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XV КОНФЕРЕНЦИЈА СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Изводи радова

XV CONFERENCE OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY
Abstracts

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2008.

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PLENARY LECTURES
ПЛЕНАРНА ПРЕДАВАЊА

SOLVENT MOLECULES OF CRYSTALLIZATION -- CHALLENGES IN X-RAY CRYSTALLOGRAPHY

Christoph Janiak

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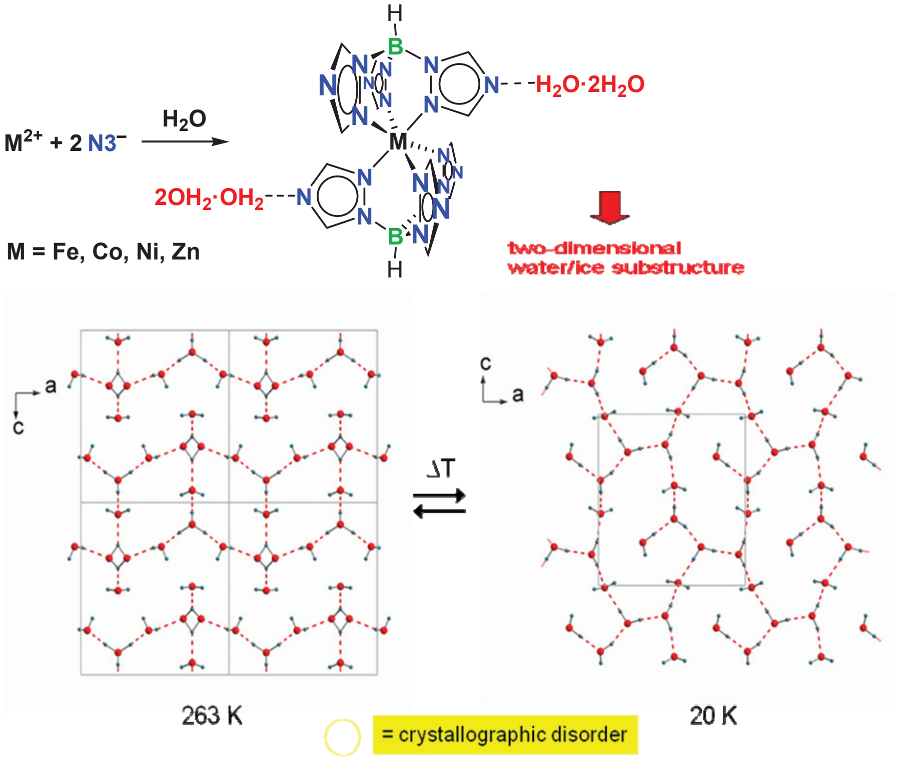
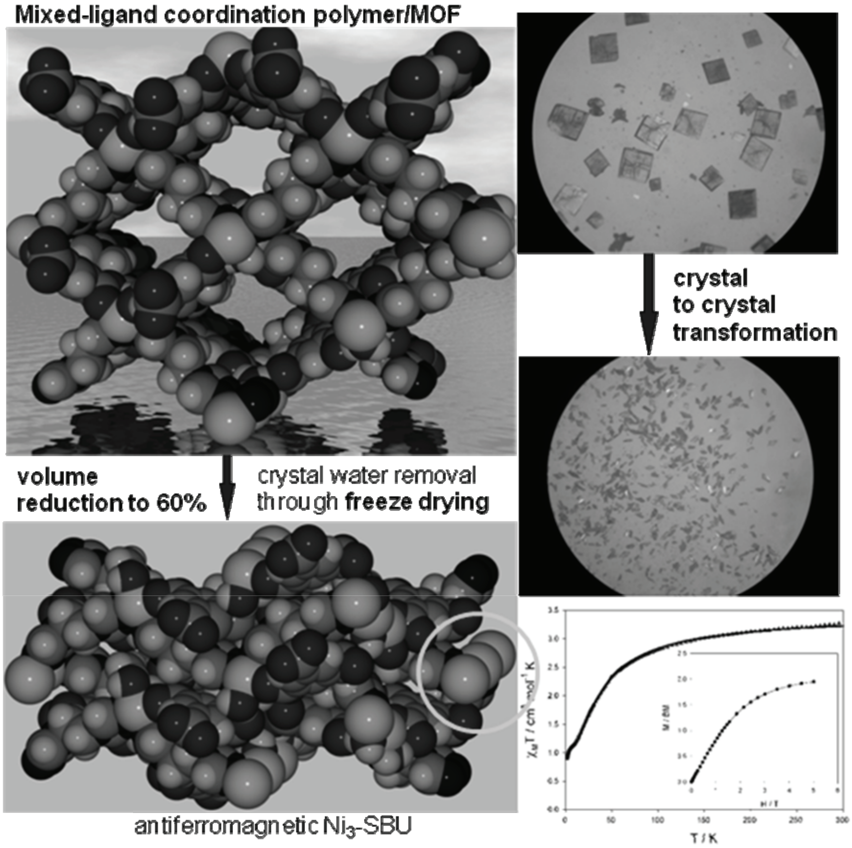
We will present examples from our recent work where the solvent molecules of crystallization have played a prominent rule – in terms of separate solvent substructure, special effects and in terms of crystallographic problems associated with disorder.

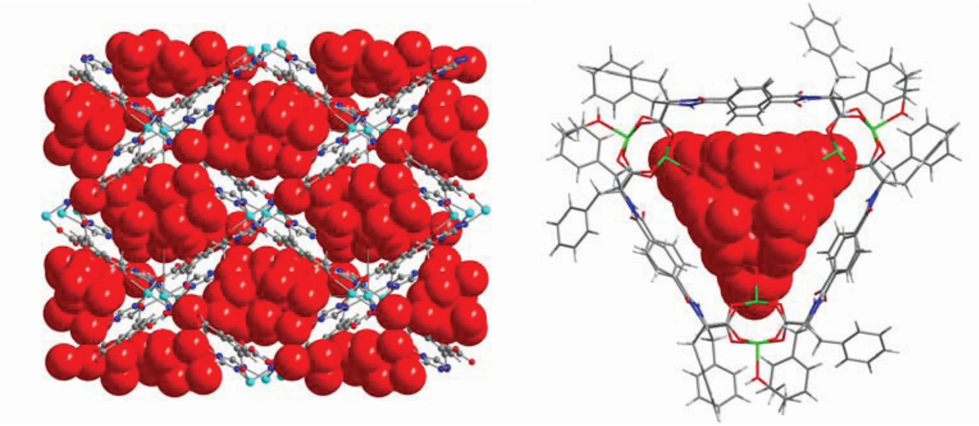
These examples include:
1) Two-dimensional water and ice layers – (neutron) diffraction studies at 278 K, 263 K, and 20 K [1].



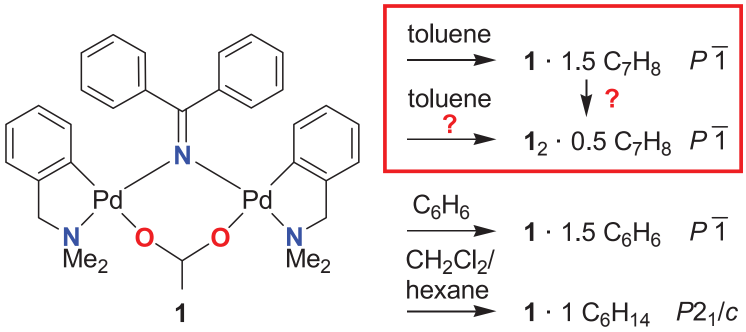
2) 3D coordination and supramolecular networks with water-filled channels and crystal-to-crystal transformation upon dehydration [2,3].



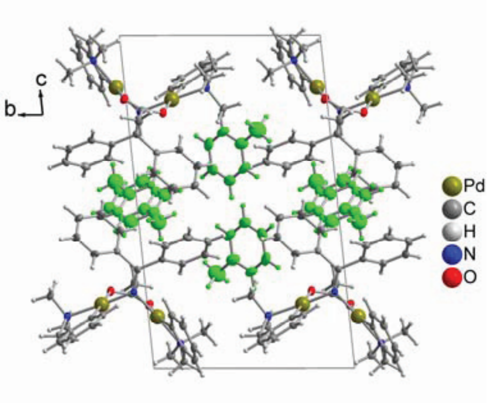
water-filled networks [2,3]:



(3) Dimeric palladacycle pseudo-polymorphs and a vanishing polymorph.



1·1.5 toluene:



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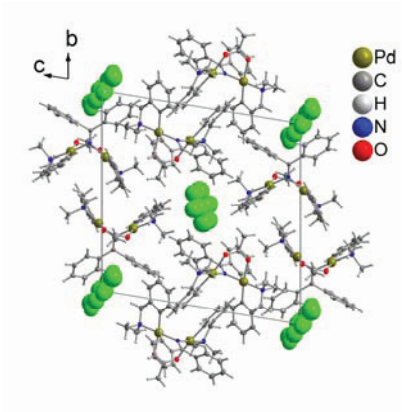
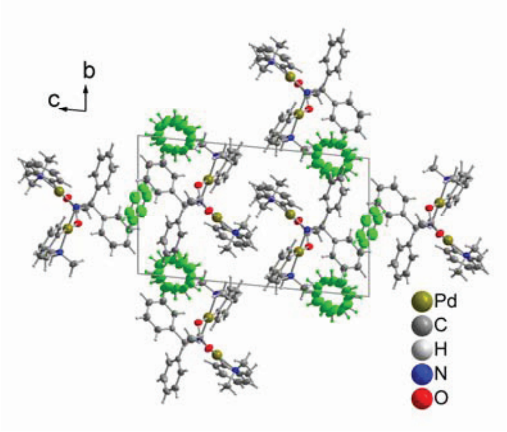


1·1.5 benzene:



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CHARGES AND FORCES IN MOLECULES

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Molecular reactivity indicators correlate with the atomic and bonding properties in molecules. Atomic bonding structures described in the theory of R. F. W. Bader (QT-AIM) gain more and more acceptance and success in the field of the molecular design [1]. In a chemical system, atoms or fragments possess intrinsic characteristics. Bader and co-workers have indeed shown that the electronic properties of atoms or fragments did not change significantly in the immediate environment [2] and therefore become transferable. These properties are fundamental for the understanding and prediction of further molecular reactivity. This also gives a sense to the molecular tailoring approach for large molecules having common fragments like polypeptides, macromolecules and proteins.

The QT-IAM Bader theory is based on a particular molecular partitioning of the electron density leading to individual atomic basins. The gradient of the electron density is used for this purpose and atomic basins are encompassed by gradient zero-flux surfaces. Properties are, in general, analytically integrated over the volumes of such basins and bonding features are highlighted by the topological analysis of the electron density.

In this lecture, we will present an original and entirely numerical approach to rationalize the molecular and atomic interactions. Atomic and molecular surfaces are defined as a cloud of points and integrated properties like charges and forces are estimated by the Gauss's theorem. Rigorous Voronoi triangulation method is used for this purpose. Instead of the electron density, we will focus on the electrostatic potential, electric field and derived properties. The experimental approach of high resolution X-ray diffraction, nowadays highly competitive to the quantum calculations, is here used to derive these properties. The computations of the electrostatic potential and field [3] are based on the Hansen-Coppens model of the electron density [4].

The features of the electrostatic potential projected on the molecular surface are used to locate the nucleophilic and electrophilic regions of a chemical system, which are essential in the molecular reactivity prediction. The electrostatic potential V is a scalar property derived from the total electron density as

$$V(\vec{r}) = \int \frac{\rho\left(\vec{r}'\right)}{\left|\vec{r} - \vec{r}'\right|} dr'$$

The electric field assists in predicting the path of reactants in the vicinity of a molecule. Being a gradient of the electrostatic potential [5], the electric field permits to accurately analyze the topology of V and reveals novel atomic basins where the total charge is zero (neutralization of the nuclear charge).

