Third National Crystallographic Symposium
with International Participation

program and abstracts

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

Institute of General and Inorganic Chemistry – BAS
Geological Institute – BAS

with the assistance of:
Sofia University, Faculty of Chemistry
Institute of Mineralogy and Crystallography – BAS

October 3–5, 2011, Sofia, Bulgaria
Earth and Man National Museum
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**SYMPOSIUM PROGRAM**

**Monday 3 October**

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<td><strong>Session 1</strong>&lt;br&gt;Chairing: Danela Kovacheva&lt;br&gt;9:30–10:00&lt;br&gt;Mois Aroyo&lt;br&gt;<em>University of the Basque Country, Spain</em>&lt;br&gt;Structure relationships studies by the Bilbao crystallographic server</td>
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<td>10:00–10:30</td>
<td><strong>Vesselin Tonchev</strong>&lt;br&gt;<em>Institute of Physical Chemistry, BAS, Sofia, Bulgaria</em>&lt;br&gt;Self-organization on vicinal crystal surfaces with competing interactions: Kinetics of pattern formation</td>
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<td><strong>Session 3</strong>&lt;br&gt;Chairing: Boris Shivachev&lt;br&gt;13:30–14:00&lt;br&gt;Ognyan Petrov&lt;br&gt;<em>Institute of Mineralogy and Crystallography, BAS, Sofia, Bulgaria</em>&lt;br&gt;Analysis of structure factors (F$_{hkl}$) of meaningful XRD diffraction intensities for chemical determinations after ion-exchange and isomorphic substitutions in crystal structures</td>
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<td>14:00–14:30</td>
<td><strong>Thomas Kerestedjian</strong>&lt;br&gt;<em>Geological Institute, BAS</em>&lt;br&gt;The thermal device of the image foil Guinier camera in the Geological Institute, BAS: Calibration and usage experience</td>
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Tuesday 4 October

Session 5  
Chairing: Rositsa Petrova  
9:30–10:00  
Peter Tzvetkov  
*Institute of General and Inorganic Chemistry, BAS, Sofia, Bulgaria*  
New perovskites-based PbBaFe$_{2−x}$Mn$_x$O$_5$ (0≤X≤1.5)

10:00–10:30  
Kiril Krezhov  
*Institute for Nuclear Research and Nuclear Energy, BAS, Sofia, Bulgaria*  
Structural investigations of magnetoelectric materials by neutron diffraction

10:30–11:00  
Coffee break

Session 6  
Chairing: Galina Gentcheva  
11:00–11:30  
Annie Shoumkova  
*Institute of Physical Chemistry, BAS, Sofia, Bulgaria*  
Synthesis of zeolite A from Bulgarian rice husk and waste aluminum

11:30–12:00  
Kamen Kamenov  
*Bruker AXS, Germany*  
Presentation of Bruker-AXS GmbH

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Session 7  
Chairing: Vladislav Kostov-Kytin  
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Milen Gateshki  
*PANalytical V.B.*  
EasySAXS: Nanoparticle size distribution determination on a multi-purpose X-ray diffractometer

14:00–14:30  
Ivan Tomov  
*Sofia, Bulgaria*  
Nullification of extinction effects in XRD characterizations of real structure of materials

14:30–15:00  
Coffee break

15:00–15:30  
Group Photo

Session 8  
Chairing: Ognyan Petrov  
15:30–17:00  
Annual meeting of BCS. Annual report of the BCS steering committee and planning of BCS further activities.
Wednesday 5 October

Lab visits

- Labs located in the Institute of General and Inorganic Chemistry – BAS.
- Labs located in the Geological Institute – BAS.
- Labs located in the Faculty of Chemistry, Sofia University.
- Labs located in the Institute of Mineralogy and Crystallography – BAS.

POSTER SESSION – Monday 3 October 16:00–18:00

P_1  V. Antonov, I. Georgieva, N. Trendafilova, D. Kovacheva, K. Krezhov
First principles investigations of structure and properties of modified multiferroic BiFeO₃

P_2  R. Atanassova, R. Vassileva, M. Kadiyski, Z. Zlatev
Crystallographic, chemical and structural characteristics of harmotome from Zlatolist, Eastern Rhodopes, Bulgaria

Texture and residual stress of chemically and electrochemically deposited copper layers

P_4  B. S. Boyanov, A. B. Peltekov
X-RAY, DTA and TGA study of zinc sulfide concentrates and their roasting in fluidized bed furnace

P_5  Zh. Bunzarov, T. Dimov, I. Iliev, P. Petkova, Y. Tzoukrovski
Birefringence spectrum of magnesium sulfite hexahydrate

P_6  Z. Cherkezova-Zheleva, K. Koleva, I. Mitov
Preparation, characterisation and properties of nano-sized ferrite materials

P_7  S. Dimitrovska-Lazova, D. Kovacheva, P. Tzvetkov, S. Aleksovska, M. Marinëk
Synthesis and structural details of perovskites within the serie PrCo₁₋ₓCrₓO₃ (x = 0, 0.33, 0.5, 0.67, 1)

P_8  S. Dimitrovska-Lazova, D. Kovacheva, S. Aleksovska, P. Tzvetkov
Structural characteristics of GdCo₁₋ₓCrₓO₃ (x = 0, 0.33, 0.5, 0.67, 1) perovskites

P_9  L. Dimowa, B. Shivachev
Occlusion and in-situ temperature powder XRD of ZnCl₂ in clinoptilolite

P_10  N. Dodoff, B. Shivachev, R. Nikolova, M. Lalia-Kantouri, V. Miletic, T. Pajpanova
Synthesis and structure of bc-dichloro-af-dihydroxo-de-bis(N-3-pyridinylmethanesulfonamido) platinum(IV) dihydrate

P_11  I. Georgieva, N. Dancheva, S. Gutzov, N. Trendafilova
DFT structure modeling of Zn(IV) acetylacetonate complexes as building units of sol–gel materials with optical properties

P_12  Zh. Georgieva, B. Shivachev, R. Nikolova, V. Skumryev, S. Zareva, S. Varbanov, T. Tosheva, E. Tashev, G. Gencheva
New copper complexes of tertiary phosphine oxide and functionalized nitrogen-containing phosphine oxide ligands – study of structure and properties
P_13  D. Goranova, R. Rashkov  
Growth instabilities and pattern formation in complex systems far from equilibrium: Electrodeposition of Cu-Ni alloys

P_14  P. Gorolomova, R. Nikolova, B. Shivachev, V. Skumryev, D. Tsekova, V. Ilieva, S. Varbanov, T. Tosheva, E. Tashev, G. Gencheva  
Series of manganese(II) coordination polymers containing dimethyl(methylenoxyaryl) phosphine oxide-bridges and inorganic ligands: Synthesis, single-crystal structure and magnetic properties

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Ganglia like ZnO structures for biosensor applications

P_16  N. Kaneva, C. Dushkin, A. Bojinova  
ZnO thin films preparation on glass substrates by two different sol–gel methods

P_17  D. Karashanova, D. Kostadinova, S. Vasilev, N. Petrova  
Size and distribution of Pt NPs in LDH nanocomposites under heating

P_18  V. Kostov-Kytin, R. Nikolova, N. Lihareva  
Two-stage protonation of a small-pore microporous zirconosilicate Na₂ZrSi₂O₇·H₂O

P_19  M. Kuneva  
Rare-earth doped optical waveguides in LiNbO₃

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Synthesis and crystal structures of zinc phosphates doped with samarium and manganese

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NANOSIZED SOLID SOLUTIONS Al$_{2-x}$Me$_x$(WO$_4$)$_3$, WHERE Me = Sc or In WITH ORTHORHOMBIC STRUCTURE .................. 50
A. Yordanova, I. Koseva, V. Nikolov
The bismuth perovskite family is of special interest due to the fact that rhombohedral (Space group R3c) BiFeO$_3$ shows magnetoelectric properties at room temperature. In view of the importance of such materials, the effects of modifying the BiFeO$_3$ by substituting Fe$^{3+}$ by Mn$^{3+}$ and Bi$^{3+}$ by La$^{3+}$ are investigated by first principles calculations. Density functional theory (DFT) realized with plane wave basis, ultrasoft pseudo potentials and GGA+U/PBE functional was used to predict the possible crystallographic structures and their electronic, magnetic and optical properties. The chemical formulae of the proposed compounds are Bi$_{1-x}$La$_x$FeO$_3$ and BiFe$_{1-x}$Mn$_x$O$_3$, where x vary between 0 and 0.3. To investigate the process of substitution an orthorhombic supercell was created to contain six unit cells of rhombohedral BiFeO$_3$. The substitution was modeled by replacement of one, two and three atoms of Bi or Fe by La or Mn. The most favored substituted structures were predicted from energetic point of view. Substitution of Bi by La tends to preserve the original crystal structure and reduces the c crystal axis. Small La concentration increases the band gap however it decreases as the La concentration increases. The magnetic moment of the cell does not change. Substitution of Fe by Mn leads to decrease of the cell parameters along both a and c axis (or to a deformation of the crystal cell). Due to the different magnetic moments of Fe$^{3+}$ and Mn$^{3+}$ a small ferrimagnetism is introduced which increases linearly with the concentration of Mn$^{3+}$. Substitution with Mn does not change the band gap. The calculations of the dielectric tensor showed that BiFeO$_3$ is uniaxial crystal. The optic axis is parallel to the axis of magnetization. In the La substituted BiFeO$_3$ the real part of the dielectric tensor decreases, regardless on the direction. The imaginary part, responsible for the light absorption also decreased. In the Mn substituted BiFeO$_3$ the real part of the dielectric tensor slightly increases in the IR region but with decreasing the wavelength it is being decreased. The same trend is observed for the imaginary part. This behavior does not depend on the orientation to the magnetization (optic) axis. The dielectric tensor calculations suggest that La and Mn substitutions affect the optical properties of BiFeO$_3$.

