absorption tunability in dilute and high concentrated solutions, as well as in thin films. However, emission tunability changes from weak at low concentration (397–408 nm) to strong at high concentration and solid state (487–625 nm). In addition, concentrated solution and solid-state emission maxima depend linearly on the donor/acceptor strength of the substituents indicating the influence of the 5-position.

In order to gain a deeper insight into the unusual concentration and substituent dependence, we have performed DFT/TDDFT investigation on the absorption and emission properties of the compounds. For this purpose, ground (S₀), first excited singlet (S₁) and triplet (T₁) states of the homoleptic Pt(II) complexes and their dimers were optimized in implicit solvent environment by using the PBE0 functional. Theoretical results attribute the “turn-on” emission tunability to the formation of excimers with strong Pt(II)---Pt(II) metalophilic interactions and to a change in the excited state character going from isolated complexes (1MLCT) to dimers (1MMLCT). Moreover, the simulations reveal that due to the excimerization process the S₁-T₁ energy difference decreases and varies as a function of the donor/acceptor strength of the substituent (from 0.25 to 0.1 eV). The latter suggests that the modification of the substituent could affect the probability for thermally delayed fluorescence and therefore to has positive impact on the quantum yield.


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

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

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

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Keywords: quaternary ammonium salts, 4,4’-bipyridine, quinoline, 2-bromoacetyl-naphthalene.
COMPARISON OF THE CRYSTAL STRUCTURES OF DNA SEQUENCE D(CGTGAATTCACG) WITH AND WITHOUT DAPI

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The crystal structures of the oligonucleotide d(CGTGAATTCACG) has been crystallized in the presence of the fluorescent molecule DAPI. Single crystals with and without DAPI were obtained by slight variation of the crystallization conditions.

The structures with and without ligand were determined at resolution of 2.00 Å and 2.2 Å respectively in space group \( P2_12_12_1 \). The main effect of the DAPI molecule is associated with the decrease of water molecules participating in the first hydration shell. The \( \text{Mg}^{2+} \) ions responsible for the compensation of the DNA backbone negative charge is also missing. The typical Watson-Crick hydrogen bonding interaction (Fig. 1) and the non-classical interstrand \( G \cdots G \) ones between adjacent DNA duplexes are conserved in both structures.

Fig. 1. a) Representation of DNA sequence with DAPI, b) observed non typical \( G \cdots G \) interactions

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Keywords: DNA, single crystal, DAPI, fluorescent.
SYNTHESIS AND CRYSTAL STRUCTURE OF BENZO[B]IMIDAZO[1,5-D][1,4]-OXAZEPINES

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Benzoxazepine ring systems are common pharmacophores, which can be found in many structures with biological activity. A number of compounds with benzoxazepine scaffold have been described as potent antiviral, anticonvulsant and neuroleptic agents. In recent years several tricyclic pyrrolo-1,5-benzoxazepines (PBOXs) stand out as promising anticancer candidates because of their ability to induce microtubule depolymerisation and apoptosis in different cancer cell lines. These hopeful results inspired us to design new tricyclic ring systems as PBOX analogues.

As a part of our research on the design and the synthesis of novel heterocyclic systems with potential biomedical application, we developed a convenient five-step approach for the preparation of tricyclic benzoxazepines, containing fused imidazolone ring. In this report we present a useful method for the synthesis of target compounds, which involves the use of benzoxazolones as easy available starting reagents. The key points of our approach are the ring transformation of 3-(2-oxopropyl)-2(3H)-benzoxazolones to the corresponding phenoxyacetic acids following by reaction of intramolecular acylation in PPA, leading to the formation of seven-membered oxazepine ring. The target compounds were obtained in good yields and their structures were established by spectroscopic methods (IR, NMR) and X-ray crystallography.