From the electric field E and using the divergence theorem, atomic charges can be accurately determined by the flux of *E* across the atomic surface. Furthermore, the general continuity equation can also be used to derive the total electrostatic force acting on a part (atoms or fragments) or the whole chemical system. The electrostatic force contains the contribution of both Feynman force acting on the nuclei and Ehrenfest force acting on the electrons. This latter can be derived from the quantum mechanics equation of motion of the momentum operator $\vec{\mathrm{p}}$. Using the divergence th rem, this force can be estimated by the flux across the molecular or atomic surface $\vec{F} = \int \sigma_M d\vec{S}$ where σ_M is the Maxwell stress tensor [6]

$$\sigma_M = \frac{1}{4\pi}\begin{pmatrix} E_x E_x & E_x E_y & E_x E_z \\ E_x E_y & E_y E_y & E_y E_z \\ E_x E_z & E_y E_z & E_z E_z \end{pmatrix} - \frac{1}{2}\begin{pmatrix} E^2 & 0 & 0 \\ 0 & E^2 & 0 \\ 0 & 0 & E^2 \end{pmatrix}$$

In order to show the efficiency of such a method, we will give the results obtained form different types of molecules of different size and nature in the solid state. Advantages and pitfalls of the present approach will be discussed as well as future perspectives.

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TETRAHEDRAL FRAMEWORK ALUMINATES UNDER NON-AMBIENT CONDITIONS: PHASE TRANSITIONS AND HIGH PRESSURE BEHAVIOUR

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Among inorganic compounds with a large variety of structures based on tetrahedral [TO_4] building units, silicates are by far the most thoroughly investigated materials. However, a similar structural complexity can be found also in alkaline earth aluminates and gallates with formula AO-B_2O_3 (A: Ca, Sr, Ba; B: Al, Ga) where the [TO_4] groups (T: Al, Ga) are the principal building units. So far, compounds with isolated tetrahedra, T_3O_{10}- and T_6O_{19}- groups, rings (T_6O_{18}, $T_{12}O_{36}$), chains, layers, as well as three-dimensional framework have been reported.

Furthermore, compared to Si^{4+}, which adopts a coordination number larger than four mainly at high pressure, Al^{3+} and Ga^{3+} generally occur in four-, five- and six-fold coordination, even under ambient conditions. In case of Al^{3+}, the structural variability strongly increases if two or all three types of coordination polyhedra are present in the same structure.

Investigation on the chemistry of alkaline-earth aluminates and gallates with special emphasis on phase transitions at non-ambient conditions was triggered from the need to: (i) obtain reliable phase diagrams: concerning a number of existing phases, melting points, melting behaviour; (ii) investigate changes of the coordination numbers of Al^{3+}, depending on pressure and temperature, (iii) study the influence of cation radii in observed structure types using (Ca, Sr, Ba) O - Al_2O_3 as a system model.

The corresponding high-pressure and high-temperature experiments have been performed at the Institute of Mineralogy and Petrography (University of Innsbruck) using a Boyd and England type piston cylinder, a Walker type multi-anvil device, and a diamond anvil cell. Structural characterisation of the samples was based on laboratory single crystal / powder X-ray diffraction and micro-Raman spectroscopy.

Starting from polycrystalline material three new high pressure/high temperature modifications have been obtained for monocalcium aluminate. At ambient conditions $CaAl_2O_4$ has a structure based on a three-dimensional corner-linked network of [AlO_4] tetrahedra (Figure 1a). This form is stable also at 2 GPa and 600 °C. At the same pressure but higher temperature (800 °C) the first quenchable polymorph was synthesized with a similar framework structure but with different arrangements of the tetrahedra. Its structure was refined from X-ray powder data using the isotypic, ambient-pressure modification of $CaGa_2O_4$ [1] as a starting model. With increasing pressure and temperature a novel polymorph of $CaAl_2O_4$ formed at 3.5 GPa and 1000 °C [2]. This polymorph has a layer-type structure with Ca atoms linking the sheets of double-layers of edge sharing [AlO_6] octahedra (Figure 1b). At even higher pressure and temperature (10 GPa and 1000 °C)

$CaAl_2O_4$ adopts a tunnel structure [2]. The main building blocks of this form are double rutile-type chains of $[AlO_6]$-octahedra with Ca atoms located inside the tunnels (Figure 1c). This third high pressure/high temperature modification is isotypic to the ambient pressure polymorph of $CaFe_2O_4$.

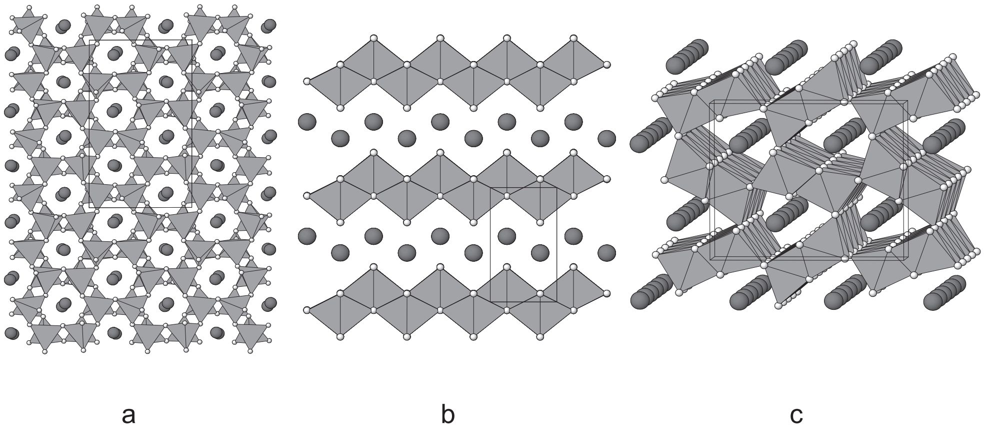

Fig.1 Crystal structures of the three polymorphic forms of $CaAl_2O_4$: a) ambient pressure form, b) HT/HP form with a layer-type structure, c) HT/HP form with tunnel-type structure.

In the course of a similar high-pressure study on corresponding $CaGa_2O_4$, in contrast to the aluminate, only one high pressure form was observed at 4.0 GPa and 700 °C, isostructural with monocalcium ferrite $CaFe_2O_4$ [3].

High-pressure experiments on the calcium aluminates were completed by an exploratory study on $Ca_2Al_2O_5$. Single crystals of this compound were prepared at 2.5 GPa and 1000 °C. *In-situ* diffraction studies at high temperature revealed an incommensurately modulated polymorph. The structure of this modulated form ($Imma(00\gamma)s00$) is isotypic to the HT form of $Ca_2Fe_2O_5$[4] and arises from an aperiodic sequence of two different configurations of tetrahedral chains with a modulation wave-vector parallel to c* ($\mathbf{q} = \gamma\, c^*$, $\gamma = 0.595$ na 825 °C).

The crystal structure of $Ba_3Al_2O_6$ was re-investigated because the existence of pseudo-symmetry created considerable problems in previous structure determinations. Basic building units are highly puckered 12-membered rings of $[AlO_4]$-tetrahedra, cross-linked via the Ba cations. The Al, O and most of the Ba-atoms fulfill the symmetry requirements of the cubic space group $Pa\bar{3}$ within a few standard uncertainties. There is only one Ba atom without a centro-symmetrically related partner lowering the true symmetry from space group $Pa\bar{3}$ to $P2_13$.

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TETRAEDARSKE MREŽASTE STRUKTURE ALUMINATA PRI NEAMBIJENTALNIM USLOVIMA: FAZNI PRELAZI I PONAŠANJE NA VISOKIM PRITISCIMA

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Među neorganskim jedinjenjima koja imaju različite vrste struktura izgrađene od [TO_4] jedinica silikati prestavljaju najistraživanije materijale. Slična kompleksnost strukturnih tipova, međutim, može se naći u zemno-alkalnim aluminatima i galatima sa formulom AO-B_2O_3 (A: Ca, Sr, Ba; B: Al, Ga), gde su [TO_4] grupe (T: Al,Ga) osnovne izgrađivačke jedinice. Do sada su objavljene kristalne strukture jedinjenja sa izolovanim tetraedrima, T_3O_{10}- i T_6O_{19}- grupama, prstenovima (T_6O_{18}, $T_{12}O_{36}$), kao i lančane, slojevite i trodimenzionalne mrežaste strukture.

U poređenju sa Si^{4+}, koji se pojavljuje u koordinaciji većoj od četiri uglavnom samo pod visokim pritiscima, Al^{3+} i Ga^{3+} se pojavljuju u koordinaciji četiri, pet i šest čak i u ambijentalnim uslovima. U slučaju aluminijuma, verovatnoća pojavljivanja različitih vrsta struktura je još veća ako se uzme u obzir da Al^{3+} može da se pojavi u dve ili sve tri različite koordinacije u okviru iste kristalne strukture.

Kristalohemijsko istraživanje zemnoalkalnih aluminata sa posebnim osvrtom na fazne prelaze u neambijentalnim uslovima proizašla je iz potrebe da se: (i) dobiju pouzdani dijagrami faza: tačan broj faza, temperature topljenja i vrste topljenja; (ii) istraži kako promena koordinacije Al^{3+} zavisi od pritiska i temperature; (iii) utvrdi uticaj radijusa katjona na različite strukturne tipove koristeći sistem (Ca, Sr, Ba)O - Al_2O_3 kao model.

Eksperimenti na visokim pritiscima i temperaturama izvedeni su na Institutu za mineralogiju i petrografiju (Univerzitet u Insbruku) koristeći Boyd and England piston cilindar, Walker tip multianvil prese, i diamond-anvil ćeliju. Karakterizacija struktura je urađena na osnovu podataka dobijenih rendgenskom difrakcijom na prahu ili monokristalu kao i mikroramanskom spektroskopijom.

Polazeći od polikristalnog monokalcijum aluminata na visokim pritiscima i temperaturama su dobijene tri nove modifikacije. U ambijentalnim uslovima $CaAl_2O_4$ ima strukturu izgrađenu od trodimenzionalne mreže [AlO_4] tetraedara, međusosobno povezanih preko rogljeva (Slika 1a). Ovaj struktura je stabilna i na 2 GPa i 600 °C. Na istom pritisku ali na malo višoj temperaturi (800 °C) sintetisan je prvi polimorf sa sličnom mrežastom strukturom ali različitom orjentacijom tetraedara. Ova struktura je utačnjena iz dijagrama na prahu, koristeći izotipičnu modifikaciju $CaGa_2O_4$ stabilnu na ambijentalnim uslovima [1] kao polazni model. Sa povećavanjem pritiska i temperature novi polimorf $CaAl_2O_4$ je formiran na 3.5 GPa i 1000 °C [2]. Ovaj polimorf ima slojevitu strukturu gde Ca atomi povezuju slojeve dvoredo poređanih [AlO_6] oktaedara povezanih preko ivica (Slika 1b). Na još višim temperaturama i pritiscima (10 GPa i 1000 °C) $CaAl_2O_4$ dobija tunelski tip strukture [2]. Osnovne jedinice koje izgrađuju ovu strukturnu formu su dvostruki lanci rutilskog tipa izgrađeni od [AlO_6] oktaedara sa Ca atomima raspoređenim unutar tunela (Slika 1c). Ova treća modifikacija sintetisana na visokim pritiscima i temeraturama je izotipična sa polimorfom $CaFe_2O_4$ stabilnim u ambijentalnim uslovima.