Keywords: multiferroic, substituted BiFeO$_3$, DFT, optical properties.
STRUCTURE RELATIONSHIPS STUDIES BY THE BILBAO CRYSTALLOGRAPHIC SERVER

M. I. Aroyo, J. M. Perez-Mato, D. Orobengoa, E. S. Tasci, G. de la Flor, S. V. Gallego

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The Bilbao Crystallographic Server (http://www.cryst.ehu.es) [1] is a free web site offering online crystallographic tools and databases. The server offers referential crystallographic information including data from the International Tables for Crystallography, Vol. A: Space Group Symmetry; Vol. A1: Symmetry Relations between Space Groups and Vol. E: Subperiodic Groups, as well as the wave-vector database with the Brillouin-zones figures for all space groups. There are tools for the study of group-subgroup relations between space groups, their representations and applications in solid-state physics and chemistry. The present contribution focuses on some basic structure utilities available on the server as well as on more complex computer tools necessary for comparisons of structures or studies of their relationships.

The set of basic structure-utility tools includes the programs CELLTRAN and TRANSTRU that transform unit-cell parameters or atomic coordinates into another space-group setting while SETSTRU converts alternative settings structure description to a standard setting and vice versa. EQUIVSTRU applies the space-group normalizers to derive all the equivalent descriptions of the same structure. For a given pair of structures, STRAIN is used to calculate the linear and finite-strain tensors as well as the degree of the lattice deformation. The program COMPSTRU offers a quantitative description of the similarity of two structure models. The program is also helpful for the recognition of identical or nearly identical atomic arrangements of different compounds that is essential for the crystal-structure classification problem. The program STRUCTURE RELATIONS quantifies the relations between two phases of the same compound by computing the homogeneous strain and the atomic displacement field characterizing the crystal-structure relationship. The structures can be visualized in an interactive 3D environment via the VISUALIZE tool. Where applicable, the tools support the CIF file format both for input and output, making it easy to exchange information between various related software packages.


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Keywords: crystal-structure descriptions, Bilbao Crystallographic Server.
Intense collision-related volcanism took place in the East Rhodopes, South Bulgaria during the Paleogene. Eruptive products, both lava and volcaniclastic rocks, are assigned to four intermediate to basic phases alternating in time with five acidic ones. Large volumes of pyroclastics erupted during the volcanic phases were deposited in a shallow marine environment and were transformed into clays, adularia, opal-CT and zeolites [1]. Unusual mineralization was observed in voids and in some microdruses and cavities of basaltic rocks near the Zlatiolist village, Eastern Rhodopes. The voids, now amygdales are filled predominantly by calcite, quartz and several zeolites (harmotome, analcime, chabasite, mordenite and heulandite). Among these zeolites harmotome occurs as remarkably well-defined prismatic crystals ranging from several mm to 1–1.5 cm. Exceptionally, crystals up to 2 cm in length have been collected. Harmotome has been characterized using optical microscopy, X-ray, SEM/EDS, EPMA, LA-ICP-MS and DTA. This paper describes morphological, chemical and structural properties of the mineral.

Harmotome is transparent with vitreous luster, and though crystals are typically colourless, some fragments may be yellow-brownish or pale beige. The crystal habit is characterized by short prismatic pseudo-orthorhombic forms. The crystals are always pseudo-orthorhombic penetration twins according to the morvenite law. Complex twinning results in an optical heterogeneity and characteristic uneven extinction under crossed polars. The morvenite twin is a fourling twin present in all investigated crystals. It is composed of four individuals, arranged across the twin planes (001) and (20–1), and it displays the {100}, {010}, {001}, {110}, and small {–201} forms. The four sets of intersecting striations, which indicate the presence of the four individuals, are seen only on the (010) faces. Morvenite twins are commonly elongated along the a-axis, and flattened on the (010). The average chemical formula analyzed using EPMA is as follows: \( \text{Ba}_{2.46}\text{Ca}_{0.17}\text{K}_{0.26}[\text{Al}_{5.89}\text{Si}_{10.19}\text{O}_{32} \cdot 12\text{H}_2\text{O}}. \) Trace elements are registered also by LA-ICP-MS. Up to 1.3 wt.% Na, 200 ppm Sr, 15 ppm Fe, and 26 ppm Ti are determined. The thermal behavior of harmotome, with five different water sites in the structure, represents water loss in three steps: at 125, 210, and 280 °C, and complete dehydration at 400 °C.

Although morphological and optical studies on minerals of the phillipsite family indicate monoclinic symmetry, the symmetry of harmotome was often discussed during 19th and 20th centuries [2]. A single crystal fragment of harmotome with dimensions 0.25 × 0.22 × 0.20 mm was measured with X-ray diffraction. Reliable model with satisfactory R-values (\( R_1 = 0.0403; R_{(all)} = 0.0473 \)) was obtained using the \( P2/\overline{1}m \) space group and it was chosen for the structure refinements. The obtained unit cell dimensions are: \( a = 8.6713(3), b = 14.1394(3), c = 8.6914(3) \text{ Å}, \beta = 110.552(4) \)° and \( V = 997.80(5) \text{ Å}^3 \). The final refinement included all atomic coordinates and anisotropic thermal displacement parameters. The fundamental framework of harmotome is orthorhombic, but Ba ions have some flexibility with respect to their position in the channels [3]. Barium deviates slightly from the (100) mirror plane, reducing the symmetry to monoclinic [2]. It is well known that harmotome individuals invariably consist of complex twins and twinning may simulate single tetragonal crystal forms. It is suggested that the non-existence of untwined crystals means that the twinning exists already in the crystallites at the time of nucleation.

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Keywords: crystal morphology, zeolites, refinement
TEXTURE AND RESIDUAL STRESS OF CHEMICALLY AND ELECTROCHEMICALLY DEPOSITED COPPER LAYERS

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X-ray diffraction methods are used for analysis of the structure, texture and residual stress of chemically and electrochemically deposited copper coatings. These coatings are used for formation of metal matrix for incorporation therein of high hardened particles, production of multilayer printed circuit boards (PCBs), implementation of adhesion securing (copper) sublayer building multilayer (sandwich type) structures for protective and decorative metal systems of non-metallic and metallic substrates, etc. Chemically deposited copper thin films can also be used as flexible conducting layers in electronic industry. This wide area of application depends on the structure and physicomechanical properties of the copper thin films obtained by different methods. Texture and residual stress of the chemically deposited layers are compared to well known electrochemically deposited copper entities. This comparison shows that the chemically deposited Cu and electrochemically deposited bright Cu layers exhibit similar crystallite sizes; the preferable orientation of chemically deposited copper is along the <111> while the texture of the bright copper coatings is mixed, <311> and <110>, the dominant axis of preferable orientation being along the <311> direction, and different residual stress.

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Keywords: texture, residual stress.
Bulgaria is a major producer of zinc in the Central and East Europe (about 100 000 tons per year). The two zinc plants in KCM S.A., Plovdiv and LZC S.A., Kardjali deliver the necessary raw materials from Bulgaria and abroad.

The oxidizing roasting of zinc concentrates exert substantial influence of the subsequent processes leaching and electrolysis in the zinc production by hydrometallurgical method. In this respect unusually important is the full characteristic of the processed Bulgarian and import zinc concentrates. In addition to the chemical composition, their phase composition and behavior in oxidizing conditions is of great importance.

In this connection Bulgarian and import zinc concentrates have been investigated with use of X-ray phase analysis and DTA and TGA. With an X-ray phase analysis (apparatus "TUR-M62" (Dresden, Germany) equipped with a computer-controlled HZG-4 goniometer with Co-Kα radiation and Bragg-Brentano geometry) it is established that the following phases are present: β-ZnS; nZnS.mFeS; CuFeS₂; PbS; SiO₂ (α-quartz). The phase β-ZnS is present in all concentrates and the other established phases are represented differently in the studied concentrates.

The results obtained are interpreted from the standpoint of receipt by roasting of an appropriate zinc calcine on the basis of its chemical and phase content. For this purpose a Web-based program system developed by mathematicians and technologies from Paisii Hilendarski University of Plovdiv for calculating the mixes of zinc concentrates at a fixed optimizing criterion was used. This enables during roasting of concentrates in fluidized bed furnace appropriate mix materials to be processed. This contributes obtaining of a zinc calcine with minimum insoluble zinc ferrite and content of admixture components below a certain technology requests.

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Keywords: zinc concentrates, X-ray analysis, DTA and TGA, roasting.
BIREFRINGENCE SPECTRUM OF MAGNESIUM SULFITE HEXAHYDRATE

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Magnesium sulfite hexahydrate (MgSO₃·6H₂O) is an anisotropic gyroropic crystal of class C₃ symmetry. Birefringence is investigated in (1–210) crystallographic direction. The crystal is placed in a “diagonal position” between a crossed polarizer-analyzer set. (The “diagonal position” is characterized by angle π/4 between the crystal optical axis and the polarization plane of the polarizer.) Two elliptically polarized electromagnetic waves propagate in the crystal in the mentioned direction. The elliptically polarization of the waves depends on crystal’s gyroropic properties. Spectra of the transmitted light through polarizer-crystal-analyzer set are analyzed and discussed. The birefringence spectrum, determined by the difference Δn between the refraction indices nₒ of the ordinary and nₑ of the extraordinary wave in the crystal, is obtained. The ratio between the gyroropic parameter ρ and the birefringence parameter Δn is estimated.