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Keywords: benzoxazepines, X-ray.
IR-SPECTRAL STUDY OF VITREOUS AND CRYS TALLINE VANADATE MATERIALS

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Glasses with compositions xMnOm(35-x)BaO.65V2O5 (x = 15 and 20 mol %) and (M = B, Ti, Ni and Zn) are prepared using a conventional melt-quenching method. The glass transition temperature Tg and crystallization temperature Tx is determined by DTA/DSC analysis. The glasses possess Tg of 230–260 °C and Tx of 270–320 °C. The composition fixed as glasses are heat-treated to full crystallization at temperature of 270–320 °C. The amorphous and crystalline nature of the samples are confirmed by XRD. 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 analysis of IR spectra confirmed the presence of weak chemical bonds such as M-O-V, Ba…O=V, V-NBO (nonbridging oxygen) and V-O-V. The role of ionic radii of the cations and the cation polarizability on the position of the IR absorption bands in the spectra are also discussed.

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Keywords: IR spectra, vanadate glasses, vanadate crystals, structure.
The synthesis of unsymmetrical urea and oxazinone derivatives is of growing interest due to the wide range of their applications in industry, engineering, agriculture, and medicine. Both moieties are often found as structural motif in numerous biologically active products and have displayed promising coordination properties as well. The need of new more efficient ligands has provoked enormous synthetic efforts and one of the most exploited ways to improve and control their properties is based on the insertion of diverse substituents on the heterocyclic scaffold.

The current study is focused on the rational design and synthesis of new structures combining dihydrooxazinone and unsymmetrical urea fragments in a common molecule. The target compounds were obtained by applying fast and efficient protocol going via the corresponding carbamoyl chloride intermediates. Single crystals suitable for X-ray analysis were obtained for selected samples.

The overlay of the molecules present in the ASU of the crystal structures revealed that the geometry of the benzoxazinone unit is highly conserved. In 2 a donor and acceptor are present and the crystal structure stabilization is “dominated” by hydrogen bonding NH…O interaction. In 1 only an acceptor (C=O) is available and the molecular geometry minimizes its surficial area/interactions by closing on itself in order to promote halogen bonding and π…π/CH3 interactions. Thus the preferred orientation of the side chain is strongly dependent on the properties of the substitution pattern at the carbonyl function.

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**Keywords:** unsymmetrical NH-ureas, dihydrooxazinones, polydentate ligands, XRD
EXAMINATION OF THE SECONDARY EXTINCTION
BY CONVERTING XRD DATA FROM STEP SCAN
INTO CONTINUOUS SCAN

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Secondary extinction (SE) is inherently related to the pole density, P. The latter represents a crystalline volume fraction normalised to random distribution that contributes to reflection. In fact, any measured point inside the reflection range 2Δθ is affected to a different extent by the SE due to variation of both pole density and energy distribution of the incident beam intensity, I₀. However, to evaluate a SE effect of the reflection as a whole, its integral intensity must be expressed by the counting rate corresponding to pole density, P, being dependent on integral breadth of reflection. In this context, an approximate equation was derived by means of which the step scan measurement data of reflection may be converted to integral intensity corresponding to a continuous scan. Thus, reformed data can be used for sensitive treatment of the SE effect in textures and powders including nanoscale materials as well.

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Keywords: secondary extinction, step scan, continuous scan.
CRYSTALLOGRAPHIC STRUCTURE OF BIOCOMPATIBLE NANOCOATINGS DEPOSITED ON Co-Cr SUBSTRATE

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In contemporary dental medicine titanium and its alloys deposited on Co-Cr substrate is widely used and applied. They are used in the manufacturing of joints, implants, endodontic instruments etc. For this purpose, they should have high mechanical properties, wear resistance, resistance to corrosion and biocompatibility [1].

In this study TiN/TiO₂ layers, known as biocompatibility materials, with thickness of 3 µm were applied on Co-Cr substrate by DC (direct current) magnetron sputtering. The crystallographic structure has been studied by XRD (X-ray diffraction) with Cu Kα characteristic radiation (1.54 Å). The measurements were conducted in Bragg-Brentano (B-B) symmetrical mode, from 20° to 80° at 2θ scale. The step has been chosen 0.1° with counting time 10 sec. per step.