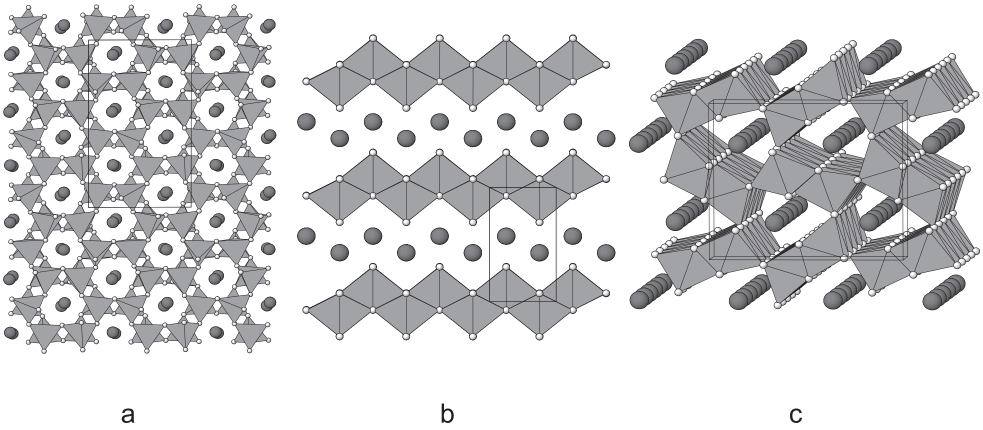

Fig.1 Kristalne strukture tri polimorfne modifikacije $CaAl_2O_4$: a) struktura stabilna na ambijentalnim uslovima, b) VP/VT forma sa slojevitom strukturom, c) VP/VT forma sa tunelskom strukturom.

U sličnom israživanju na visokim pritiscima sa odgovarajućim $CaGa_2O_4$, za razliku od aluminata, dobijen je samo jedan polimorf na pritisku od 4.0 GPa i temperaturi od 700 °C. On je izostrukturan sa $CaFe_2O_4$ [3].

Eksperimenti na visokim pritiscima sa kalcijum aluminatom su zaokruzeni istraživanjem na $Ca_2Al_2O_5$. Monokristali su pripremljeni na 2.5 GPa i 1000 °C. *In-situ* visokotemperaturna difrakcija na monokristalu je pokazala neproporcionalno modulisani polimorf. Struktura ovog modulisanog polimorfa ($Imma(00\gamma)s00$) je izotipična sa visokotemperaturnom formom $Ca_2Fe_2O_5$ [4], koja proizilazi iz aperiodične sekvence dve različite konfiguracije tetraedarskih lanaca sa vektorom modulacije paralelnim sa c* ($\mathbf{q} = \gamma\, c^*$, $\gamma = 0.595$ na 825 °C).

Usled problema u ranijim pokušajima sa se odredi, ponovo je istražena kristalna struktura $Ba_3Al_2O_6$ zbog uočenog postojanja pseudosimetrije. Osnovne jedinice koje izgrađuju su izuzetno nabrani prstenovi sastavljeni od 12 [AlO_4] tetraedara, ukrštenih preko Ba-katjona. Svi Al, O i većina Ba-atoma simetrijski odgovara prostornoj grupi $Pa\bar{3}$. Samo jedan Ba atom bez centrosimetričnog para snižava simetriju od prostorne grupe $Pa\bar{3}$ do prostorne grupe $P2_13$.

[1] B. Lazic, V. Kahlenberg, J. Konzett, Z. Kristallogr., 222 (2007), str. 696-704.
[2] B. Lazic, V. Kahlenberg, J. Konzett, R. Kaind, Solid State Sci., 8 (2006), str. 589-597.
[3] B. Lazic, V. Kahlenberg, J. Konzett, Z.Anorg. Allg. Chem., 631 (2005), str. 2411-2415.
[4] H. Krüger, V. Kahlenberg, Acta Cryst., B61 (2005), str. 656-662.

COMBINED RAMAN SPECTROSCOPIC AND X-RAY DIFFRACTION STUDY OF THE MODULATED STRUCTURE OF $Ca_2Al_2O_5$

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The brownmillerite solid solution series $Ca_2(Fe_{1-x}Al_x)_2O_5$ has been studied frequently since the members with $x \approx 0.5$ are one of the main phases in Portland cement clinkers. Structurally, brownmillerite-type compounds consist of two main building units: layers of perovskite-like corner-sharing $[(Fe,Al)O_6]$-octahedra and *zweier* single chains of $[(Fe,Al)O_4]$-tetrahedra. Alternating stacks of perovskite-type layers and sheets of tetrahedral chains form a three-dimensional network interconnected by Ca cations. The iron-rich compositions up to $x = 0.235$ adopt space group *Pnma*, whereas the more Al-rich members crystallise in space group *I2mb* [1]. For $Ca_2Fe_2O_5$, a transformation to an *Imma* structure was reported to occur at about 700°C [2]. However, a more detailed study showed [3], that the HT-phase actually exhibits an incommensurately modulated structure where the modulation is caused by an ordering process between two orientation states (L,R) of the tetrahedral chains. The Al-endmember $Ca_2Al_2O_5$ can be prepared only at high pressures and temperatures, but can be quenched to ambient conditions [4]. We investigated its high-temperature behaviour and detected a phase transition to a modulated structure, which is isotypic to the HT-phase of $Ca_2Fe_2O_5$. The temperature as well as the character of the transition was studied by micro-Raman spectroscopy and single crystal X-ray diffraction.

In situ high-temperature Raman experiments were performed in a ceramic crucible of a heating stage through a quartz window, mounted to a Raman micro-spectrometer. Spectra were recorded between 100-800 in steps of 100°C. Temperature precision and accuracy, checked by measuring the thermal shift of the TO-LO phonon of a (100) polished single crystal silicon wafer, was around ± 5 °C. A prismatic transparent crystal with good optical quality was excited by the 514.5 nm emission line of an Ar^+-laser through a 50x objective. Accuracy of the determined Raman shifts was around 0.5 cm^{-1}. For the high-temperature single-crystal diffraction experiments, a hot nitrogen gas *Heatstream* furnace mounted on an IPDS-2 diffractometer was used. Data for the structure determination of the modulated phase were collected at 817(10) °C. Furthermore, a series of 28 single crystal diffraction experiments covering a temperature range from 657 to 812°C were performed, in order to narrow down the temperature of the phase transition.

In the unmodulated room temperature structure of $Ca_2Al_2O_5$, 15 Raman bands with relative intensities ≥ 1 (normalized to the most intense band at 506 cm^{-1}) could be detected. Two intense bands with Raman shifts of 772 and 739 cm^{-1} were assigned to stretching modes of AlO_4-tetrahedra and AlO_6-octahedra. The most intense band at 506 cm^{-1} is related to bending modes of the AlO_4-tetrahedra. Bands with Raman shifts below 500 cm^{-1} result from Ca- and Al-O translations.

With some exceptions the temperature dependence $\partial\nu/\partial T$ of most of the vibrational modes are approximately linear and within a narrow interval: (1) $\partial\nu/\partial T$ of the AlO_6-octahedra stretching modes is significantly lower compared to the AlO_4 tetrahedra (Figure 1a). Furthermore, the $\partial\nu/\partial T$ of the AlO_4 bending mode at 476 cm^{-1} is low (Figure 1b). This is consistent with higher bond forces and shorter bond lengths within the tetrahedra and is confirmed by the X-ray diffraction study. (2) At 400 and 700°C disappearance of modes can be observed (Figure 1b), which may be an indication for symmetry change from the *I2mb* room temperature structure to the modulated phase [(3+1)-dimensional superspace group *Imma*(*00γ*)*s00*], detected in the high-temperature diffraction patterns of $Ca_2Al_2O_5$. The changes are related to tetrahedral distortions and ordering of L- and R-oriented tetrahedral chains [3]. However, the influence of the structural modulations of crystals to their vibrational spectra needs further theoretical and experimental investigations.

In summary, a phase transition and the incommensurate high-temperature ordering of tetrahedral chains in brownmillerite-type $Ca_2Al_2O_5$ could be confirmed. Both, $Ca_2Al_2O_5$ and $Ca_2Fe_2O_5$ show a phase transition to isotypic high-temperature structures and are end-members of the solid solution series $Ca_2(Fe_{1-x}Al_x)_2O_5$, thus we assume intermediate compositions to behave similar[1;5]. The exact nature of the phase boundary for $x > 0.325$ is still unknown and requires further studies.

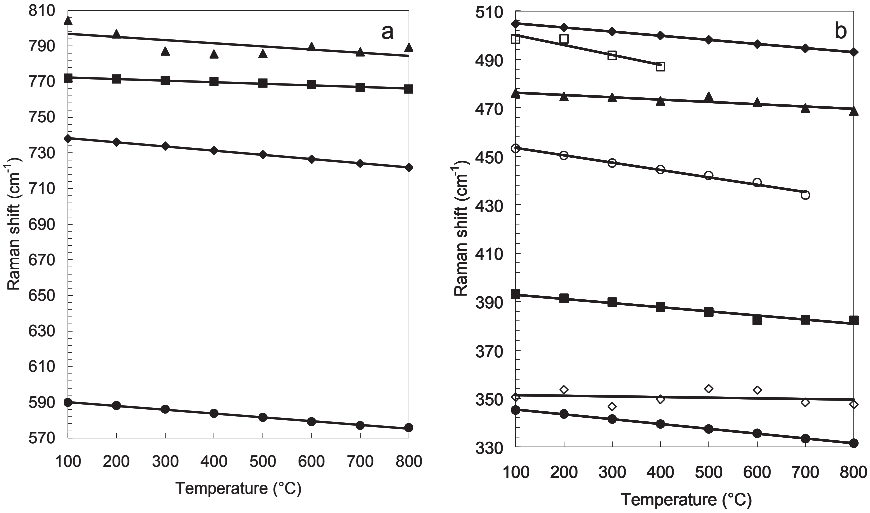

Figure 1: a) $\partial\nu/\partial T$ of Raman bands of $Ca_2Al_2O_5$ in the range 570-810 cm^{-1}; b) in the range 330-510 cm^{-1}.

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STRUCTURAL PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) COORDINATION COMPOUNDS WITH ANIONS OF POLYCARBOXYLIC ACIDS

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Cobalt, nickel and copper can be regarded as representatives of the first row transition elements and are known for constructing numerous complexes. Accordingly, they are of great interest for the coordination chemists and crystallographers. A considerable number of described mixed-ligand structures belongs to phthalate (dianion of 1,2-benzenedicarboxylic acid) [1] and terephthalate (dianion of 1,4-benzenedicarboxylic acid) complexes [2] and their intensive research has begun in the 1970s of the 20th century. Pyromellitate (tetraanion of 1,2,4,5-benzenetetracarboxylic acid) [3] and especially isophthalate (dianion of 1,3-benzenedicarboxylic acid) compounds [4] are less considered. It is known that a large number of ternary complexes with polycarboxylate ligands are Cu(II) compounds, whereas the number of the structures with other transition elements is smaller. To date, researches have shown that the anions of polycarboxylic acids mostly behave as bridging polydentate ligands producing binuclear or polymeric complexes: one-dimensional (linear, zig-zag or spiral chains), two-dimensional (layers, ribbons, ”ladders”) and three-dimensional networks. The fact that from 2000 about twenty articles on this type of structures are published each year validates that the subject is very advanced. Regardless of the numerous investigations, the possibilities for formation of structurally diverse compounds with different coordination of polycarboxylate ions are still unlimited.

In this study, the results of the synthesis of series of ternary Co(II), Ni(II) and Cu(II) complexes with anions of isophthalic, terephthalic and pyromellitic acid and some aromatic diamine ligands such as 2,2′-dipyridylamine, 2,2′-bipyridine and 1,10-phenanthroline are presented in detail [5]. The structural properties of compounds determined by X-ray analysis are discussed and compared. Based on these data, the complexes are systematized.