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Keywords: class C₃ symmetry, gyroropic crystal, birefringence.
Nano-sized materials are used as magnetic fluids, catalytic agents and ceramics, for information storage, light-emitting diodes, pigments in paints and cosmetics. Much attention has been paid to their preparation in respect to different application – in energetics, medicine, electronics, catalysis, etc. Magnetite ($\text{Fe}_3\text{O}_4$) and $\text{Me}_x\text{Fe}_{2-x}\text{O}_4$ ferrites (where $\text{Me}$ denotes a divalent cation) are members of solid solution series. This provides a possibility to prepare series of samples with different electronic properties. The aim of this investigation is to synthesise and characterise different nano-sized magnetite-type samples of general formula $\text{Me}_x\text{Fe}_{2-x}\text{O}_4$, $0 \leq x \leq 1$ ($\text{Me} = \text{Mg}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}$, etc.).

Nano-sized magnetite-type ferrite samples were prepared by co-precipitation method. The phase composition and dispersity of synthesised samples were studied by number of physicochemical methods – X-ray diffraction, Mössbauer spectroscopy at room temperature (RT) and liquid nitrogen temperature (LNT), infrared spectroscopy and transmission electron microscopy/selected area electron diffraction. The obtained results showed the formation of single phase ferrite materials with respective composition – $\text{Me}_{0.5}\text{Fe}_{2.5}\text{O}_4$, where $\text{Me} = \text{Fe}^{2+}, \text{Mg}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}$, etc. Their particle size is nano-dimensional – about 3-12 nm and changes varying chemical composition in the following order:

$$\text{Fe}_3\text{O}_4 > \text{Mg}_{0.5}\text{Fe}_{2.5}\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4 > \text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4.$$

All particles have spherical shape and close size-distribution. Study of magnetic properties of prepared materials showed collective magnetic excitation behavior of magnetite sample at RT and superparamagnetic behavior of all magnetite-type materials at RT and at LNT. Initial catalytic tests revealed their god catalytic activity and the potential to use them as catalytic materials.

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Keywords: nano-sized magnetite-type materials, relaxation phenomena, catalysis.
SYNTHESIS AND STRUCTURAL DETAILS OF PEROVSKITES WITHIN THE SERIE PrCo$_{1-x}$Cr$_x$O$_3$ ($x = 0$, 0.33, 0.5, 0.67, 1)

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Within the field of material science one of the most interesting group of compounds belong to perovskite structural type. Namely, perovskite compounds exhibit diversity of properties which are connected with different possibilities for practical application [1]. Continuing our work on praseodymium perovskites, compounds with general formula PrCo$_{1-x}$Cr$_x$O$_3$ (with $x = 0$, 0.33, 0.5, 0.67 and 1) were synthesized using solution combustion method.

In order to obtain perovskites with desired composition and purity, the synthesis were performed using two different fuels: urea and glycine. The amount of fuel was calculated on the basis of the propellant chemistry and the ratio F/O was set to one. After the initializations of the reaction mixture, the obtained powders were heated at different temperatures for different periods of time. The annealed samples were identified using X-ray powder diffraction. The purity of the compounds obtained using glycine as a fuel were better and for further investigations perovskites obtained with this fuel were used. The crystal structure was refined by Rietveld method, and the morphology of the particles was investigated using SEM. Structural investigations of the perovskites revealed that all compounds crystallize in orthorhombic system, within the space group $Pnma$ ($Z = 4$). The effect of the substitution of Co$^{3+}$ ion with Cr$^{3+}$ was investigated by analyzing different crystallochemical parameters (deformation of the polyhedra around cations, bond valence of the ions, global instability index etc). Most of the obtained results are in accordance with expected change in parameters based on the difference in ionic radii of Co$^{3+}$ ($r$(Co$^{3+}$) = 0.545 Å, low spin) and Cr$^{3+}$ ($r$(Cr$^{3+}$) = 0.615 Å).


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Keywords: perovskites, powder X-ray diffraction, SEM.
STRUCTURAL CHARACTERISTICS OF GdCo$_{1-x}$Cr$_x$O$_3$  
($x = 0, 0.33, 0.5, 0.67, 1$) PEROVSKITES

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The perovskite structure (ABO$_3$) can accommodate different ions in the positions of the cations (A, B). The most pronounced influence on physico-chemical properties of perovskites have the ions in the B-position, and among them perovskites with Co$^{3+}$ ion exhibit variety of interesting properties. Investigating the influence on the substitution of cobalt ion with chromium, perovskites with formula GdCo$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.33, 0.5, 0.67$ and $1$) were synthesized and characterized.

Gadolinium perovskites were synthesized using solution combustion method. The reaction mixture containing nitrates of corresponding metals was mixed with urea, which was used as a fuel for the combustion. In order to obtain the highest reaction temperature during the combustion, the ratio between the fuel ant total oxidants (F/O) was set to one. The obtained voluminous powders were heated at 800 °C for 4 hours. The obtained samples were analyzed by powder X-ray diffraction. The crystal structure of these perovskites was refined by Rietveld method.

The analysis of the X-ray diffraction patterns showed that continuous series of solid solutions within the system GdCo$_{1-x}$Cr$_x$O$_3$, was formed. The obtained perovskites belong to the orthorhombic crystal system. The crystal structure has been refined in space group $Pnma$ ($Z = 4$). The relationship between lattice cell parameters of all compounds are $a>b>/sqrt{2}>c$, and these compounds belong to O-type perovskites. Also, with enhancement of the substitution of cobalt ion with slightly bigger chromium ion, the cell parameters increase gradually. The tilting angles of the octahedral ($\theta$ and $\Phi$) increase with enlargement of the substitution of cobalt ion. On the other hand, the tilting angle $\varphi$ stays almost the same. It may be noticed from the analyzed results that although the cell distortion is increasing through the series the global instability index is decreasing.

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Keywords: perovskites, combustion synthesis, powder X-ray diffraction.
Most of clinoptilolite (CPT) deposits are opencast making it a very prospective raw material for industrial application. In addition to this fact clinoptilolite possesses a microporous Si/Al framework and is structurally isotypical with heulandite. Thus, it is not surprising that clinoptilolite structure, properties and respective alterations have been extensively studied. Here we present ZnCl$_2$ molten exchange in clinoptilolite, as an alternative of the ion-exchange, and the thermal behavior of the obtained Zn form. The conditions for optimal molten exchange were adjusted and it was found that the process of ZnCl$_2$ incorporation is less time consuming than the ion-exchange while the amounts of Zn in the CPT structure are comparable. As the exchange process requires the treatment of clinoptilolite with relatively elevated temperatures (~380 °C) we investigated the stability of clinoptilolite structure in function of temperature. The results showed that natural CPT structure is conserved up to 550 °C while the Zn form is even more stable.

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Keywords: zeolite, microporous materials, cation substitutions.
SYNTHESIS AND STRUCTURE OF \(bc\)-DICHLORO-af-DIHYDROXO-de-BIS(N-3-PYRIDINYL METHANESULFONAMIDE) PLATINUM(IV) DIHYDRATE

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Pt(IV) complexes attract much attention as potential anticancer agents, because of their better profile of pharmacokinetics and toxicity with respect to cisplatin and other Pt(II) analogues, and some of them have shown promising results in clinical trials \([1]\). In continuation of our previous studies on the coordination chemistry \([2–4]\) and cytotoxic effect \([5]\) of platinum-group metal complexes with N-3-pyridinylmethanesulfonamide (PMSA), now we report the synthesis and crystal structure of the title compound, \(cis,cis,trans\)-[Pt(PMSA)\(_2\)Cl\(_2\)(OH)\(_2\)·2H\(_2\)O \((1)\). The compound was prepared by oxidation of \(cis\)-[Pt(PMSA)\(_2\)Cl\(_2\)] by \(H_2O_2\), and was characterized by elemental analysis, molar electric conductivity and IR spectroscopy.

Crystals of \(1\) (monoclinic, \(C2/c\) \(a = 16.5424(7), b = 8.6973(3), c = 16.6079(6)\) Å, \(\beta = 117.185(5)^\circ\), \(Z = 4\)) contain complex molecules (\(C_2\) symmetry) of in which the Pt is almost octahedrally surrounded and the pyridine rings are inclined (64.6(1)\(^\circ\)) in the same direction with respect to the plane defined by the Pt, the Cl and N donor atoms, and the sulfonamide groups are in a transoid orientation between each other.