The microstructure of the obtained layers was investigated by Scanning Electron Microscopy (SEM), as backscattered electrons have been used. The accelerated voltage was 20 kV. The chemical composition was studied by Energy-Dispersive X-ray Spectroscopy (EDX).

The mechanical properties (i.e. hardness and Young’s modulus) were measured, as the experiments were performed using Nanomechanical tester (Brucker, USA). Prior to the indentation, the surface of the studied samples was polished.

The obtained results demonstrate the possibility of formation of biocompatible coatings of TiN/TiO₂ by DC magnetron sputtering. It was found that the application of the discussed method with the respect technological parameters is able to form the examined nanocoatings with good stoichiometry and mechanical properties.


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Keywords: biocompatibility, nanocoatings, magnetron sputtering, XRD.
AN ANION DEPENDENT SYNTHESIS OF ZINC(II) COORDINATION POLYMERS OF BIS(DIMETHYLPHOSPHINYL METHYLENOXY)-BENZENE LIGANDS

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The wide spread application of coordination polymers and metal organic frameworks (MOF’s) as absorbents, catalysis, new material for linear optic, electronic and other areas of industry necessitated the synthesis of different new coordination polymer compounds. The specific structural characteristic and the properties of the coordination compound are determined from the metal ion chemistry. Zinc(II) proved to be very suitable for constructing a variety of coordination polymers. The ligand choice (polydentate nature, donor atoms) is also of great importance. The present study summarizes the influence of the mutual positions of the substituents in three isomeric bidentate tertiary phosphine oxide ligands (namely o-, m- and p-bis(dimethylphosphinylmethylenoxy)-benzene) and the size of halide ions from the initial zinc salt on the diversity of the structures obtained. The newly zinc coordination compounds obtained have polymeric structures with only one exception of a monomeric zinc complex of the o-isomer with iodide ions due to a steric hindrance of the close situated substituents in the ligand and the bulky iodide anions. The solid state structures of the zinc coordination polymers were determined by X-ray analysis and IR spectroscopy. The coordination mode of the ligand through the phosphoryl oxygen atom and solution chemistry of some of the complexes was studied by ¹H and ³¹P{¹H} NMR spectroscopic investigation.

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Keywords: coordination polymers, MOF, Zn(II) complexes.
DEFORMATIONS OF ETS-4 Ti-Si FRAMEWORK AFTER ION EXCHANGE AND TEMPERATURE LOWERING

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Crystal structures of Na-K-ETS-4 and ion-exchanged of Ag-, Cs-, Mg-, Ba-, Mn-, Ni- Cu-samples are solved from single-crystal X-ray diffraction data. Experiments are carried out on the same sample at room (RT-290 K) and low (LT-150 K) temperature.

The results show that ion-exchange and temperature lowering cause deformations of the channel systems formed by 6-, 7- and 8-membered rings. The deformations are evaluated by comparing geometrical parameters of the rings for the as synthesized Na-K-ETS-4 and the ion-exchanged samples and for the RT and LT structures. The ion exchange affects the rings shape without changing the area of their cross sections. Thus the unit cell volume for the as synthesized and ion-exchanged samples remains almost the same. The only exception is Ba-ETS4 which volume is reduced by about 5%. The 6- and 8-membered rings alternate along [100] and their deformations at this direction compensate each other, whereas the 7-membered rings are in another orientation (Fig. 1).

The temperature lowering reduces the pores size in most of the studied samples with the exception of Ba-ETS4. The highest degree of deformation is realized in Ni-ETS-4. The Ti-Si framework behavior upon ion-exchange and temperature lowering is discussed in terms of ETS-4 structure peculiarities and the specific features of the exchanged cations.

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Keywords: ETS-4, single crystals analyses.
THE INVESTIGATION OF LONGITUDINAL AND TRANSVERSE PHONONS OF NiO:K

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In this work, we have investigated the absorption of NiO and NiO:K thin films in the spectral region 400–1600 nm. Nickel oxide thin films were deposited on glass substrates by a simple mini spray technique at 460°C. The damping ratio is calculated in the all investigated spectral region. The frequencies of longitudinal and transverse phonons are also determined. The conductivity of electrons and their effective mass are presented as a function of frequency. The important conclusions about the microstructure of the investigated thin films are made.