The geometry of molecules (bond distances and angles), the geometry of hydrogen bonds and packing arrangements were also considered. The coordination modes of different polycarboxylate ligands and factors determining their coordination modes are discussed. Common structural properties were noticed and the main structural properties are: centrosymmetry of structures, bridging role of polycarboxylate ions, presence of hydrogen bonds and π–π interactions, as well as three-dimensional networks. A correlation between synthesis, structure and properties of the compounds is established.

Beside common structural properties, a large number of specific structural characteristics related to the donor possibilities of aromatic polycarboxylate ions were found, such as: presence of polycarboxylate ligands coordinated in different modes in the same structure, simultaneous existence of a binuclear complex cation and a binuclear complex anion, different degree of distortion of coordination polyhedra around Cu(II), presence of hydrophobic and hydrophilic parts of the layers in the packing arrangements and channels filled with solvent molecules, *etc*.

The number of donor O atoms, the number of O–M bonds, the angles in coordination polyhedron and COO^- groups, *etc.* in synthesized compounds are very versatile.

It was determined that the packing arrangements of molecules and chains in the crystals were very different. Three-dimensional networks are defined and contributed by network systems of hydrogen bonds and π–π interactions, as well as by the type of N-donor ligand present therein, *i.e.* by its bulkiness and rigidness. In the polymeric compounds, the spiral chains are held together by π–π interactions forming two-dimensional layers, which construct three-dimensional framework via system of hydrogen bonds. In the complexes where zig-zag chains exist, three-dimensional network is formed by hydrogen bonds and π–π interactions between the chains. Similar non-covalent interactions exist in the crystal arrangements of binuclear units, where hydrogen bonds exist within layers and π–π interactions exist between layers, or hydrogen bonds and π–π interactions are formed at the same time within layers. It was concluded that factors influencing the packing arrangements of molecules are numerous and complex and that they are often specific for each structure.

The complexes with pyromellitate ligands were additionally subjected to the TG and DSC analysis. The dehydration process and thermal decomposition of anhydrous compounds were investigated. Results of the thermal analysis were in accordance with the results determined by X-ray structure analysis and could be used as the basis for potential investigation of the kinetic of thermal decomposition in the systems metal – polycarboxylate – diamine.

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STRUKTURNE KARAKTERISTIKE KOORDINACIONIH JEDINJENJA KOBALTA(II), NIKLA(II) I BAKRA(II) SA ANJONIMA POLIKARBOKSILNIH KISELINA

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Kobalt, nikal i bakar mogu se smatrati reprezentativnim predstavnicima prvog prelaznog niza elemenata i poznati su kao graditelji izuzetno velikog broja kompleksnih jedinjenja, pa se kao takvi nalaze u središtu interesovanja koordinacionih hemičara i kristalografa. Najveći broj do sada opisanih mešovito-ligandnih struktura odnosi se na ftalat- (dianjon 1,2-benzendikarboksilne kiseline) [1] i tereftalat- (dianjon 1,4-benzendikarboksilne kiseline) komplekse [2], čije intenzivno proučavanje počinje sedamdesetih godina XX veka, dok su piromelitat- (tetraanjon 1,2,4,5-benzentetrakarboksilne kiseline) [3], a naročito izoftalat- (dianjon 1,3-benzendikarboksilne kiseline) jedinjenja [4] zastupljena u znatno manjoj meri. Takođe je poznato da se najveći broj ternernih kompleksa sa pomenutim polikarboksilat-ligandima odnosi na Cu(II)-jedinjenja, dok je broj poznatih struktura ostalih prelaznih elemenata manji. Dosadašnja istraživanja pokazuju da se anjoni polikarboksilnih kiselina najčešće ponašaju kao polidentatni ligandi mostovnog tipa i da su nastali kompleksi binuklearni ili polimerni, i to: jednodimenzionalni (linearni, cik-cak ili spiralni lanci), dvodimenzionalni (slojevi, trake, „merdevine”) i trodimenzionalno umrežene strukture. Aktuelnost problematike najbolje ilustruje činjenica da se u periodu od 2000. godine svake godine objavljuje po dvadesetak radova u kojima su opisani kompleksi sa ligandima koji su predmet ovog rada, kao i da uprkos brojnim istraživanjima još uvek nisu iscrpljene mogućnosti stvaranja strukturno različitih jedinjenja sa drugačijom koordinacijom polikarboksilat-jona.

U ovom radu detaljno su prikazani rezultati sinteze serije ternernih kompleksa prelaznih metala Co(II), Ni(II), Cu(II) sa anjonima izoftalne, tereftalne i piromelitne kiseline i nekim aromatičnim diaminskim ligandima, kao što su 2,2′-dipiridilamin, 2,2′-bipiridin i 1,10-fenantrolin [5]. Diskutovane su i poređene strukturne karakteristike jedinjenja dobijene rendgenskom strukturnom analizom, na osnovu čega su kompleksi sistematizovani.

Razmatrana je geometrija (dužine veza i uglovi) molekula, geometrija vodoničnih veza i pakovanje molekula. Diskutovani su načini koordinacije različitih polikarboksilat-liganada i faktori koji određuju njihove načine koordinacije. Uočene su zajedničke strukturne karakteristike, od kojih su glavne sledeće: centrosimetričnost, mostovna uloga polikarboksilat-jona, prisustvo vodoničnih veza i π–π interakcija, trodimenzionalna umreženost. Utvrđena je korelacija između sinteze, strukture i osobina jedinjenja.

Pored navedenih zajedničkih svojstava, nađen je i veći broj specifičnih strukturnih karakteristika, koje su u neposrednoj vezi sa donorskim mogućnostima aromatičnih polikarboksilat-jona, kao što su: prisustvo različito koordiniranih polikarboksilat-liganada u istoj strukturi, istovremeno postojanje binuklearnog kompleksnog katjona i binuklearnog kompleksnog anjona, različit stepen deformisanosti koordinacionog poliedra oko Cu(II), postojanje slojeva pri pakovanju molekula koji se odlikuju hidrofobnim i hidrofilnim delovima, postojanje kanala ispunjenih molekulima rastvarača i dr.

Broj donorskih atoma O, broj O–M veza, vrednosti uglova u koordinacionom poliedru i COO^{-}-grupama i dr. u sintetisanim jedinjenjima vrlo su raznovrsne.

Utvrđeno je da su pakovanja molekula i lanaca u kristalu vrlo različita. Trodimenzionalno umrežavanje određuju i umnogome mu doprinose razgranati sistemi vodoničnih veza i π–π interakcija, kao i vrsta prisutnog N-donorskog liganda, tj. njegova veličina i krutost. Kod polimernih jedinjenja, spiralni lanci se međusobno drže π–π interakcijama i formiraju dvodimenzionalne slojeve, koji preko sistema vodoničnih veza grade trodimenzionalnu strukturu. Umrežavanje kod kompleksa koji sadrže cik-cak lance nastaje preko vodoničnih veza i π–π interakcija koje se javljaju između lanaca. Slične nekovalentne interakcije postoje i pri pakovanju binuklearnih jedinki, gde vodonične veze postoje unutar slojeva i π–π interakcije između slojeva, ili se unutar slojeva istovremeno javljaju i vodonične veze, i π–π interakcije. Tako je zaključeno da su faktori koji određuju pakovanje molekula mnogobrojni i složeni, kao i da su često specifični za svaku strukturu.

Kompleksi koji sadrže piromelitat-ligande dodatno su podvrgnuti TG- i DSC--analizi. Praćen je tok termičke dehidratacije i razlaganja anhidrovanih jedinjenja. Dobijeno je da su rezultati termijskih analiza u saglasnosti sa rezultatima strukturne analize i da bi mogli da posluže kao osnov za potencijalna istraživanja kinetike termičke dekompozicije u sistemima metal – polikarboksilat – diamin.

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STRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES OF PEROVSKITES $AFe_{2/3}B_{1/3}O_{3-\delta}$ (A = Pb, Sr, Ca, Ba; B= W, Te)

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Materials known as magnetoelectrics, which are simultaneously ferroelectric and ferromagnetic (or at least show some type of magnetic ordering), have recently become the focus of much research. These compounds present opportunities for a wide range of potential applications. Aside from device design, the fundamental physics of magnetoelectrics is rich and fascinating. However, ferroelectricity and magnetism hardly coexist and very few magnetoelectrics exist in nature, or have been synthesized in the laboratory. In general the existence of transition metal d electrons, which are essential for magnetism, reduces the tendency for polar ferroelectric distortions. Thus, an additional electronic and structural driving force must be present for ferroelectricity and ferromagnetism to occur simultaneously. The present contribution is a survey of our recent results on experimental structural, dielectric and magnetic investigations of new magnetoelectric perovskites $AFe_{2/3}B_{1/3}O_{3\text{-delta}}$ (A= Pb, Sr, Ca, Ba; B= W, Te; delta= 0-0.2), prepared by convential solid state synthesis and using magnetic, dielectric and neutron powder diffraction (NPD) measurements. It was shown that this class of the ferroelectric magnets exhibits both electric-dipole and magnetic ordering in definite temperature range. NPD patterns have been collected at the Swedish Research Reactor R2 (Studsvik) at different temperatures (10-1000 K). The data was analysed with the FULLPROF software in order to characterize the temperature-induced phase transformations and determine the nuclear and magnetic structures. The size of the A and B-type cations is directly related to different structural distortions. The structural peculiarities of distorted perovskite phases are discussed in details and possible mechanisms of phase transitions are presented. Structural studies have shown that the room temperature structures of the A= Pb, Sr and Ca phases are cubic (Pm-3m), tetragonal (I4/m) and monoclinic ($P2_1/n$), respectively, whilst the A= Ba compound is hexagonal ($P6_3/mmc$). In the Pb compound the Fe and W (Te) cations are randomly distributed over the B sites while in the case of Sr and Ca compounds a partial crystallographic order was established. The dependence of the magnetic phase transition temperature T_N on the type and concentration of nonmagnetic A, O and magnetic B sublattices are outlined. It was found that T_N values appear to depend mainly on the nature of the A-cation (ion size and electronic configuration), the degree of cation ordering of Fe/W (Te) and on the oxygen content. Magnetic moment ordering~~s~~ of Fe^{3+} cations, distributed between two different crystallographic sites in these systems are analysed. All compounds have the antiferromagnetic G-type structure. The introduction of Te^{6+} into the B-site has a strong negative effect on the magnetic properties. In the Ba compound the oxygen concentration has a significant effect on structural and magnetic properties. The correlation between the structural polar distortions, B-site ordering, oxygen stoichiometry and a ferrimagnetic orbital ordering is also briefly discussed and may possibly provide additional insight into the magnetoelectric coupling in these perovskites.

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ORAL PRESENTATIONS
САОПШТЕЊА

SYNTHESIS AND CRYSTAL STRUCTURE OF 2(*S*)-(-2-OXOTETRAHYDRO-1,3-OXAZIN-3-YL)-PROPIONIC ACID

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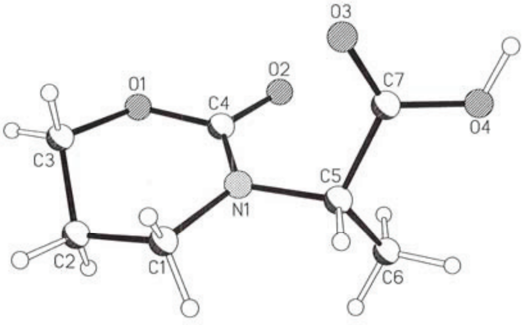
In reaction of *S*-alanine and 1,3-dibrom-propane (1:1), in presence of NaOH and Na_2CO_3, with adjusting pH to 3,5 a new compound 2(*S*)-(2-oxotetrahydro-1,3-oxazin-3-yl-)-propionic acid was obtained. After recrystalization from water solution the white crystals suitable for X-ray analysis were prepared. *Anal. Calc. for* $C_7H_{11}NO_4$ (FW = 173.17): C, 48.54; H, 6.41; N, 8.09 %. Found: C, 47.98; H, 6.40; N, 8.13 %.