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Keywords: platinum(IV), sulfonamide, cytostatic.
Theoretical and spectroscopic studies of a series of monomeric and dimeric complexes formed by the modification of the zirconium butoxide precursor with acetylacetone and subsequent hydrolysis and/or condensation have been performed applying DFT/B3LYP/6-31++G(d) and high accurate RI-ADC(2) methods as well as IR and UV/Vis transmittance and diffuse reflectance spectroscopies. Based on DFT model calculations and simulated and experimental UV-Vis and IR spectra of all the studied structures, the most probable building units of the Zr(IV)-AcAc gel were predicted: the dimeric double hydroxo-bridged complex $\text{Zr}_2(\text{AcAc})_2(\text{OH})_4(\text{OH})_2$, 9 and the mono-oxo bridged complex $\text{Zr}_2(\text{AcAc})_2(\text{OH})_4\cdot\text{H}_2\text{O}$ 12. In both structures the two AcAc ligands are coordinated to one Zr atom. It was shown that the building units 9 and 12 determine the photophysical and vibrational properties of the gel material. The observed UV-Vis and IR spectra of Zr(IV)-AcAc gel were interpreted and a relation between the spectroscopic and structural data were derived. The observed UV-Vis bands at 315 nm and 298/288 nm were assigned to a partial ligand – metal transitions and to intra-/inter AcAc ligand transitions, respectively.
NEW COPPER COMPLEXES OF TERTIARY PHOSPHINE OXIDE AND FUNCTIONALIZED NITROGEN-CONTAINING PHOSPHINE OXIDE LIGANDS – STUDY OF STRUCTURE AND PROPERTIES

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The tertiary phosphine oxides are widely used in the practice: in analytical chemistry as extragents, in organic synthesis – to introduce functional groups, in technologies – for obtaining of nano-structural materials, etc. Recently, tertiary phosphine oxide ligands were applied for preparation of coordination polymers [1–4]. These compounds based on infinite networks of transition metals and multifunctional ligands possess potentially interesting properties for different areas such as hydrogen storage, molecular adsorption and separation, ion exchange, luminescence, magnetism, catalysis, etc. The studies in the filed of crystal engineering of coordination frameworks are focused on using of proper ligand systems, assuring both structural rigidity and pore size.

The research of our group was started with bidentate aromatic tertiary phosphine oxides. Thus, series of coordination polymers of Mn\textsuperscript{2+}, Cu\textsuperscript{2+} и Zn\textsuperscript{2+} with different dimensionalities and structures have been synthesized and characterized. In this paper we are presenting the synthesis and structural characterization of two copper(II) complexes with tridentate tertiary phosphine oxides, namely, 1,3,5-tris(dimethylphosphinylmetoxy)benzene (L1) – with an aromatic link between the three substituents bearing the donor phosphine oxide groups and N,O-containing ligand \textit{bis}((dimethylphosphinyl)-methyl)amine (L2), where the secondary amine group is the link between the two phosphine oxide groups. The results obtained showed that the crucial factor for formation of metal-organic frameworks is the ligand structure. A copper coordination polymer with a Cu\textsubscript{3}(L1)\textsubscript{3}Cl\textsubscript{6}-spacer was formed only using 1,3,5-tris(dimethylphosphinylmetoxy)benzene. In the polymer, there are two kinds of divalent copper atoms, i.e. almost regular square-planar CuO\textsubscript{4}–units alternate distorted tetrahedral CuOCl\textsubscript{3}–units (Fig. 1). The polymer crystallizes in the monoclinic space group P2\textsubscript{1}/c. At the same reaction conditions, the chelating N,O-ligand (L2) gave only a mononuclear five-coordinate copper(II) complex, having the tridentate ligand as a capping ligand in the CuO\textsubscript{2}NCl\textsubscript{2} units. The compound crystallizes in the orthorhombic Pca\textsubscript{2}\textsubscript{1} space group. The stereochemistry of copper(II) in this compounds can be described as a square-based pyramid with trigonal bipyramidal distortion. The structure and properties of the newly synthesized complexes have been studied by instrumental methods for structural analysis: X-ray diffraction and magnetic measurements, UV-Vis and IR Spectroscopy.

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The aim of this study is to obtain growing patterns incorporating two metals. Alkaline and acid electrolytes with various concentrations of copper and nickel ions are studied. We found the suitable concentrations of basic components for obtaining dendritic structures at potentiostatic condition. The morphology and distribution of components in the alloy are investigated by SEM and EDX analysis. Different content of both metals is found along the dendritic structures - while the copper prevails in the initially grown parts, the nickel takes over in the late stages of the growth.
SERIES OF MANGANESE(II) COORDINATION POLYMERS CONTAINING DIMETHYL(METHYLENOXYARYL)PHOSPHINE OXIDE-BRIDGES AND INORGANIC LIGANDS: SYNTHESIS, SINGLE-CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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Research on the synthesis of metal-organic frameworks by copolymerization of metal ions and organic ligands is of growing significance, mostly owing to their intriguing structural features and promising properties for potential technological and industrial application. On the other hand, the interest in the crystal engineering is determined from both the synthetic routes and the art of structural design. One of the challenges in this field is to forecast the crystal structure and properties on the basis of the nature of the building units. Recently, three bis-(dimethylphosphinylmethoxy) benzenes have been already employed for the synthesis of coordination polymers [1-3]. Thus, series of cooper(II) and zinc(II) frameworks with different structures and properties were obtained. The ligands used have bidentate nature and coordinate through the two phosphoryl oxygen donors from the substituents, disposed in α-, m- and p-positions in aromatic ring [4]. The structural diversity of the polymers obtained was determined primary by the metal ion nature, as well as from the mutual disposition of the two tertiary phosphate oxide groups in the ligands and the size and coordination ability of the counterions used.

In this report, the synthesis and characterization by magnetic measurements, EPR, IR spectroscopies and elemental analysis of five new manganese(II) coordination polymers with bis(dimethylphosphinylmethoxy)benzene-bridges are described. The compounds were obtained by reactions of the phosphate oxide-like-digands and corresponding salts MnCl₂·4H₂O and MnSO₄ in alcoholic medium and in any cases, counterions such as AsF₆⁻, ClO₄⁻, etc. were used for precipitation. The structures of three of the compounds were determined by single-crystal X-ray crystallography (Fig. 1). The structural studies show that the metal atoms in the polymers with different dimensionalities have six-coordinate geometry MnO₆ with a distorted octahedral environment. The inner coordination sphere of the Mn(II) ions are constructed with different numbers of O-donors belonging to tertiary phosphate oxide-linkers and oxygens from the sulfate-ion bridges and solvents molecules such as C₂H₅OH and H₂O. Magnetic measurements proved significant antiferromagnetic coupling between Mn(II) ions in the hexa-coordinated Mn(II) 2D polymers.

Fig. 1. Octahedral coordination environments of Mn(II) in the coordination polymers studied.

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GANGLIA LIKE ZnO STRUCTURES FOR BIOSENSOR APPLICATIONS

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Zinc oxide (ZnO) is a wide band gap semiconducting material that has various applications including optical, electronic, biomedical, corrosion protection and biosensors. It is usually synthesized via processing routes, such as vapor deposition techniques, sol–gel, spray pyrolysis and thermal evaporation, oxidation and anodizing. ZnO-based thin films have potential application in the biological field as biosensors. The applications of ZnO thin films surfaces in biosensors require a variety of different functionalities in order to immobilize biomolecules without cells interference. The interaction of a surface with cells is usually dominated in the initial stage by adhesion of proteins onto the biomaterial surface, which occurs rather rapidly. For this reason it is important to study the interactions of cells with ZnO-based surfaces and not to tailor them, if necessary, by suitable surface modifications.

Here, we reported synthesis of nanostructured ZnO film directly from a solution precursor using sol-gel method. Nanostructured ZnO coatings were deposited from the sol precursor prepared using zinc acetate, monoethanolamine and 2-methoxyethanol. This solution was deposited on glass substrates via dip-coating technique. The resulting thin films were characterized by different methods XRD and SEM. Biocompatibility of the films were investigated by optical microscopy.

X-ray diffraction confirmed polycrystalline nature and hexagonal wurtzite crystal structure of the coatings. There is ganglia typical surface structure of the obtained film, which was shown by SEM. They are evenly distributed over the entire surface of the film. In this study, we also investigated the biocompatibility of nanostructured ZnO films using human hepatocellular carcinoma (Hep G2) and endothelial (EA.hy 926) cells. The results with optical microscopy showed that ZnO films do not favor the cells’ attachment and adherence. Cell viability assays indicates that the growth rate was significantly reduced compared to the controls making them a suitable material to tune the surface properties which can promote specific biomolecule adsorption and/or suppress biofouling with potential application in biosensors preparations.

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Keywords: zinc oxide thin films, dip coating, sol-gel method, biocompatibility, biosensors.
ZnO THIN FILMS PREPARATION ON GLASS SUBSTRATES
BY TWO DIFFERENT SOL–GEL METHODS

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Zinc oxide is a modern material known for its numerous applications in research and practice. Here we present thin films of ZnO with photocatalytic application in purifying water from organic pollutants. The films were obtained from stable colloidal precursor sol, prepared by two sol–gel method using zinc acetate and various solvents. These solutions are deposited on glass substrates via dip-coating technique. The resulting nanostructured films are characterized by different methods (XRD, SEM, FTIR). By XRD show that the zinc oxide is with hexagonal crystal structure. The three characteristic peaks clearly proof the existence of ZnO, which correspond to different crystallographic orientations of the crystal lattice of vyuurtit (from left to right) (100) – at $2\theta = 31.76^\circ$; (002) – at $2\theta = 34.39^\circ$ and (101) – at $2\theta = 36.24^\circ$.

A comparison of the determined morphology, composition and structure for the prepared by two different method films is studied. The morphology of films obtained with 1-propanol and 1-butanol, as shown is not homogeneous. The film surface is not uniform and there are many cracks and bubbles. Layers in such films is very easy to peel off after their ignition. Therefore, a third synthesis of the first sol-gel method is performed, with any changes in the formulation, only alcohol is substituted by 2-propanol. There is ganglia typical surface structure of the so obtained film, which is established by SEM. They are evenly distributed over the entire surface of the film. The film surface in the second sol-gel was investigated by SEM. The film surface has characteristic ganglia-like patterns. The resulting samples are more uniform show much better adhesion of the layers and higher density, compared to films from the first sol-gel method.

FTIR spectroscopy provides information about the presence of remaining organics. This was deduced from the resulting absorption groups, which are received and can be established to which functional groups are responsible. Both films contain only ZnO.

The difference in the films morphology has influence their photocatalytic performance.