![Absorption spectra of NiO and NiO:K thin films](image)

Fig. 1. The absorption spectra of NiO and NiO:K thin films in the spectral region 400–1600 nm

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Keywords: thin films, damping ratio, frequencies of longitudinal and transverse phonons, conductivity of electrons, effective mass of electrons.
VIBRATIONAL AND STRUCTURAL ANALYSIS OF COPPER (II) COMPLEX WITH 3-HYDROXY FLAVONE

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This report presents the first attempts to synthesize and study the structure of the complexes of monohydroxyflavones and transition metals by vibrational spectroscopy and quantum chemical methods.

In the course of the studies were prepared complexes of 3-hydroxyflavone with Cu^{2+} ions, incorporated by sulfate and selenate compounds. For this purpose, trials were carried out for selection of the optimal solvent that provides maximum solubility of the salts, containing Cu (II) and, the influence of the concentration and the pH of the stock solutions and the time of reaction, the structure and stability of the complexes.

Received optimized structures of copper complexes with coordination number 4 and 6 and metal ratio: 3-hydroxyflavone 1:1. The additional ligands are molecules of the solvent used – MeOH. Found structural differences between free ligands and coordination compounds are compared with the resulting differences in vibrational and electronic spectra (IR and Raman spectra).

The impact of coordination on the structure of the ligand is assessed by Becke’s 3-Parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP), with the standard 6-311++G(d,p) basis set in the software package Gaussian09. The same orbital basis is used for preliminary optimization of ligands.

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Keywords: 3-hydroxyflavone, copper(II) complex, vibrational spectroscopy, structural analysis.
NEUTRON DIFFRACTION STUDY OF THE CRYSTALLOGRAPHIC STRUCTURE OF Ti–Al–Nb ALLOYS AT HIGH TEMPERATURES

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The combination of attractive mechanical properties, light weight and resistance to corrosion makes Ti–Al based alloys applicable in the modern industry – e.g. aircraft, automotive etc. It was found that incorporation of niobium additional improves the high temperature performance and mechanical properties [1].

In this study, Ti–Al–Nb alloys were synthesized by electron-beam surface alloying technique, as on commercially pure aluminium substrate, titanium and niobium layers with thickness of ~2μm were deposited. The obtained sample was then alloyed with scanning electron beam.

The crystallographic structure of the specimen was investigated by neutron diffraction, as the experiments were performed on IBR-2 pulsed reactor, located at Frank Laboratory of Neutron Physics (FLNP) in Joint Institute for Nuclear Research (JINR), Dubna, Russia. The measurements were conducted at 6a channel, equipped with oven for precise high temperature dependent structural investigations. In our study, the obtained specimen was measured in a temperature interval from 300° K up to 800° K.

The obtained in the study results demonstrate that Al–Ti–Nb surface alloy was successfully produced by the discussed technology with (Ti,Nb)Al3 intermetallic phase. The shift of the lattice parameters of (Ti,Nb)Al3 as well as the thermal expansion coefficient, strains and residual stresses were examined with respect to each temperature point.


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Keywords: surface alloys, neutron diffraction, crystallographic measurements at high temperatures.
COMPOSITIONAL AND STRUCTURAL DIFFERENCES OF APATITE FROM ENAMEL AND DENTINE

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Longitudinal sections of 9 human teeth are prepared by cutting with microtome and subsequent polishing. Different vibrational micro-spectroscopic techniques were used to investigate the structural differences of enamel and dentin apatite, as well as scanning electron microscopy to visualize morphological and chemical differences.

The results indicate that the enamel is composed of predominantly B-type carbonate substituted hydroxylapatite and to a lesser extent A-type. The degree of carbonate substitution gradually increases from the surface enamel toward dentine-enamel junction and significantly increases in dentine apatite. The amount of the organic component detected in dentine depends on its type. Unlike enamel, hydroxyl group is absent in dentine. The reasons for these differences are discussed from a structural point of view.