Crystallographic data: $C_7H_{11}NO_4$, orthorhombic system, space group $P2_12_12_1$, a = 5.3622(2), b = 9.5723 (9), c = 15.1906 (14) Å, α = β = γ= 90º, V = 779.71(11) $Å^3$, Z = 4, D_c=1.475 Mg/m^3, μ(Mo*Kα*) = 0.122 mm^{-1}, F(000)=368, crystal size 0.23 x 0.21 x 0.14 mm, no. of parameters: 142, R1 = 0,0263 and wR2 = 0,0645 (for 1172 reflections with I>2σ (I)).

In the crystal there exist very strong intermolecular hydrogen bond between O(4)-H(4A)---O(2)#1 (H---A = 2,6122 Å)



SINTEZA I KRISTALNA STRUKTURA 2(S)-(-2-OKSOTETRAHIDRO-1,3-OKSAZIN-3-IL)-PROPANSKE KISELINE

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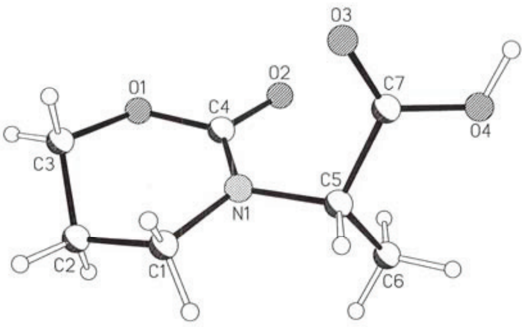
U reakciji *S*-alanina i 1,3-dibrom-propana (1:1), u prisustvu NaOH i Na_2CO_3, sa podešavanjem pH na 3,5 dobijeno je novo jedinjenje 2(S)-(2-oksotetrahidro-1,3-oksazin-3-il-)-propanska kiselina. Posle prekristalisavanja iz vodenog rastvora dobijeni su beli kristali pogodni za rendgensku strukturnu analizu. *Anal. Izrač. za* $C_7H_{11}NO_4$ (Mr = 173,17): C, 48,54; H, 6,41; N, 8,09 %. *Nadjeno.*: C, 47,98; H, 6,40; N, 8,13 %.

Kristalografski podaci: $C_7H_{11}NO_4$, ortorombični sistem, prostorna grupa $P2_12_12_1$, a = 5,3622(2), b = 9,5723 (9), c = 15,1906 (14) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 779,71(11) $Å^3$, Z = 4, D_c=1.475 Mg/m^3, μ(Mo*Kα*) = 0.122 mm^{-1} , F(000)=368, veličina kristala 0,23 x 0,21 x 0,14 mm, br. parametara: 142, R1 = 0,0263 i wR2 = 0,0645 (za 1172 refleksije u opsegu $I > 2\sigma(I)$).

U kristalu postoji veoma jaka intermolekularna vodonična veza između O(4)-H(4A)---O(2)#1 (H---A = 2,6122 Å).



CRYSTAL STRUCTURE OF *uns-cis*-DIBROMO-(ETYLENEDIAMINE-*N,N*`-DI-*S,S*-2-PROPIONATO)-PLATINUM(IV) COMPLEX, *uns-cis*-[Pt(*S,S*-eddp)Br_2]

Srećko R. Trifunović[a], **Verica V. Glođović**[a], **Gordana P. Vasić**[a], **Vesna M. Đinović**[b], **Tibor J. Sabo**[b], **Olivera Klisurić**[c] **and Slobodanka Stanković**[c]

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The title compound was obtained in reaction of potassium hexabromoplatinate(IV), ethylenediamine-*N,N*`-di-*S,S*-2-propionic acid dichlorhydrate (H_2-*S,S*-eddp·2HCl) and lithium hydroxide in molar ratio 1:1:4 at 50 ºC. The yellow prismatic compound was crystallized from mother solution at room temperature.

Crystallographic data: $C_8H_{14}Br_2N_2O_4Pt$, [Pt(*S,S*-eddp)Br_2], M_r = 557.12, orthorhombic system, space group $P2_12_12_1$, ρ_x = 2.755 g cm^{-3}, μ(Mo Kα) = 16.40 mm^{-1}, $\Delta\rho_{max}$ = 0.67 e Å^{-3} and $\Delta\rho_{min}$ = –0.96 e Å^{-3}. The diffraction data for this complex were collected at room temperature on a Gemini S diffractometer using grafite-monochromated Mo Kα radiation (λ = 0.71073 Å) and $\omega/2\theta$ scans. Crystal size: 0.35×0.11×0.14 mm. Unit cell dimensions: a = 7.221(5), b = 13.378(5), c = 13.905(5) Å, V = 1343.3(12) Å^3.

The structure was solved by direct methods on the basis of 3073 independent reflections and refined using full-matrix least-squares [1]. All calculations were performed using SHELXL97, PARST and PLATON, as implemented in the WinGX system of programs. The final R factor is 0.025 for 2769 reflections with $I > 2\sigma(I)$.

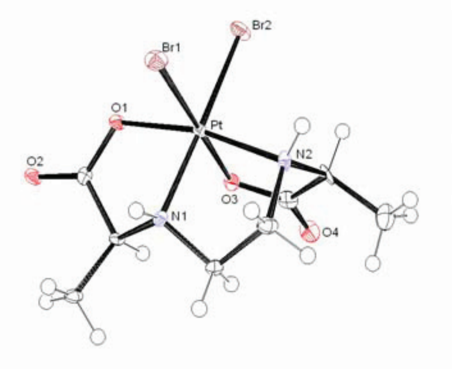

Figure 1. A view of the molecular structure of *uns-cis*-[Pt(*S,S*-eddp)Br_2] complex

[1] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

KRISTALNA STRUKTURA *uns-cis*-DIBROMO-(ETILENDIAMIN-*N,N`*-DI-*S,S*-2-PROPIONATO)PLATINA(IV) KOMPLEKSA, *uns-cis*-[Pt(*S,S*-eddp)Br_2]

<u>Srećko R. Trifunović</u>[a], Verica V. Glođović[a], Gordana P. Vasić[a], Vesna M. Đinović[b], Tibor J. Sabo[b], Olivera Klisurić[c] i Slobodanka Stanković[c]

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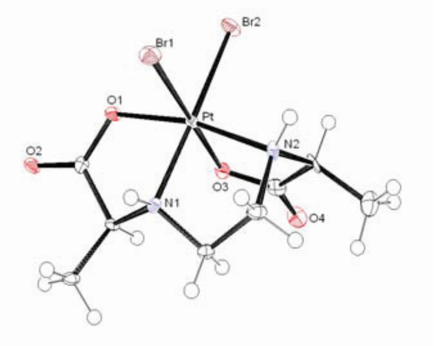
Kompleks *uns-cis*-[Pt(*S,S*-eddp)Br_2] dobijen je u reakciji kalijum-heksabromoplatinata(IV), etilendiamin-*N,N`*-di-*S,S*-2-propionske kiseline dihlorhidrata i litijum-hidroksida u molskom odnosu 1:1:4 na 50 ºC. Postepenim uparavanjem matičnog rastvora na sobnoj temperaturi dobijeni su žuti, prizmatični kristali.

Kristalografski podaci za dobijeni kompleks: $C_8H_{14}Br_2N_2O_4Pt$, [Pt(*S,S*-eddp)Br_2], M_r = 557,12, rombični sistem, prostorna grupa $P2_12_12_1$, ρ_x = 2,755 g cm^{-3}, μ(Mo Kα) =16,40 mm^{-1} sa $\Delta\rho_{max}$ = 0,67 e $Å^{-3}$ i $\Delta\rho_{min}$ = -0,96 e $Å^{-3}$. Difrakcioni podaci za ovaj kompleks sakupljeni su na sobnoj temperaturi na Gemini S difraktometru koristeći monohromatsko Mo Kα zračenje (λ = 0,71073 Å). Dimenzije kristala su 0,35×0,11×0,14 mm, dok su parametri jedinične ćelije *a* = 7.221(5), *b* = 13.378(5), *c* = 13.905(5) Å, *V* = 1343.3(12) $Å^3$.

Struktura kristala rešena je primenom direktnih metoda na bazi 3073 nezavisnih refleksija i utačnjena metodom najmanjih kvadrata sa potpunom matricom [1]. Sva izračunavanja vršena su koristeći SHELXL97, PARST i PLATON, kao delove WinGX programa. Konačna vrednost *R*-faktora je 0,025 za 2769 refleksija sa $I > 2\sigma(I)$.



Slika 1. Prikaz molekulske strukture *uns-cis*-[Pt(*S,S*-eddp)Br_2] kompleksa

[1] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

ELECTRONIC PROPERTIES OF THE SULFUR ATOM IN THE 4-METHYL-3-THIOSEMICARBAZIDE

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The high-resolution single-crystal X-ray diffraction experiment was performed at 100.0(1) K. The 115688 reflections collected in this experiment have been sorted and averaged, giving a total of 10361 unique reflections with final R_{int} = 2.31 %. The experimental electron density distribution in the titled compound has been determined from a multipole refinement based on the Hansen-Coppens formalism. Here we report the final results of the multipole refinement, which outcomes in R = 1.78 % for 7503 reflections and 437 refined parameters.

This work represents the continuation of our systematic study on the electronic properties of the thiosemicarbazide based compounds [1]. The previous investigation of thiosemicarbazide derivate, salicylaldehyde thiosemicarbazone [1], established that the valence electrons of the S atom which are not engaged in covalent bonds have inhomogeneous distribution of the electron density within the sulfur's torus. The static deformation density maps of the S atom in the title compound (Fig. 1.) indicate that the deformation density of the sulfur's free electron pairs is more polarized than in the case of salicylaldehyde thiosemicarbazone [1]. The accumulation of deformation electron density is particularly emphasized in the directions of the strongest N–H…S intermolecular interactions.

The analysis showed significant differences in magnitude and disposition of the electrostatic potential around the sulfur atoms of the two independent molecules. It also indicates that the most negative regions of the electrostatic potential on the molecular surfaces are directed toward the H atoms which form interactions with sulfur atoms.

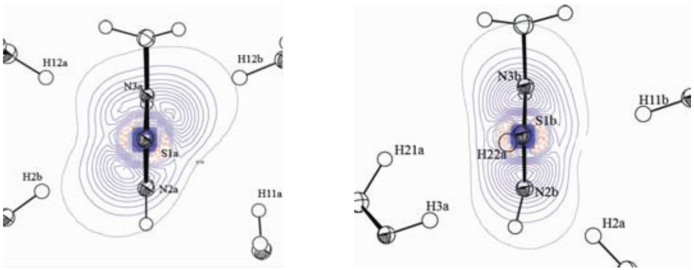

Fig. 1. Intermolecular interactions of X–H…S types for the both independent molecules of 4-methyl-3-thiosemicarbazide with static electron deformation density around the sulfurs in the plane perpendicular to the molecule and C–S bond.

[1] S. B. Novaković, B. Fraisse, G. A. Bogdanović, A. Spasojević-de Biré, Crystal Growth Design, 7 (2007), 191-195.