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Keywords: zinc oxide, thin films, crystallites, glass substrate, dip coating, sol-gel method.
SIZE AND DISTRIBUTION OF Pt NPs IN LDH NANOCOMPOSITES UNDER HEATING

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Nanocomposites were successfully synthesized from multicationic layered double hydroxides (LDHs) and platinum nanoparticles (Pt NPs). Specific experimental conditions for control of the NPs mean diameter were established. The particle size and the phase composition of the samples were investigated by means of XRD and TEM while the thermal behaviour of the LDH nanocomposite by DTA-TG analysis.

Topotactic transformations of the LDH support in mixed oxide and in spinel were observed after heat treatment at 500 °C and 1000 °C, respectively. In addition of this well-known phenomenon, the change of the mean size and the size distribution of the Pt NPs was established. The intercalated in the support Pt NPs were coalesced under heating. Rough and granular aggregates were formed after treatment at 500 °C while large, dense and well-faceted, particles were observed at 1000 °C. The size distribution of the Pt NPs was improved with the increase of the temperature.

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Keywords: LDH and Pt NPs nanocomposite; structure and phase composition.
WHAT HAPPENS AFTER X-RAY STRUCTURE IS SOLVED – LESSONS FROM PROTEIN IONISATION EQUILIBRIA

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There is no doubt that X-ray crystallography is among the most powerful methods helping us understand fundamentals of life. The pioneering works of Rosalind Franklin, Watson and Crick (three-dimensional structure of DNA) and Max Perutz (three-dimensional structure of haemoglobin) have shown that biomacromolecules are molecular machines bearing and reproducing information; catalysing processes; binding, transporting and releasing chemical material, transforming energy. The works of these and many other scientists from the 50-ies – 60-ies of the last century uncovered a huge research area, namely structure-function relationships in biomacromolecules, including of course structure-function relationships in proteins.

It turns out that three-dimensional crystalline structures of proteins may differ from those of the corresponding molecules in solution - their more natural state. The obvious reasons for this effect are the crystal contacts and the electrostatic influence of counterions trapped in the crystal structure. All these are not present when proteins are in solution. Other phenomena are more delicate and do not follow directly from the crystal environment, neither can be detected unambiguously by X-ray crystallography. Such a phenomenon is the conformational flexibility of proteins.

Conformational flexibility turns out to be a major factor determining the ionisation equilibria in proteins. The complexity of this phenomenon arises from the fact that proteins are poly ions with large number of mutually dependent ionisable sites. The solution of this task, based on X-ray structure only, often leads to misleading interpretations. The introduction of the conformational flexibility helps to avoid such undesirable situations. Two cases of successful introduction of conformational flexibility will be presented: 1) the correct prediction of pH dependence of unfolding free energy and 2) the improvement of the theoretical prediction of ionisation constants of functional groups in protein. Finally, an example of pH dependent conformational changes will be illustrated.
THE THERMAL DEVICE OF THE IMAGE FOIL GUINIER CAMERA IN THE GEOLOGICAL INSTITUTE, BAS: CALIBRATION AND USAGE EXPERIENCE

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The thermal device of the Image Foil Guinier camera in the Geological Institute, BAS is a powerful tool for recording powder diffraction patterns at any given temperature in the range ambient → 900 °C. Along with the simple registration of solid state phase transitions, the tool allows precise determination of the thermal expansion behavior of the studied substance. Combined with some Rietveld refinement, the peak shape changes close to transition points can also provide additional information about the symmetry transition mechanisms. Less routine applications of the device include recording of the reverse homogenization temperatures of admixed bi-phase samples: a problem of high importance in geology. In-situ observation of solely heat induced solid state reactions of bi- or poly-phase samples can be of particular interest in some cases too.

The sample is loaded in a quartz glass capillary tube, 0.5 mm thick and with 0.01 mm wall thickness. Given the 10 mm optimal length of the tube, the amount of substance required for the study is just 1.8 mm$^3$.

The method, however, has some restrictions and specifics, one of the most important ones being the calibration of the tool. Due to its open design, the temperatures reported by the feed-back thermo-couple differ (significantly in the high temperature range) from those in the capillary with the sample. Since temperature in both points is transferred by infrared irradiation, the specific (rather different) heat capacity of the glass and the Pt play important role for the resulting temperatures of these two objects. The magnitude of this difference is specific for each individual heating device. This is why, a correction curve should be carefully generated, prior to put the device in use. The generation of the curve is based on the differences between reported (by the thermo-couple) and real (known phase transition temperatures of chosen substances) temperatures of the sample tested.

Along with calibration, a good deal of experience is required, for obtaining reliable results. The capabilities, restrictions and our own experience in calibration and using the thermal device will be communicated and discussed in the presentation.

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Keywords: thermal device, calibration, Guinier camera, capillary sample.
Two-stage protonation of a small-pore microporous zirconosilicate $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$

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The synthesis, crystal structure and temperature behaviour of the small-pore zirconosilicate $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$ were reported earlier [1]. It was found that the structural framework is built up of $\text{ZrO}_6$ octahedra and $\text{SiO}_4$ tetrahedra in a manner that results in the formation of $\alpha$-$\text{ZrP}$ type of layers. The adjacent layers are related by rotation and are connected via oxygen atoms creating $[\text{Si}_2\text{O}_7]$ pyrogroups. The structure is thus three-dimensional framework and possesses a system of interconnected channels where the sodium ions and water molecules reside. Here we present the pH-dependent protonation behaviour of the titled compound. Several protonated samples were prepared using different reaction mediums. Subsequently two of the samples were chosen for further investigations designated as HM-1 and HM-2, 1 and 2 meaning the initial pH value of the leaching solution. The studied samples were characterized by powder XRD, DTA-TG and chemical analyses. The crystal structures of the HM-1 and HM-2 were refined and compared with that one of the studied compound. Although the monoclinic arrangement of the structure is preserved the crystal structures becomes pseudo-orthorhombic with values of $\beta = 89.519(9)^\circ$ and $89.872(3)^\circ$ for HM-2 and HM-1 respectively. It was found that sodium leaching causes morphological changes of the framework channels and consequent mutual shifting of the adjacent layers.


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Keywords: crystal structure, protonation, zirconosilicate.

Fig. 1. Crystal structures of the initial and protonated samples: A – initial; B – HM-1; C – HM-1
STRUCTURAL INVESTIGATIONS OF MAGNETOELECTRIC MATERIALS BY NEUTRON DIFFRACTION

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We describe the possibilities to identify new materials with multiferroic and magnetoelectric behaviour, based primarily on considerations of symmetry and the knowledge of the magnetic structure. The systems studied were from the ReMnO$_3$ and ReMn$_2$O$_5$ series (Re is a rare earth ion or Yttrium) with perovskite-like structure and other structurally unrelated materials like Y-type hexaferrites. The materials are magnetic insulators that display a sequence of magnetic phase transitions. The ferroelectric polarization is explained by the Dzyaloshinski-Moriya interaction and non-collinear magnetic order with strong chiral components. The coupling of magnetic and ferroelectric order parameters is not well understood, and it may be related to competing ground states in these materials.
RARE-EARTH DOPED OPTICAL WAVEGUIDES IN LiNbO$_3$

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Doping of dielectric hosts with laser-active ions, such as the rare earth ones, is widely researched recently. The great interest has been provoked by the miniature waveguide solid state lasers obtained that way, and the opportunity for monolithic integration of these lasers and other elements on a common substrate.

The present article is a data review on the doping of LiNbO$_3$ with ions of rare-earth elements. Here, an attempt is made to summarize the most important results on technologies for doping with rare earths of optical waveguides in LiNbO$_3$ substrates and for obtaining of optical waveguides in rare-earth doped LiNbO$_3$. The sequence of the technological steps depends on the methods of doping and particularly on the temperature. The main methods of doping are described: ion implantation, diffusion from a layer deposited on the LiNbO$_3$ crystal substrate, diffusion from a melt. The main points of consideration are the effect of substrate orientation and of the initial doping on the subsequent diffusion processes, mechanism of rare-earth ion penetration and the possible positions they occupy in the lattice, structural changes due to the doping versus technological parameters, etc. A special attention is paid to the low-temperature methods of diffusion; they imply ion exchange or diffusion without ion exchange when the doping ions are situated in existing vacations of the host. The influence of the melt composition, temperature and duration of the diffusion on the concentration of the dopant in the waveguide is discussed, as well as the conditions at which that kind of anisotropic diffusion process becomes self-restricted.

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Keywords: Rare earths, Optical waveguides, LiNbO$_3$. 
SYNTHESIS AND CRYSTAL STRUCTURES OF ZINC PHOSPHATES DOPED WITH SAMARIUM AND MANGANESE

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Recently there has been significant interest in rare-earth doped zinc phosphates due to their potential applications in advanced devices such as laser sources, sensors, photodiodes, X-ray imaging plates etc [1].

Our research on rare earth doped zinc phosphates has demonstrated UV and X-ray exited photo-luminescence in the visible spectra for glass ceramics materials formed in the ZnO-rich compositions. We believe the strong photoluminescence is due to the stabilisation of rare earth ions within the host glass-ceramic matrix, including within the crystalline phases. It is of particular interest to investigate these crystalline phases and to study their structures, in order to understand their relationship with the photo-luminescence properties.

The doped zinc phosphates were prepared by a typical high-temperature solid state syntheses where ZnO, NH₄H₂PO₄ and Sm₂O₃ (or MnO) of pre-determined ratios were powdered, mixed and placed in alumina crucibles. The synthesis was performed in the range of 850–950 °C for 3 to 5 hours in a muffle furnace. Samples were quenched out of the melt to room temperatures and after that annealed at 250 °C for 2 hours. Rare earth doping varied between 0.03 and 0.28 mol %.