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Keywords: enamel, dentine, apatite mineral, vibrational spectroscopy.
SURFACE AND INTERNAL CRYSTALLIZATION IN GLASS CERAMICS WITH A LOW THERMAL EXPANSION PHASE

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Recently developed solid solutions $\text{Ba}_{1-x}\text{Sr}_x\text{Zn}_2\text{Si}_2\text{O}_7$ ($0.1 \leq x \leq 0.9$) exhibit low or negative thermal expansion in a wide temperature range above room temperature. Materials which have low or negative thermal expansion find applications as cook panels, telescope mirrors, gyroscopes, and others. Since the already mentioned phase has promising application in the industry, we are interested in the crystallization behavior of a base glass system $\text{BaO-SrO-ZnO-SiO}_2$. Because of the high anisotropy of the coefficients of thermal expansion, the obtained materials from this phase have strong tendency to micro cracking. In order to overcome this problem, we need small crystal size and homogenous distribution in the volume. In the present work, we study the effect of one of the most common nucleation agents $\text{ZrO}_2$ in varying concentrations to the basic system. For characterization of the glass ceramics, we used X-ray diffraction with which we determined the obtained crystalline phase and scanning electron microscopy to characterize the microstructure.

By applying different heating rates in a differential scanning calorimetry device, we were able to calculate the activation energy using the equation of Ozawa and Kissinger and determining the Avrami parameters, which provide further information on the crystallization process. An appropriate adjustment of the type and amount of nucleation agents is necessary in order to optimize the crystallization behavior.

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Keywords: activation energy, crystallization, low thermal expansion.
PARAMAGNETIC POLYNUCLEAR PLATINUM COMPLEXES OF 5-FLUOROURACIL.
I. SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIPROLIFERATIVE EFFECTS

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The antitumor activity of the “platinum blues” – paramagnetic mixed valent polynuclear complexes is associated with their depot function, that providing the release of low molecular weight Pt\textsuperscript{II}-species with time in biological environmental. It is rather surprising that although much of the ‘platinum blues’ chemistry has come as a results of the serendipitous discovery of the first “platinum pyrimidine blue” which proved to have high antitumor activity as well as low renal toxicity, research on the antitumor properties of these compounds has not started until very recently.

This study deals with synthesis of “platinum blues” complexes with antitumor drug 5-fluoruracil, their structural characterization and exploration of their antiproliferative properties. Two paramagnetic polynuclear platinum complexes have been synthesized in the following conditions: molar ratio Pt:5-fluorouracil 1:1, Pt:NaOH 1:1 in two different reaction paths. In the first one, the ligand was added in solid state, in the second one – as an aqueous solution. The structure of the complexes in solid state and in a solution has been characterized with the methods of UV-Vis, IR, mass spectrometry, EPR, elemental analysis. The initial test of the antiproliferative properties have demonstrated much higher effects comparable and better than that of cisplatin. The complex-formation in solution has been studied in order to obtain platinum complexes with definitive chain length. The processes of complex-formation were studied with the method of the UV-Vis and the reaction systems were analyzed with computational methods. The absorption bands belongs to the unreacted ligand were analyzed in the range of 250–320 nm.

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Keywords: 5-fluorouracil, platinum blues, antiproliferative effects.
NANOSIZED Cr$^{3+}$ DOPED Sc$_{2-x}$In$_x$(WO$_4$)$_3$
SOLID SOLUTIONS

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Me$_2$(WO$_4$)$_3$ tungstates, where Me = Y, In, Sc, Al, Ga, Cr have received considerable attention due to their negative thermal expansion (NTE) properties, ionic conductivity and interesting physical phenomena such as temperature- and pressure-induced phase transitions and pressure-induced amorphization. These compounds doped with Cr$^{3+}$ ions are also attractive as laser media for tunable lasers. Generally, for laser applications, single crystals are used, but the production of single crystals from these materials is related to a number of problems. One alternative is high-density ceramic with the same chemical compositions. On the other hand solid solutions within the frame of the considered class of compounds provide the possibility to tailor properties by varying the chemical compositions.