ЕЛЕКТРОНСКА СВОЈСТВА АТОМА СУМПОРА У 4-МЕТИЛ-3-ТИОСЕМИКАРБАЗИДУ

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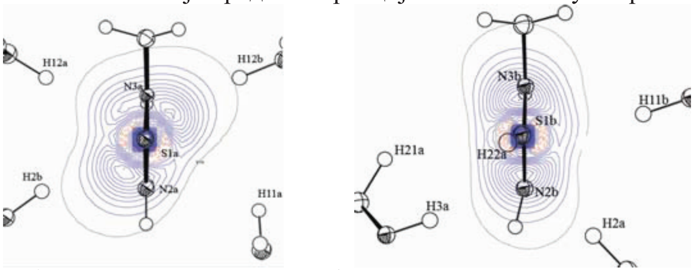
Експериментални подаци високе резолуције добијени су дифракцијом рендгенског зрачења са монокристала при радној температури од 100,0(1) K. У овом експерименту је сакупљено 115688 дифракционих максимума, који сортирањем и усредњавањем дају укупно 10361 независних рефлексија са крајњим R_{int} = 2,31 %. Расподела експерименталне електронске густине у молекулу 4-метил-3-тиосемикарбазида одређена је методом мултипол-утачњавања заснованом на Хансен-Копенсовом формализму. У овом раду представљамо финалне резултате мултипол-утачњавања, где је 437 параметара утачњено до коначног R-фактора од 1,78 % за 7503 рефлексија.

Овај рад представља наставак истраживања која се односе на електронска својстава једињења тиосемикарбазида [1]. Претходним испитивањима деривата тиосемикарбазида, тиосемикарбазона салицилалдехида [1], утврђено је да валентни електрони атома S који не учествују у ковалентним везама имају нехомогену расподелу електронске густине унутар торуса сумпора. Мапе статичке деформационе густине нашег једињења (слика 1.) указују да је поларизација деформационе густине слободних електронских парова атома сумпора израженија, него код тиосемикарбазона салицилалдехида. Нађено је да је акумулација деформационе електронске густине нарочито наглашена у правцима најјачих N–H…S међумолекулских интеракција.

Анализа такође открива значајне разлике у вредностима и распореду електростатичког потенцијала у околини атома сумпора два независна молекула. Најнегативнија област електростатичког потенцијала на површини молекула усмерена је ка H атомима који граде интеракције са атомима сумпора.



Слика 1. Међумолекулске интеракције X–H…S типа независних молекула 4-метил-3-тиосемикарбазида са деформационом електронском густином око атома сумпора у равни нормалној на молекул и на C–S везу.

[1] S. B. Novaković, B. Fraisse, G. A. Bogdanović, A. Spasojević-de Biré, Crystal Growth Design, 7 (2007), 191-195.

THE CRYSTAL STRUCURE OF THE *s-cis*-DICHLORO-(ETHYLENEDIAMINE-*N,N'*-DI-*S,S*-2-PROPIONATO)-PLATINUM(IV) COMPLEX, *s-cis*-[Pt(*S,S*-eddp)Cl_2]·$2H_2O$

<u>Gordana P. Vasić</u>[a], Srećko R. Trifunović[a], Verica V.Glođović[a], Vesna M. Đinović[b], Tibor J. Sabo[b], Olivera Klisurić[c] and Slobodanka Stanković[c]

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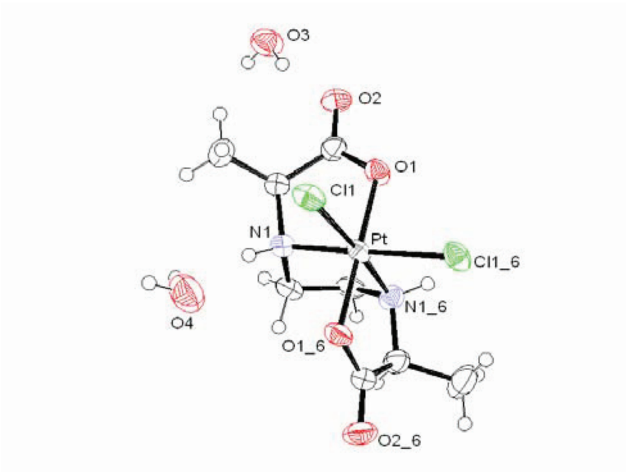
In reaction of $K_2[PtCl_6]$ and tetradentate H_2-*S,S*-eddp ligand (H_2-S,S-eddp = ethylenediamine-*N,N′*-di-*S,S*-2-propionic acid) (1:1 molar ratio) the octaedral complex, *s-cis*-[Pt(*S,S*-eddp)Cl_2]·$2H_2O$, was prepared. The yelow crystals of the comlex suitable for X-ray analysis were obtained during crystallization from the mother solution.

Ligand S,S-eddp is coordinated as a tetradentate ligand forming three five-membered chelate rings to platinum(IV) central metal ion. The results of X-ray analysis indicate that the complex crystallizes as dyhidrate. This compound crystallizes in the bipyramidal crystal form. In the crystal packing numerous hydrogen bonds of the N-H···O, C-H···O and C-H···Cl type exist.

Crystallographic data: formula $C_8H_{22}Cl_2N_2O_8Pt$, M_r = 270.13, tetragonal, space group $P4_12_12$, $a = b = 6.878(5)$, $c = 35.699(5)$ Å, $V = 1688.8(18)$ Å^3, $Z = 8$, $D_x = 2.125$ Mg m^{-3}, $\mu = 8.66$ mm^{-1}, $T_{min} = 0.638$, $T_{max} = 0.383$, $S = 1.17$, $R_1 = 0.046$ for 1810 reflections with $I > 2\sigma(I)$, w$R_2 = 0.086$ for 1934 independent reflections and 113 refined parameters. All calculations were performed using SIR92, SHELXL97, PARST and PLATON, as implemented in the WinGX system of programs.



KRISTALNA STRUKTURA *s-cis*-DIHLORO(ETILENDIAMIN-*N,N'*-DI-*S,S*-2-PROPIONATO)PLATINA(IV) KOMPLEKSA, *s-cis*-[Pt(S,S-eddp)Cl_2]·$2H_2O$

<u>Gordana P. Vasić</u>[a], **Srećko R. Trifunović**[a], **Verica V. Glođović**[a], **Vesna M. Đinović**[b], **Tibor J. Sabo**[b], **Olivera Klisurić**[c] **i Slobodanka Stanković**[c]

[a]Prirodno-matematički fakultet, Univerzitet u Kragujevcu, R. Domanovića 12, p.pr. 60, Srbija; [b]Hemijski fakultet, Univerzitet u Beogradu, Studentski trg 16, p.pr. 158, 11001 Beograd, Srbija; [c]Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 4, 21000 Novi Sad, Srbija
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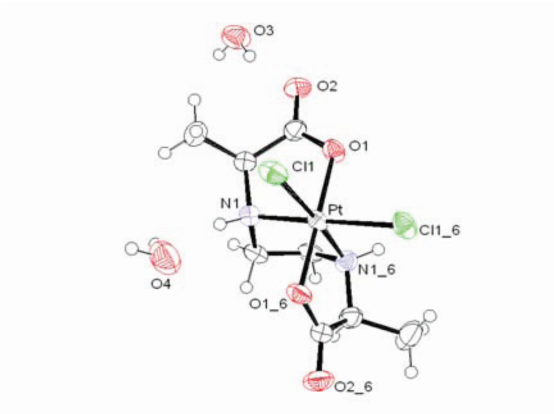
Oktaedraski kompleks *s-cis*-[Pt(*S,S*-eddp)Cl_2]·$2H_2O$ sintetisan je u reakciji između $K_2[PtCl_6]$ i tetradentatnog liganda *S,S*-eddp (eddp ═ anjon etilendiamin-*N,N'*-di-*S,S*-2-propionske kiseline) u molskom odnosu 1:1. Žuti kristali kompleksa pogodni za rendgensku analizu dobijeni su kristalizacijom iz matičnog rastvora.

Ligand *S,S*-eddp je koordinovan za Pt(IV) centralni metalni jon kao tetradentatni ligand formirajući tri petočlana helatna prstena. Rezultati rendenske strukturne analize ukazuju na to da ovaj kompleks kristališe kao dihidrat. Kristali ovog jedinjenja su bipiramidalne kristalne forme. U kristalnom pakovanju postoje brojne vodonične veze tipa N-H···O, C-H···O i C-H···Cl.

Kristalografski podaci: formula $C_8H_{22}Cl_2N_2O_8Pt$, $M_r = 270{,}13$, tetragonalni sistem prostorna grupa $P4_12_12$, $a = b = 6{,}878(5)$, c = 35.699(5) Å, $V = 1688.8(18)$ Å^3, $Z = 8$, $D_x = 2{,}125$ Mg m^{-3}, $\mu = 8{,}66$ mm^{-1}, $T_{min} = 0{,}638$, $T_{max} = 0{,}383$, $S = 1{,}17$, $R_1 = 0{,}046$ za 1810 refleksija sa $I > 2\sigma(I)$, $wR_2 = 0{,}086$ za 1934 nezavisnih refleksija i 113 utačnjavanih parametara. Sva izračunavanja su vršena korišćenjem programa SIR92, SHELXL97, PARST i PLATON kao delovima WinGX sistema.



INFLUENCE OF METAL AND LIGAND TYPES ON STACKING INTERACTIONS OF PHENYL RINGS WITH SQUARE-PLANAR TRANSITION METAL COMPLEXES

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Recently, it was shown that chelate rings with delocalized π-bonds can be involved in noncovalent interactions in ways similar to aromatic organic molecules. Chelate rings can be involved in CH/π interactions as hydrogen acceptors with organic moieties[1] and in stacking interactions with aryl rings.[2-4] Our previous results show that there are stacking interactions between chelate and aryl rings containg six carbon atoms (C_6-aryl) in crystal structures of square-planar transition-metal complexes.[2] These observations could be connected with an assumption that planar chelate rings with delocaliyed π-bonds can have aromatic character. In order to find out whether metal type influences the stacking interactions of phenyl rings in square-planar complexes, geometrical parameters for Cu, Ni, Pd and Pt complexes, with and without chelate rings, were analyzed and compared.[3] By searching the Cambridge Structural Database, 220 structures with Cu complexes, 211 with Ni complexes, 285 with Pd complexes, and 220 with Pt complexes were found. The results show that the chelate ring has a tendency to make the stacking interaction with the phenyl ring independent of metal type in the chelate ring. However, there are some differences among metals for complexes without a chelate ring. There are a number of structures containing Pd and Pt complexes, without chelate rings, that have short carbon-metal distances and parallel orientations of the phenyl ring with respect to the coordination plane. It was found that some of these complexes have a common fragment, CN, as a part of the ligands. This indicates that the CN supports stacking interactions of square planar complexes with the phenyl ring.