Using powder X-ray diffraction, we have found that the obtained crystalline phases are isostructural with α-Zn₂P₂O₇ [2], illustrated in Figure 1, where samarium and manganese ions substitute for Zn²⁺. Some of Zn²⁺ sites in the structure are 5-coordinated and others are 6-coordinated. This corroborates with the observed photo-luminescence spectra which also confirm that all samarium ions are present in 3+ valence state.

In our work we present crystal structure studies of samarium and manganese doped zinc phosphate ceramics, we examine the difference between the two dopant structures, and we correlate them to the observed photo-luminescence properties.


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Keywords: doped zinc phosphates, samarium, manganese.
THE ELECTRON-PHONON INTERACTION IN Bi$_{12}$SiO$_{20}$
DOPED WITH Fe$^{2+}$, Cr$^{3+}$ AND P$^{5+}$ IONS

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The absorption coefficient of Bi$_{12}$SiO$_{20}$:Fe, Bi$_{12}$SiO$_{20}$:P and Bi$_{12}$SiO$_{20}$:Cr+P single crystals is measured in the spectral region of Urbach’s rule at room temperature. The parameters of electron-phonon interaction [1], Urbach’s energy [2] and the constants of Urbach’s rule [3] are calculated. It is established the mode of decomposition of bound excitons with the ionized donors Fe$^{2+}$ and Cr$^{3+}$ in the crystal lattice. It is reported the behavior of the acceptor P$^{5+}$ in Urbach’s rule region.


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Keywords: electron-phonon interaction, Urach’s rule, doped sillenites.
THE OPTICAL INFLUENCE OF Cr$^{3+}$ AND P$^{5+}$ IONS ON THE PROPERTIES OF DOPEd Bi$_{12}$SiO$_{20}$

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The absorption coefficient of Bi$_{12}$SiO$_{20}$:Cr+P and Bi$_{12}$SiO$_{20}$:P single crystals [1, 2, 3, 4] is measured in the visible and far IR spectral regions. The influence of P$^{5+}$ ions is determined in double doped sillenite. The energy level diagram of Cr$^{3+}$ is produced. The Jahn-Teller effect and spin-orbit interaction are explained in the concrete crystals. The Racah parameters have been calculated also. The magnitude of the composite oscillations is determined in far IR region.


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Keywords: doped sillenites, Jahn-Teller effect, spin-orbit interaction, Racah parameters.
ANALYSIS OF STRUCTURE FACTORS ($F_{hkl}$) OF MEANINGFUL XRD DIFFRACTION INTENSITIES FOR CHEMICAL DETERMINATIONS AFTER ION-EXCHANGE AND ISOMORPHIC SUBSTITUTIONS IN CRYSTAL STRUCTURES

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Clinoptilolite case

Ion-exchange of clinoptilolite with heavy cations (Sr, Ba, Pb, Ag, Cs, Tl) results in large intensity changes in the powder XRD pattern. These intensity changes can be interpreted using the known crystal structure of clinoptilolite. For 0k0 type reflections, the structure factor change in relation to the number of cations (or the number of electrons) in the mirror plane of the structure (space group C2/m). Variations in $F(020)$ depend mainly on the cationic part of the structure, the contribution of which in the structure factor is always positive and depende on the type and quantity of the exchangeable cations. Using the derived simplified equation, $F(020)= - 250 + \sum n_f$, and applying corrections for mass absorption coefficients ($\mu^*$) quantification of the degree of ion-exchange can be achieved by measuring I(020) of clinoptilolite before and after cation exchange.

Fluorite case

Powder XRD studies of Ca$_{1-x}$Sr$_x$F$_2$ single crystals (0.007≤$x$≤0.674) are important to evaluate the influence of Sr-concentration in such single crystals, which are promising materials for optoelectronics. In a typical powder XRD pattern for Ca$_{1-x}$Sr$_x$F$_2$ sample the most intense peak is (111). In what follows, we inspect the dependencies of the XRD intensity ratio $I_{111}/I_{222}$, which is a suitable crystal chemical parameter when studying the fluorite structure. Diffraction maxima $I_{111}$ and $I_{222}$ correspond to parallel atomic planes and, in general, the ratio $I_{111}/I_{222}$ should be a constant. However, the intensities $I_{111}$ and $I_{222}$ would strongly depend on the isomorphic substitution of Ca$^{2+}$ by Sr$^{2+}$ in the cationic position of the fluorite structure.

The intensity of an X-ray diffraction maximum $I_{hkl}$ is directly proportional to the square of the corresponding structural factor $|F_{hkl}|^2$ expressed as:

$$F_{hkl} = \sum n_f \exp(2\pi i \sum hx \pm ky \pm lz),$$

where $i$ stands for the imaginary unit, $n_f$ for the number of atoms per position; $f_j$ for the X-ray atomic scattering factor for an element (ion) in the structural position; $x$, $y$, $z$ are the coordinates of the atomic position; and $h$, $k$, $l$ are Miller indices of a diffraction line.

Further, using these formulae and knowing the ion coordinates ($x$, $y$, $z = 1/4$ for F$^-$ and $x$, $y$, $z = 0$ for Ca$^{2+}$ (Sr$^{2+}$)) in the fluorite structure (space group Fm$\overline{3}$m) one can calculate $F_{111}$ and $F_{222}$: $F_{111} = 4f(M)$ and $F_{222} = 4f(M) - 8f(F)$, where $M$ stands for cations occupying the (4a) Wyckoff position.

It is clear that for Ca$_{1-x}$Sr$_x$F$_2$ compounds $f(M)$ depends strongly on $x$ and, consequently, the ratio $I_{111}/I_{222}$ should vary with $x$. The conclusion is that $F_{111}$ and $F_{222}$ (and respectively $I_{111}$ and $I_{222}$) depend only on the isomorphic substitution of Sr$^{2+}$ for Ca$^{2+}$ and, as $f$(Ca) < $f$(Sr), the ratio decays exponentially with $x$. So, one can judge for the Sr$^{2+}$ content in the fluorite structure based on the ratio $I_{111}/I_{222}$. 
SYNTHESIS OF ZEOLITE A FROM BULGARIAN RICE HUSK AND WASTE ALUMINIUM

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Zeolite A [Na_{12}Al_{12}Si_{12}O_{48}.27H_2O] is the most widely used synthetic zeolite. It has found broad range of industrial applications as ion-exchanger, molecular sieve and catalysis, but the largest-volume application of zeolite A is as water softening “builder” in detergent formulations. Zeolite A could be synthesized from a variety of Si and Al – bearing row maretials, including waste ones. Several recent studies have demonstrated that high-grade zeolite A could be synthesized from silica-rich (85%-98% SiO_2) rice husk ash generated during the burning of rice husk, one of the largest agricultural wastes, in power production plants [1,2].

Bulgarian rice husk and waste aluminium cans were used as silicon and aluminium source for the synthesis of zeolite Na-A by conventional alkali hydrothermal treatment method. Six different procedures for the preparation of the initial synthesis gel were tested. It was demonstrated that pure zeolite Na-A can be synthesized from both rise husk and rise husk ash.

The morphology and particle sizes distribution of the synthesized products were observed in details by scanning electron microscopy (SEM). In all cases well shaped cubic crystals of micron size (1-5 micrometers) were obtained. Rarely, the presence of smaller ball-like crystals build of blade-shaped intersecting plates was detected. The bulk composition of the products was evaluated on the base of integral spectra of several thousands crystals, and the elemental composition of dozens of zeolite crystals was examined by energy-dispersive X-Ray analyses. X-Ray Diffraction (XRD) spectroscopy analyses confirmed the presence of zeolite Na-A (cubic crystals). In some samples Sodalite (balls) was identified as an admixture phase.

Investigations on the optimization of treatment conditions in order to obtain zeolite A of the commercial quality required for laundry detergent production are in progress.


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Keywords: Rice husk, Zeolite Na-A, SEM-EDX
MORPHOLOGICAL EVOLUTION OF ZEOLITIZED FLY ASH FROM “MARITSA 3” TPP – BULGARIA

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Fly ash (FA) from electrostatic precipitators in “Maritza 3” thermal power plant, Dimitrovgrad, was hydrothermally activated at 130 °C with duration from 1 to 7 hours; with or without preliminary or post temperature aging. At these conditions a process of transformation of fly ash aluminosilicates into various types of zeolites is taking part. The crystallization of zeolites goes simultaneously with the dissolution of Si$^{4+}$ and Al$^{3+}$ and gel-formation processes [1, 2].

The morphology and elemental composition of several hundred zeolite particles have been studied using Scanning Electron Microscope, equipped by Energy Dispersive X-Ray Detector. The active crystallization of zeolite phases begins in the third hour of alkali treatment. Four morphologically different types of zeolite crystals (blades, strobiles, pyramids and cubes) have been distinguished [3]. They could be associated with the zeolite types of Sodalite, Na-P, Na-X and Na-A, respectively.

The formation and growth of these different zeolites have been tracked out on the base of the investigation of morphology and composition of dozens of individual crystals of each type. It was found that Sodalite is the most abundant phase in all samples, and it co-exists with the other zeolite phases. Na-A crystals were found to present only in samples subjected to a long post temperature aging. The elemental composition of Sodalite crystals is quite constant, while their morphology evolutes during the thermal treatment from aggregates of randomly oriented rods to well-shapes intersecting blades.