The aim of our investigation was to obtain pure phases of nanosized powders of Cr$^{3+}$:Sc$_{2-x}$In$_x$(WO$_4$)$_3$, (x=0÷2) with controlled sizes and size distribution of the particles, suitable for obtaining of high density ceramics.

Nanosized solid solutions with the formula Sc$_{2-x-y}$In$_x$Cr$_y$(WO$_4$)$_3$, where x varies from 0 to 2 were synthesized for the first time by co-precipitation method from aqua solutions of Na$_2$WO$_4$.2H$_2$O and Me(NO$_3$)$_3$.xH$_2$O nitrates of corresponding metals: In, Sc and Cr. The obtaining of pure tungstates phases was established by X-Ray analysis. Monophasic products of the solid solutions were obtained by strict maintenance of pH between 2.8 and 5.4. The synthesized solid solutions of Sc$_{2-x}$In$_x$Cr$_y$(WO$_4$)$_3$ are orthorhombic at room temperature for value of x between 0 and 1, and are monoclinic for value of x greater than 1; for value equal to 1 the samples possess both polymorphic modifications. Deferential thermal analysis was used to determine the crystallization temperature of precipitates as well to establish the phase transition temperature. The well crystallized powders at 900°C for 3 h were used to determine structure, cell parameters and lattice volume.

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Keywords: nanostructured materials, tungstates, X-ray diffraction, thermal analysis.
SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF CATALYSTS BASED ON MIXED OXIDES

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Catalytic oxidation is one of the most important processes for VOC elimination in waste gases. Noble metals catalysts have greater activity than other used catalysts, but their price cost is high. The metal oxides of transition elements are good alternative. Complete oxidation of volatile organic compounds over bulk metal oxide systems was studied. Cobalt and manganese mixed oxides with different ratio were synthesized by co-precipitation method. The materials were characterized by XRD, XPS, TPR and BET. Methane combustion reaction was chosen for catalytic tests because methane is the second chemical compound responsible for the global warming, after carbon dioxide. The obtained samples appear good catalytic activity in this reaction.

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Keywords: Co-Mn mixed oxide, catalytic oxidation.
SYNTHESIS OF CHIRAL AMINOBENZYNAPHTHOLS – STRUCTURE AND CONFIGURATION

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The process known as “Betti reaction” presents an easy to perform condensation between three components – 2-naphthol, aldehyde and amine. The condensation reaction may occur with remarkable diastereoselectivity by using of a suitable chiral amine and has significant synthetic potential for preparation of new complex chiral compounds through variation of the components. These compounds are suitable building blocks for various asymmetric syntheses and could be applied as ligands in metal catalyzed processes.

We are presenting here the synthesis of aminobenzynaphthol derivatives through condensation between steroidal 2-naphthol analogue, (S)-(−)-1-phenylethylamine and aromatic aldehydes. The condensation reaction is stereoselective and the isolation of pure individual diastereoisomers has been achieved by easy to perform purification methods (crystallization or flash chromatography).

The configuration of newly formed stereogenic centres within the aminobenzynaphthols isolated has been determined by advanced NMR experiments. The correctness of the method has been proved by X-ray crystallography.