[1] G. A. Bogdanović, A. Spasojević-de Bire, S. D. Zarić, *Eur. J. Inorg. Chem.* (2002), 1599
[2] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, Crystal Growth & Design, (2005), 6, 29-31
[3] D. N. Sredojević, Z. D. Tomić, S. D. Zarić, Cent. Eur. Journal of Cemistry, (2007), 5, 1-11
[4] D. N. Sredojević, G. A. Bogdanović, Z. D. Tomić, S. D. Zarić, CrystEngComm, (2007), 9, 1-7

УТИЦАЈ МЕТАЛА И ВРСТЕ ЛИГАНАДА НА СТЕКИНГ ИНТЕРАКЦИЈЕ ИЗМЕЂУ ФЕНИЛ ГРУПЕ И КВАДРАТНО-ПЛАНАРНИХ КОМПЛЕКСА ПРЕЛАЗНИХ МЕТАЛА

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Недавно је показано да хелатни прстенови са делокализованим π-везама могу бити укључени у нековалентне интеракције на начин који је особен за ароматичне органске молекуле. Хелатни прстенови могу бити укључени у грађење CH/π интеракција као акцептори водоника са органским лигандима[1,4] и у стекинг интеракције са арил прстеновима.[2-4] Наши предходни резултати показују да постоје стекинг интеракције између хелатних и арил прстенова који садрже шест атома угљеника (C_6-aryl) у кристалним структурама квадратно-планарних комплекса прелазних метала.[2] Ова опажања могу бити повезана са предпоставком да планарни хелатни прстенови са делокализованим π-везама могу да поседују ароматични карактер. У циљу испитивања да ли тип метала има утицаја на стекинг интеракције између фенил групе и квадратно-планарних комплекса прелазних метала, геометријски параметри за Cu, Ni, Pd и Pt комплексе, који садрже и који не садрже хелатне прстенове, су анализирани и поређени.[3] Претражујући Кембричку кристалографску банку података (CSD) , пронађено је 220 структура комплекса Cu, 211 структура Ni комплекса, 285 структура Pd комплекса, и 220 структура Pt комплекса. Резултати показују да хелатни прстенови поседују тенденцију за грађење стекинг интеракција са фенил групом независно од типа метала у хелатном прстену. Међутим, постоје одређене разлике дуж метала за комплексе који не садрже хелатне прстенове. Постоји одређен број структура Pd и Pt комплекса, који не садрже хелатне прстенове, а код којих се јављају блиски контакти између метала и угљеника фенил групе и код којих су равни фенил групе паралелно оријентисане у односу на средњу координациону раван. Пронађено је да већина ових комплекса садржи заједнички фрагмент, CN, као део лиганда. Ово указује на то да CN фрагмент доприноси грађену стекинг интеракција квадратно планарних комплекса који не садрже хелатне прстенове.

[1] G. A. Bogdanović, A. Spasojević-de Bire, S. D. Zarić, *Eur. J. Inorg. Chem.* (2002), 1599
[2] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, Crystal Growth & Design, (2005), 6, 29-31
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[4] D. N. Sredojević, G. A. Bogdanović, Z. D. Tomić, S. D. Zarić, CrystEngComm, (2007), 9, 1-7

ARCHEOMINERALOGICAL AND CRYSTALLOGRAPHIC ANLYSIS OF SAMPLES FROM SOME LOCATION IN SERBIA

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Material sciences and the material culture becomes the base of the contemporary archeology. From the methods of the investigations in the archeology and in material sciences emphasised: XRF, SEM and EDS[1]. The aims of the investigations are identification of the structure of the archeological remains and the determination of their chemical and mineralogical content. On the base of this analysis, without demages of investigated samples, we can get importanat informations about ages, origin and properties of archeological remains. In this work there are investigated petrified animal fossils originated from location of Risovača and Petrovaradin, also microcristalline structures of artefacts, potteries and building materials from bricks[2]. The origin of this samples are from Felix Romuliana and from some of location near Bor the Timok Valey. In this work are investigated the micro-crystallic structures of bronze objects originated from Celtic and Roman periods. The archeological locations where the semples originated are the Region Srem what means western part of Vojvodina. The samples originated from the period of 1st century BC and 3rd century AD trough Migration of Nations. The microcrystallic structures of artefacts, decorative and rite things and coins are important informations for archeologists. On the base of this dates they could conclude about technologies of the materials were used in production of the investigated archeological samples, as well as about their surface treatment by handycraft. In this work by means of microcrystallography analysis are determinated the surface structure of romans coins known and unknown origines.

[1] S. Fitzgerald, **The 10 micron innovation –X-ray Fluorecence micro-analysis**, 49. Magyar Spektorkemiai Vandorgyules, Miskolc (2006) str. 65
[2] T. Halasi, S. Kalamković, J. Adamov, R. Halaši, M. Segedinac, **MICROSCOPIC INVESTIGATION OF ARCHEOLOGICAL SAMPLES OF PETROVARADIN RISOVAČA AND FELIX ROMULIANA**, 3rd Serbian Congress for Microscopy, Sept. 25-28, Belgrade, Serbia, p.69-70.

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ARHEOMINERALOŠKA I KRISTALOGRAFSKA ISPITIVANJA UZORAKA SA NEKIH ARHEOLOŠKIH LOKACIJA U SRBIJI

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Materijalne nauke i materijalna kultura postaju osnove savremene arheologije. Od metoda istraživanja i u arheologiji i u materijalnim naukama se ističu: XRF, SEM i EDS[1]. Ciljevi istraživanja su identifikacija strukture arheoloških ostataka i određivanja njihovog hemijskog i mineraloškog sastava. Na osnovu tih analiza, bez značajnijeg oštećenja ispitivanih uzoraka, se mogu dobiti važne informacije o starosti, poreklu i osobinama arheoloških ostataka. U ovom radu su ispitivani okamenjeni životinjski fosili poreklom sa arheoloških lokacija Risovača i Petrovaradin, zatim mikrokristalne strukture artefakta, grnčarskih posuda i građevinskog materijala od opeke[2]. Poreklo tih uzoraka su Feliks Romuliana i neke druge arheološke lokacije iz Borskog okruga, odnosno Timočke Krajine. U ovom radu su ispitivane mikrokristalne strukture brončanih predmeta, poreklom iz keltskog i rimskog perioda. Arheološke lokacije, odakle potiču ti uzorci su Sremska regija, odnosno zapadni krajevi Vojvodine. Period nastajanja tih uzoraka je od 1. veka pne do 3. veka ne i perioda Seobe naroda. Mikrokristalna struktura površine artefakta, dekorativnih i obredskih predmeta kao i metalnih novčića su važne informacije arheolozima. Na osnovu tih podataka zaključuju i o tehnologiji proizvodnje materijla od čega su izrađeni arheološki uzorci i o načinu njihove površinske obrade raznim zanatskim veštinama. U ovom radu komparativnom mikrokristalografskom analizom su utvrđivane i strukture površina rimskih novčića poznatog i nepoznatog porekla.

[1] S. Fitzgerald, **The 10 micron innovation –X-ray Fluorecence micro-analysis**, 49. Magyar Spektorkemiai Vandorgyules, Miskolc (2006) str. 65
[2] T. Halasi, S. Kalamković, J. Adamov, R. Halaši, M. Segedinac, **MICROSCOPIC INVESTIGATION OF ARCHEOLOGICAL SAMPLES OF PETROVARADIN RISOVAČA AND FELIX ROMULIANA**, 3rd Serbian Congress for Microscopy, Sept. 25-28, Belgrade, Serbia, p.69-70.

Zahvala

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CRYSTAL STRUCTURE OF *O,O'*-DIISOBUTYL-(*S,S*)--ETHYLENEDIAMMONIUM-*N,N'*-DI-2-(4-METHYL)-PENTANOATE DICHLORIDE

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O,O'-Diisobutyl-(*S,S*)-ethylenediammonium-*N,N'*-di-2-(4-methyl)-pentanoate dichloride [(*S,S*)-$H_2i$$Bu_2$eddl]$Cl_2$ was prepared by using an esterification reaction earlier described [1]. X-ray measurments were performed on crystalls obtained from mother liquor.

The compound is found to crystallize in tetragonal crystal system in the chiral space group *P*42. The molecular structure is shown in Figure 1. Emprircal formula $C_{22}H_{46}Cl_2N_2O_4$, unit cell dimensions a = 15.9534(4), b = 15.9534(4), c = 5.2491 Å, $\alpha = \beta = \gamma = 90$ °, V = 1335.95(7) Å^3, Z = 2, ρ_c = 1.177 Mg m^{-3}, μ(Mo K_α) = 0.271 mm^{-1}, F(000) = 516. Data collection: $2.86 < \theta < 30.50$ °, no. of parameters: 106, R_1 = 0.0659, wR_2 = 0.1560 for 3889 reflections with $I > 2\sigma(I)$.

The isolated crystalls consist of one dicationic species [(*S,S*)-$H_2i$$Bu_2$eddl]$^{2+}$ and two Cl^- anions. The most significant hydrogen bonds for given way of packing are N–H1N···Cl, 3.100(3) Å, 164(3) and N–H2N···Cl, 3.055(3) Å, 158(3) ° and these interactions form an infinite chain.

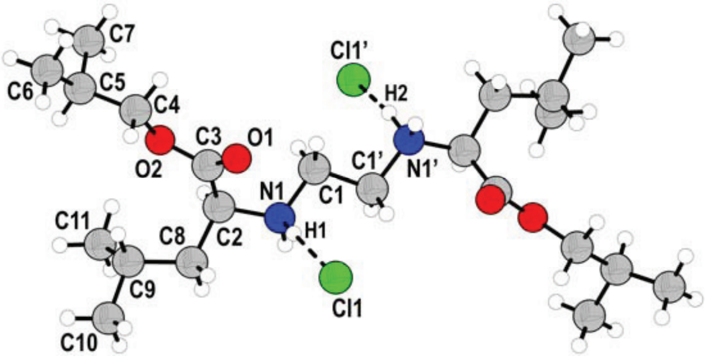

Figure 1. Crystal structure of [(*S,S*)-$H_2i$$Bu_2$eddl]$Cl_2$ (H-bonds shown by dashed lines)

[1] B. B. Krajčinović, G. N. Kaluđerović, D. Steinborn, H. Schmidt, Ch. Wagner, Ž. Žižak, Z. D. Juranić, S. R. Trifunović and T. J. Sabo, J. Inorg. Biochem., 102 (2008) 892–900.

KRISTALNA STRUKTURA *O,O'*-DIIZOBUTIL-(*S,S*)- -ETILENDIAMMONIUM-*N,N'*-DI-2-(4-METIL)-PENTANOAT-DIHLORIDA

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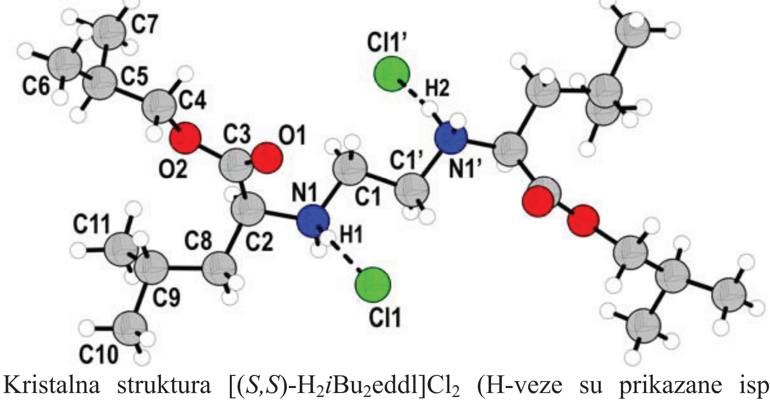
O,O'-Diizobutil-(*S,S*)-etilendiammonium-*N,N'*-di-2-(4-metil)-pentanoat-dihlorid [(*S,S*)-H_2*i*Bu_2eddl]Cl_2 dobijen je u reakciji esterifikacije, kao i srodna jedinjenja opisana u literaturi [1]. Rendgenska strukturna analiza urađena je na monokristalima dobijenim iz filtrata.

[(*S,S*)-H_2*i*Bu_2eddl]Cl_2 kristališe u tetragonalnom kristalnom sistemu u hiralnoj prostornoj grupi *P*42. Molekulska struktura prikazana je na Slici 1. Empirijska formula $C_{22}H_{46}Cl_2N_2O_4$, dimenzije jedinične ćelije a =15,9534(4), b = 15,9534(4), c = 5,2491 Å, $\alpha = \beta = \gamma = 90$ °, V = 1335,95(7) $Å^3$, $Z = 2$, ρ_c = 1,177 Mg m^{-3}, μ(Mo K_α) = 0,271 mm^{-1}, $F(000) = 516$. Opseg: $2,86 < \theta < 30,50$ °, broj parametara: 106, $R_1 = 0,0659$, $wR_2 = 0,1560$ za 3889 refleksija sa $I > 2\sigma(I)$.