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Keywords: Fly ash zeolites, SEM-EDX, crystal morphology.
The morphology assessment was made of well-formed cane sugar monocrystals with a size larger than 5 mm and reaching 10–15 mm in length with visually distinct crystal walls. The detailed morphology assessments of single cane sugar crystals firmly indicate that they are with a triclinic symmetry without symmetry elements, i.e., they belong to triclinic-monohedral class and thus differ from the monoclinic symmetry of beet sugar crystals according to literature data. Morphology studies conducted on single crystals of sugar obtained from sugar cane by three consignments showed that these crystals are mainly faceted with well-developed faces of six monohedra with indices (100) and (100) followed by (001) and (001) and (010), two vertical walls with indices (hk0) and (hk0), as well as two to four plate-like cross-walls developed to varying degree with indices (hkl), (hkl), (hkl) and (hkl). Especially typical for the single crystals is the appearance of a very typical monohedron with a less-developed face with indices (0kl), as well as a barely distinct wall with indices (0kl), which develop during the crystallization of sugar solutions without impurities at high concentrations.

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Keywords: sugar cane monocrystals, sugar beet; symmetry triclinic and monoclinic, pinakoidal and monohedral.
SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF ZnTiO$_3$
POWDERs OBTAINED BY DIFFERENT SOL–GEL METHODS

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Zinc titanate (ZnTiO$_3$) is an attractive material due to its various applications as paints pigments, fusion cast thermistors, sorbent, microwave dielectrics, dielectric resonators, catalysts, etc. There are several methods for preparing ZnTiO$_3$ powders, including conventional solid state reactions, mechanochemical activation and several variants of sol-gel technique. The most common way for obtaining ZnTiO$_3$ is sol-gel method. It provides fine and homogeneous powders with a high specific surface area. Low-temperature is required for the formation of this compound because of the decomposition of ZnTiO$_3$ to Zn$_2$TiO$_4$ and rutile at high temperature (945 °C). The purpose of this study is to synthesize nanosized ZnTiO$_3$ powders using hydrolytic and nonhydrolytic sol-gel methods and to study their structure and properties. The present study extends our previous investigations on the synthesis of nanosized powders in the ZnO–TiO$_2$ system[1].

For the synthesis of zinc titanate by hydrolytic route zinc acetate and titanium ethoxide were used as starting materials. The synthesis of nanocrystalline ZnTiO$_3$ by a nonhydrolytic route was based on the reaction between TiCl$_4$, ZnCl$_2$ and benzyl alcohol at moderate temperature, followed by calcination at 500 °C.

The structure and morphology of the resulting particles were characterized by XRD, IR and SEM analysis. The obtained ZnTiO$_3$ powders exhibit photocatalytic activity in the degradation of Malachite Green (MG) under UV-light irradiation.

Study of the antibacterial properties of the synthesized powders is in progress.

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To improve accuracy in the XRD characterizations of crystalline structures, our concern here is essentially with the exact relationship between diffraction and extinction. Extinction is due to power loses caused by removing energy from the incident X-ray beam just at producing the diffracted beam. Therefore, under diffraction condition, just as the incident beam is extinguished so also is the diffracted beam. Since measured intensities are extinction-affected, they always cause extinction-induced systematic error on the resultant derived quantity. Elimination of the extinction-induced error, in absolute sense of this term, is object of our study that outlines an analytical approach for nullification of the extinction effects. The approach is based on using the empirical extinction coefficient \( k \) that is a constant inherent of any particular reflection of the XRD pattern. The constancy of \( k \) is established by examination of its relationship with both the secondary extinction coefficient \( g \) and the diffraction process. Any of the coefficients \( k \) and \( g \) is introduced as a constant of the crystal (i.e. as parameter that is independent of the \(<hkl>\) crystal direction) by Bragg et al. [1] and Darwin [2], respectively. However, since crystal is anisotropic body, one needs to reconsider the nature of the coefficients \( k \) and \( g \). So that, accounting for crystal and textural anisotropy, we have found that these coefficients are interconnected by 
\[
g = k P l_s S / 2 \mu \quad \text{and} \quad k = 2 g u P l_s S
\]
in terms of the same parameters that control diffraction process excluding only the reflectivity \( Q \) per unit crystal volume. Depending inversely on the diffraction parameters, the coefficients \( k \) and \( g \) show different behavior with respect to the level of interaction of the diffraction process. Actually, any level of interaction is controlled by both the intensity \( I_0 \) of the incident beam and the pole density \( P \) that represents the relative volume fraction of crystallites that satisfy simultaneously the Bragg condition. For a reflection, we have deduced that whereas \( g \) is proportional to the power of the level of interaction, \( k \) is a constant independent of the same level of interaction. Particularly, the coefficients \( k \) and \( k' \) of the same reflection of textured sample and random standard are equal, i.e. \( k = k' \). Actually, just the constancy of \( k \) predetermines its capability for nullification of the extinction effects. As an example, here a technique is discussed to attainment of extinction-free values in the pole density \( P \) determination. The procedure for nullification of extinction effects starts with kinematic definitions of \( P \) and finishes with an operative formula for its calculation. This formula contains a series of intensities measured at different levels of interaction of the diffraction process of the same reflection of both a textured sample and a random sample. Taking advantage of the \( k \)-relationship between kinematic and measured intensities, the nullification of the extinction effects is defined by equalizing two expressions of \( k \). Each of the \( k \)-expressions uses couples of intensities corresponding to the textured and random samples both measured at the same XRD condition. Therefore, because all intermediate stages of the nullification procedure are strictly dependent on the requirements of the mathematical logic, the resultant derived value of \( P \) is then in exact accord with the respective kinematic definition, i.e. \( P \) is extinction free. The main advantage of this approach is to gain accuracy and, hence, to physical reality of the data. Another its advantage is that it allows for the capability of internal experimental checks that reveal simply the real ability of the XRD apparatus to supply precise and accurate data.

We present results from numerical calculations with models with increasing complexity of vicinal crystal surfaces with competing interactions – attraction and repulsion with different range (different exponent in the power law for the interaction energy).

In the beginning of the talk are briefly introduced three model of step motion with increasing complexity and containing opposite tendencies – interstep attraction and repulsion. Their linear stability is studied to find the conditions (in terms of model parameters) that make the step motion unstable.

Further these equations are integrated numerically to obtain the step trajectories until the instability is well developed. Qualitatively all models result in the specific type of step bunching characterized with constant surface slope in the bunches. The two monitoring schemes for collecting quantitative information from the surface patterns are introduced. Two types of scaling relations are thus obtained – for the minimal interstep distance in the bunch and the time-scaling of the number of steps in the bunch. The latter can distinguish between the models.

Finally, the results from the present study are compared with these from previous studies of other authors.
Wollastonite (CaSiO$_3$) occurs in several polymorphic modifications: low-temperature and high-temperature. The low-temperature modification (β-wollastonite) comprises both triclinic polytypes (1T, 3T, 4T, 5T, 7T, 1Td) and monoclinic parawollastonite (2M). These forms are not easily distinguishable except by single-crystal X-ray work, since they differ only in the reflexions with k odd, and these are always weak.

Wollastonite with crystal chemical formula (Ca$_{0.996}$Fe$_{0.05}$)$_{1.046}$SiO$_3$ from zoned calcic skarns included in monzonites of the Zvezdel pluton (Eastern Rhodopes) is investigated. The mineral occurs in association with clinopyroxene, plagioclase, and epidote. Titanite and apatite are present as accessories. A single crystal of wollastonite with dimensions 0.20 × 0.10 × 0.10 mm was mounted on a glass fiber and measured on an Oxford diffraction Supernova diffractometer equipped with Atlas CCD detector. X-ray data collection was carried out at room temperature with monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structure of studied wollastonite is monoclinic with unit cell parameters: $a = 15.3770(11)$ Å, $b = 7.2990(4)$ Å, $c = 7.0491(5)$ Å, $\beta = 95.380(6)^{\circ}$, $V = 787.68(9)$ Å$^3$, and was refined to $R_1 = 0.0462$ and $R(\text{all}) = 0.0692$ using 1970 unique reflections. Wollastonite-2M contains dreier single chains. Si–O bond lengths vary between 1.580(3) and 1.667(3) Å (mean 1.624 Å), Ca–O bond lengths between 2.251(3) and 2.662(3) Å (mean 2.390 Å), Si–O–Si angles are 140.03(17), 139.39(18) and 150.81(18)$^{\circ}$ (mean 143.31$^{\circ}$). Atomic coordinates are listed in Tables 1.

The polytype transformations nT→2M of wollastonite have been explained as a result of deformation with shear stress or with temperature increase and they are useful petrogenetic indicators for the deformation and cooling history of a rock.