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Keywords: (Betti condensation, aminobenzynaphthol, NMR spectroscopy, X-ray crystallography).
DIRECTED CRYSTALIZATION OF γ-FOOH AT LEPTOTHRIX SP. CULTURING IN MEDIUM OF LIESKE

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Iron-containing biomass obtained by Sphaerotilus-Leptothrix group bacteria cultivation in different nutrition media is most frequently multicomponent. Catalytic activity in oxidation of CO is inherent in γ-Fe₂O₃, obtained from a biogenic FeOOH precursor. A challenge to the cultivation process control is the selection of such experimental conditions so that γ-FeOOH to be a predominant compound in the composition. A template/crystal nuclei import could facilitate and assist the crystallization process of the targeted compound. Anodic alumina is used as support which is a mixture of amorphous and crystal γ-Al₂O₃, γ-AlOOH, α- and γ-Al(OH)₃. Both oxyhydroxides are isomorphous and it is supposed that γ-AlOOH can help and direct the crystallization of γ-FeOOH generated during bacteria cultivation. Samples were obtained by Leptothrix genus bacteria cultivation in Lieske medium. Anodic deposited Al₂O₃/Al lamellas were preliminary submerged in the flasks with the nutritional solution. All samples were studied by methods of infrared, Moessbauer and X-ray photoelectron spectroscopy. Analysis of the obtained data shows that two kinds of biogenic iron-containing phases were synthesized simultaneously in the medium: powdered samples with α- and γ-FeOOH and lamellas covered with γ-FeOOH modification, only. The experiment could be considered as successful but additional study is necessary to clear up the exact role of the used support. The multicomponent samples' composition complicates the analyses and application of the untreated biogenic iron. From the point view of catalysis single component samples simplify the work with biogenic iron.

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Keywords: biogenic lepidocrocite, anodic alumina, spectroscopic investigation.
DNA G-QUADRUPLEX – LIGAND INTERACTION: A COMPARISON BETWEEN FLUORESCENT INTERCALATOR DISPLACEMENT ASSAY, THERMOPHORESIS AND SINGLE CRYSTAL DIFFRACTION DATA

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Small molecules that can interact with DNA are intensively studied since they appear to inhibit the growth of cancer cells. G-quadruplex DNA (G4) and G-quadruplex ligands are intensively studied since they appear to inhibit the growth of cancer cells via an unprecedented mode of action based on structural stabilization of GC rich DNA fragments. Thus methods for rapid and reliable detection of G4-ligand interaction are needed. Herein, we would like to report on the G4 fluorescent intercalator displacement (FID) assay, thermophoresis and single crystal data from both quadruplex and duplex DNA. The FID screening method was applied based on the displacement of thiazole orange from both quadruplex and duplex DNA, while DAPI was used for B-DNA and as a negative control. Attempts including a third light probe ethidium bromide were also performed. Thus evaluation of ligand specificity and selectivity for quadruplex and/or duplex DNA can be achieved.

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Keywords: DNA, quadruplex, G4, FID, fluorescence, single crystal.
CRYSTAL CHEMISTRY AND STRUCTURAL CHARACTERIZATION OF NATURAL Cr-SPINELS

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Two natural chromian spinel samples were examined by means of single-crystal X-ray diffraction, powder X-ray diffraction, Mössbauer spectroscopy and electron microprobe chemical analysis, in order to reveal some aspects of the relationships between composition and structural parameters. The samples come from east Rhodopean ultramafic massive of Golyamo Kamenyane in Bulgaria, which is part of a dismembered ophiolite complex. They show very distinctive textural, chemical and structural features. One of the samples is chromium rich and can be regarded as chromite, whereas the other one is very rich in Fe²⁺ and Fe³⁺ (as shown by EMPA and Mössbauer spectroscopy), approximating magnetite end member of the spinel group. These contrasting compositional differences result in very pronounced differences in the structural parameters – cell edge and $u$ oxygen positional parameter, which reflect different conditions of formation and/or alteration. $U$ parameter is indicative for the thermal history of the hosting ultramafic rock. It depends on cation distribution, but not very strongly, which allows rather accurate determination of $u$ within reasonable limits of cation distribution uncertainty. Nevertheless, our results show, that diffraction studies alone are insufficient for geothermometric purposes and have to be combined with EPMA and Moesbauer data. Calculated system closure temperatures for both samples indicate 800–950 °C, which are acceptable for the pristine chromite formation conditions. For outer rims of the crystals, formed during later metamorphic events, however, should be expected lower temperatures.

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Keywords: Cr-spinels, X-ray diffraction, structural parameters.
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