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Keywords: wollastonite-2M, single crystal structure.
NEW PEROVSKITE-BASED PbBaFe$_{2-x}$Mn$_x$O$_5$ (0≤X≤1.5)

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New perovskite-based compounds with general formula PbBaFe$_{2-x}$Mn$_x$O$_5$ (0≤X≤1.5) were synthesized by solid-state reaction under argon atmosphere. The compounds were characterized by X-ray powder diffraction, TEM (SAED, HRTEM) and $^{57}$Fe Mössbauer spectroscopy. The crystal structure of PbBaFeMnO$_5$ and PbBaFe$_{0.5}$Mn$_{1.5}$O$_5$ members of the series is determined by Rietveld refinement method. The results are with good agreement with SAED data and HRTEM images. The basic crystallographic sections in orientations [100], [010] and [001] are obtained by SAED method. Two HRTEM images in orientations [100] and [010] are registered to reveal the microstructure at unit cell level. The compounds crystallize in the orthorhombic space group Pnma with unit cell parameters $a ≈ \sqrt{2}a_p$, $b ≈ a_p$, and $c ≈ 4\sqrt{2}a_p$ ($a_p$ – the parameter of the perovskite subcell). The crystal structure consists of perovskite blocks separated by $\frac{1}{2}[110]_p$ (\(\overline{T}01\))$_p$ ($p$ – the perovskites subcell) crystallographic shear planes. Inside the blocks the octahedral B-position is occupied by Fe$^{3+}$ and Mn$^{3+}$ atoms and the twelve coordinated A-position is fully occupied by Ba$^{2+}$ ions. The perovskites blocks are connected to each other by chains of edge-sharing (Fe,Mn) O5 distorted tetragonal pyramids with six-sided tunnels along the b-axis inside them. Within the tunnels Pb$^{2+}$ cations are located coordinated by six oxygen atoms and one 6s$^2$ electron lone pair of the lead atom. The tunnels and pyramidal chains adopt two mirror-related configurations (“left” L and “right” R) and layers consisting of chains and tunnels of the same configuration alternate in the structure according to an-L–R–L–R-sequence. The Mössbauer spectroscopy reveals that the antiferromagnetic ordered PbBaFe$_2$O$_5$ structure at room temperature changes to paramagnetic with the substitution of Fe$^{3+}$ by Mn$^{2+}$ cations.

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Keywords: perovskites, crystallographic shear planes, cation substitutions.
WAXS INVESTIGATIONS OF MIXTURES OF POLY(ETENOKSID) AND LOW MOLECULAR WEIGHT COMPOUNDS

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Mainly using diffraction methods and techniques are examined mixtures of low molecular weight compounds with poly(etenoksid). Used are mostly X-ray powder diffraction, electronic diffraction, micro diffraction, and small angle scattering of polarized light. Studied are mixtures of poly(etenoksid) with urea, thiourea, sodium cyanide, etc. salts of alkali metals, sucrose, sea lye, etc., with purpose to identify the molecular complexes between the polymer and low molecular weight substances. Are proposed approaches and methods for effective use of the geometrical structure sensitivity of X-ray diffraction methods for unambiguous quantitative and qualitative evaluation of existing crystalline phases meso phases and non-crystallizable complexes in the studied mixtures.

Key words: poly(etenoksid), powder diffractometry, mixtures, low molecular weight compounds.
INVERSE SODIUM-BORATE GLASSES WITH HIGH CONCENTRATIONS OF ALKALINE EARTH AND 3D-TRANSITION METAL OXIDES: PHASE FORMATION AND MICROSTRUCTURE

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Multicomponent oxide glass-ceramics with high concentrations of alkaline earth and 3d-transition metal oxides can simultaneously exhibit electric and magnetic ordering and thus, behave as multiferroics. The latter materials also undergo numerous phase transitions within the temperature interval of their application and thus, are of both fundamental and practical interest. Due to their magnetoelectric properties, the multiferroic materials can find application, depending on the size and type of the formed crystals, in microelectronics, spintronics, sensor technology and for energy storage.

The present work reports on the synthesis, phase formation and crystallization behaviour of the products, obtained in the system $\text{Na}_2\text{O}/\text{TiO}_2/\text{BaO}/\text{B}_2\text{O}_3/\text{Fe}_2\text{O}_3$. The formation of $\text{BaTiO}_3$ and/or $\text{BaTiFeO}_3$ and magnetic tiny crystals is observed for the slowly cooled melts, while for the quenched on steel plate melt only formation of tiny magnetic crystals occurs. The characteristic temperatures of the samples are determined by means of differential thermal analysis. The phase composition and microstructure are studied by x-ray diffraction and electron microscopy.

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Keywords: iron oxide, barium titanate, microstructure.
XRD STUDY OF CRYSTALLITE SIZES AND MICROSTRAINS
OF NATIVE SILVER. NEW GENETIC EVIDENCES

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A detail X-ray diffraction study of native Ag was held as an attempt to solve some problems of mineralogy and geology of Ag deposits – conditions of Ag nuggets; how to distinguish hypogenous (hydrothermal) from hypergenous Ag.

The Ag samples studied are from the following deposits: volcanogenic Au-Ag epithermal (Dukat, NW Russia); sulfide (Rubtzovoe, Altai mts.) telethermal of the 5-metal U-Ag-Bi-Ni-Co formation (Kongsberg; Prsibram; Port Radium, Canada; Sokolovskoe, Kazakhstan); silver-polymetalSuCH, (Sedmochislenitzi and Chiprovzti, Bulgaria and Sasa, Macedonia); cuprous sandstones of Zhezkazgan (Kazakhstan).

For the different genetic types of Ag the X-ray characteristics show the following values:
1. Hypergenous Ag: 1.1. Pseudomorphous Ag overchalide minerals: crystallite sizes (D): D=26.1 nm (25.5–26.85), ε = 0.093 (0.088–0.096); 1.2. Primary crystallized Ag: D=21.7 (19.6–22.4), ε = 0.139 (0.132–0.152).

The following facts were observed: 1) Crystallite sizes and microstrains of Ag coming from one and the same hydrothermal deposit are sustainable. 2) D and ε of Ag nugget and small Ag exsolutions in hydrothermal ores are identical. This proves that physic-chemical conditions of the forming of nuggets and small exsolutions are the same. 3) D, ε and FWHM of 111 reflection of hypogenous (hydrothermal) and hypergenous Ag are surely distinguishable. Also hydrothermal native Ag, product of primary crystallization, and Ag substituting argentite differ the same way hypergenous primary Ag and pseudomorphous Ag differ.

Keywords: native silver, crystallite sizes, microstrain.
In order to answer some questions about the origin of hypogenous and hypergenous gold nuggets and how to distinguish them a detail X-ray diffraction study of crystallite sizes and their microstrains has been done. The gold studied comes from some of the main ore and placers formations – plutogenous-metasomatic (bererezite-listvenite) type from N. Kazakhstan and Ural mts., excluding big nuggets; gold from Bulgaria – Etropole and E. Rhodopes; Au from gold-copper-porphyric formation; hypergenous placer Au (Bulgaria, Kazakhstan); pseudomorphous gold over Au-Ag tellurides in weathering crusts (Kazakhstan).

For different genetic types were obtained the following values of crystallite sizes (D) and microstrain (ε): 1. Hypergenous Au: 1.1. Au pseudomorphoses: D=35.2, ε = 0.075; 1.2. Au from placers: D=29.4 (28.2–31.4), ε =0.08 (0.060–0.075); 2. Hypogenous Au: 2.1. Gold-quartz formation Au: D=22.3 nm (18.9–26.3), ε = 0.141 (0.103–0.181); 2.2. Gold-copper-porphyric formation Au: D=17.9 nm (17.8–18.4), ε = 0.185 (0.184–0.186).

The results of XRD analysis of D and ε show that: 1) The sizes of nanocrystallites and the internal strains of gold samples taken from one and the same big gold-quartz deposit are sustainable; 2) D and ε of big gold nugget and those of minute Au exsolutions in hydrothermal ores are identical. So, the physic-chemical conditions of forming of both types of Au are the same; 3) nanocrystallite sizes, microstrains and the half-width of 111 reflection of native gold from hypogenous (hydrothermal) and such from hypergenous deposits differ quite distinguishably.

Keywords: native gold, crystallite sizes, microstrain.
NANOSIZED SOLID SOLUTIONS $\text{Al}_{2-x}\text{Me}_x(\text{WO}_4)_3$
WHERE $\text{Me} = \text{Sc}$ or $\text{In}$ WITH ORTHORHOMBIC STRUCTURE

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$\text{Me}_2(\text{WO}_4)_3$ belong to a class of compounds with orthorhombic structure, space group $\text{Pnca}$. The compounds have a number of potential applications as ionic conductivity, low thermal expansion coefficient and a broad emission as tunable lasers.

The present communication presents the results of our research – synthesis for the first time of nanosized solid solutions $\text{Al}_{2-x}\text{Me}_x(\text{WO}_4)_3$, where $\text{Me} = \text{Sc}$ or $\text{In}$ within the whole $\text{Al}/\text{Me}$ concentration ratio (for $x$ values from 0 to 2), as well as of these solutions, doped with 1, 2 or 5 at.% Cr.

The nanosized powders of solid solutions with a general formula $\text{Al}_{2-x}\text{Me}_x(\text{WO}_4)_3$ for values of $x = 0$, 0.5, 1, 1.5 and 2, were obtained using the co-precipitation method. Except for the pure solid solutions, three series of solid solutions doped with Cr, with a general formula $\text{Al}_{2-x-y}\text{Me}_x\text{Cr}_y(\text{WO}_4)_3$ for values of $y=0.02$, 0.04 and 0.1, with the same atomic ratios of Al and Si (2:0; 1.5:0.5; 1:1; 0.5:1.5 and 0:2) were also synthesized.

The final thermal treatment was at 550 °C for 1, 3 or 8 hours. After treatment at 550 °C the obtained powders were used to determine the particle size, shape and size distribution depending on the composition of the solid solutions and the duration of thermal treatment.

The thermal analysis was used for determination of crystallization temperature of some solid solution products. The investigations were done by combined LABSYSTM EVO DTA/TG device. Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer. The obtained data were used for determining of the solid solution lattice parameters. The mean crystallite size and unit cell parameters were calculated.

Additionally, the particle size and morphology were determined using a TEM JEOL 2100 at 200 kV. The particle size distribution was determined by TEM micrographs using Lince v2.4 – Linear Intercept program.

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Keywords: tungstate solid solutions, co-precipitation method, nanoparticles, structure
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