Dobijeni monokristali sastoje se iz jednog dikatjona [(*S,S*)-H_2*i*Bu_2eddl]$^{2+}$ i dva Cl^- anjona. Najznačajnije vodonične veze za dati način pakovanja jesu N–H1···Cl, 3,100(3) Å, 164(3) ° i N–H2···Cl, 3,055(3) Å, 158(3) ° i ove interakcije formiraju beskonačan lanac.



Slika 1. Kristalna struktura [(*S,S*)-H_2*i*Bu_2eddl]Cl_2 (H-veze su prikazane isprekidanim linijama)

[1] B. B. Krajčinović, G. N. Kaluđerović, D. Steinborn, H. Schmidt, Ch. Wagner, Ž. Žižak, Z. D. Juranić, S. R. Trifunović and T. J. Sabo, J. Inorg. Biochem., 102 (2008) 892–900.

STRUCTURE TYPES AMONG *M*1–*M*2–H-ARSENATES AND VANADATES (*M*1 = Sr^{2+}, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}; *M*2 = Mg^{2+}, $Mn^{2+,3+}$, $Fe^{2+,3+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})

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Natural as well as synthetic metal arsenates and vanadates often form tetrahedral-octahedral framework structures with potentially interesting properties (e.g., ion conductivity, ion exchange and catalytic activity). In an ongoing comprehensive study of hydrothermal synthesis, crystallography and properties of arsenate and vanadate compounds in the insufficiently known system $M1O–M2O–X_2O_5–H_2O$ (*M*1 = Sr^{2+}, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}; *M*2 = Mg^{2+}, $Mn^{2+,3+}$, $Fe^{2+,3+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; *X* = As^{5+}, V^{5+}) yielded a large number of new $M1^{2+}$–(H-), $M2^{2+}$–(H-) and *M*1–*M*2–(H-) arsenates and vanadates that are characterized structurally, and, in part, also by spectroscopic techniques. In general, the knowledge of compounds belonging to the group of *M*1–*M*2–H-arsenates and vanadates is very poor. There are only 23 compounds belonging to this group (14 arsenates and 9 vanadates) of which 11 have been synthesized within current study. Seven of them are minerals. Considering the ratio *M*1:*M*2, natural and synthetic *M*1–*M*2–H-arsenates and vanadates can be divided into the following subgroups: (i) *M*1:*M*2 = 2:1 (count two minerals belonging to the brakebushite structure type), (ii) *M*1:*M*2 = 1.5:1 (count one compound related to the class of open-framework materials showing catalytic and ion exchange properties), (iii) *M*1:*M*2 = 1.33:1 (count one compound that adopts new structure type), (iv) *M*1:*M*2 = 1:1 (count eight compounds, seven of which adopt adelite-descloizite structure type, and one mineral), (v) *M*1:*M*2 = 1:2 (count five compounds; two arsenates belong to the tsumcorite structure type, and other three arsenates adopt new structure types each), (vi) *M*1:*M*2 = 1:3 (count two minerals and one synthetic compound that adopts novel structure type, one mineral is a rare member of the crandallite group and another is similar to the bayldonite-leningradite group of compounds), (vii) *M*1:*M*2 = 1:4 (count one mineral adopting cubic pharmacosiderite type-structure, (viii) *M*1:*M*2 = 1:6 (count one mineral that has a micro-porous framework structure with similarities to common zeolites) and (ix) *M*1:*M*2 = 1:9 (count one mineral that has unique crystal structure). These new arsenates and vanadates represent either novel structure types with a potential for technically interesting physical and chemical properties, or known structure types with interesting crystal-chemical properties.

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ТИПОВИ СТРУКТУРА КОД *M*1–*M*2–H-АРСЕНАТА И ВАНАДАТА ($M1 = Sr^{2+}$, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}; $M2 = Mg^{2+}$, $Mn^{2+,3+}$, $Fe^{2+,3+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})

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Како природни, тако и синтетички арсенати и ванадати метала често кристалишу у облику тетраедарско-октаедарских 3D структура занимљивих физичко-хемијских својстава, као сто су јонска проводност, могућност измене катјона и каталитичка активност. У току истраживања хидротермалне синтезе, кристалографских и физичко-хемијских особина арсената и ванадата из недовољно познатог система $M1O–M2O–X_2O_5–H_2O$ ($M1 = Sr^{2+}$, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}; $M2 = Mg^{2+}$, $Mn^{2+,3+}$, $Fe^{2+,3+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; $X = As^{5+}$, V^{5+}) добијени су бројни $M1^{2+}$–(H-), $M2^{2+}$–(H-) и *M*1–*M*2–(H-) арсенати и ванадати. Они су испитани методом рендгенске дифракције на монокристалу и делимично коришћењем инфрацрвене и Раман спектроскопије. *M*1–*M*2–H-арсенати и ванадати су недовољно испитани. У тој групи постоји само 23 једињења (14 арсената и 9 ванадата), од којих је 11 добијено у току овог истраживања. Седам једињења су минерали. На основу односа *M*1:*M*2 катјона, природни и синтетички *M*1–*M*2–H-арсенати и ванадати могу се поделити у следеће групе: (i) *M*1:*M*2 = 2:1 (два минерала која кристалишу у бракебушит структурном типу), (ii) *M*1:*M*2 = 1.5:1 (једно једињење структурно слично супстанцама које имају 3D отворене мреже и показују каталитичке особине као мугућности измене катјона), (iii) *M*1:*M*2 = 1.33:1 (једно једињење нове структуре), (iv) *M*1:*M*2 = 1:1 (осам једињења, од којих седам припада аделит-десклоизит типу структуре и један минерал нове структуре), (v) *M*1:*M*2 = 1:2 (пет једињења; два арсената кристалишу у тсумкуритском типу структуре, а остали арсенати су сви структурно различити и нових типова структура), (vi) *M*1:*M*2 = 1:3 (два минерала и једно једињење нове структуре; први минерал је члан ретке крандалит групе супстанци, а други кристалише у бајлдонитско-лењинградској групи супстанци), (vii) *M*1:*M*2 = 1:4 (један минерал који припада тесералном фармакосидеритском типу структуре), (viii) *M*1:*M*2 = 1:6 (један минерал микропорозне структуре сличне зеолитима) и (ix) *M*1:*M*2 = 1:9 (један минерал нове структуре). Нови арсенати и ванадати метала представљају или нове типове структура или већ познате структуре са интерасантном кристалохемијом.

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ANALYSIS OF ORDER-DISORDER PHASE TRANSITION IN LIZN$_{0.5}$TI$_{1.5}$O$_4$ BY *IN SITU* XRD AND LANDAU THEORY

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Nanocrystalline spinel LiZn$_{0.5}$Ti$_{1.5}$O$_4$ has been produced by high energy ball milling. The crystal structure refinement has been performed using the Rietveld profile method and Fullprof program. Sample crystallize in disorder spinel structure in space group $Fd\bar{3}m$, and has metastable cation distribution. Due to annealing crystal symmetry has changed from $Fd\bar{3}m$ to $P4_332$. Annealing and slow cooling to room temperature led to equilibrium cation 1:3 ordering at octahedral sites O_h. The order-disorder transition was investigated by *in situ* XRD diffraction and Landau's theory of phase transition. X-ray powder diffraction patterns were collected on a STOE STADI MP diffractometer. The phase transition has occurred at $T_c = (1030 \pm 10)$ °C. The cation migration of Li^+ and Zn^{2+} ions between the tetrahedral 8*c* and octahedral 4*b* sites in ordered spinel, was accounted for beginning of disordering, but the main mechanism was cation disordering inside O_h sublattice. The linear increase of the lattice parameter, *a*, with the temperature rise was observed, with discontinuity around T_c. Landau theory was used to analyze the mechanism of the phase transition. Analysis of the topology of the order parameter vector space, Figure 1, could indicate biquadratic coupling between Q_1 and Q_2 parameters. In the temperature stability range of the ordered phase there is a linear relationship between Q_1 and Q_2, therefore linear-quadratic coupling is not excluded.

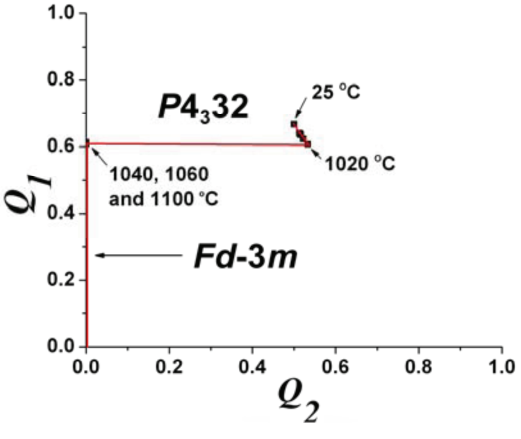

Figure 1. Thermodynamically stable states represented in the vector space of the order parameters Q_1 and Q_2.

ANALIZA FAZNOG PRELAZA RED-NERED U $LIZN_{0.5}TI_{1.5}O_4$ POMOĆU *IN SITU* RENDGENSKE DIFRAKCIJE I LANDAUOVE TEORUJE

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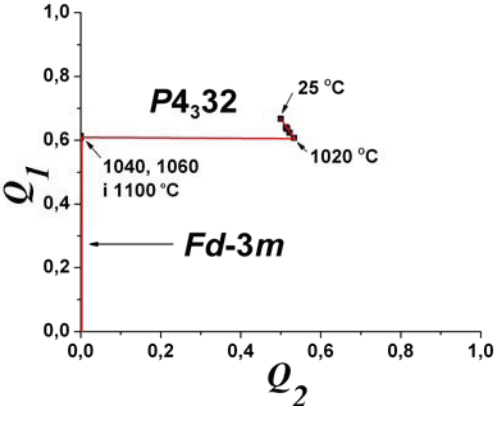
Nanokristalni spinel $LiZn_{0.5}Ti_{1.5}O_4$ dobijen je mehanohemijskim postupkom. Kristalna struktura uzorka utačnjena je korišćenjem Ritveldove profilne metode i programa Fullprof. Uzorak kristališe u neuređenoj spinelskoj strukturi opisanoj u prostornoj grupi $Fd\bar{3}m$ i ima metastabilnu katjonsku raspodelu. Usled odgrevanja došlo je do promene simetrije kristala iz $Fd\bar{3}m$ u $P4_332$. Zagrevanjem praćenim sporim hlađenjem do sobne temperature uspostavljeno je ravnotežno katjonsko uređenje tipa 1:3 unutar oktaedarske podrešetke, O_h. *In situ* rendgenska difrakcija i Landauova teorija faznih prelaza korišćene su za proučavanje prelaza red-nered. Difraktogrami su snimljeni na difraktometru STOE STADI MP. Fazni prelaz je uočen na $T_c = (1030 \pm 10)$ °C. Razuređenje počinje katjonskom migracijom jona Li^+ i Zn^{2+} između tetraedarskih 8*c* i oktaedarskih 4*b* položaja u uređenoj spinelskoj fazi, ali osnovni mehanizam razuređenja predstavlja mešanje jona unutar O_h podrešetke. Konstanta rešetke, *a*, linearno raste sa povećenjem temperature i ima prekid u okolini T_c. Mehanizam faznog prelaza analiziran je korišćenjem Landauove teorije. Analiza topološkog prostora parametara uređenja (Slika 1) ukazuje na moguće bikvadratno sprezanje Q_1 i Q_2 parametara. U temperaturnom opsegu stabilnosti uređene spinelne faze postoji linearna zavisnost izemđu Q_1 i Q_2, čime linerno-kvadtarno sprezanje nije isključeno.



Slika 1. Stanja termodinamičke stabilnosti u vektorskom prostoru parametara uređenja Q_1 i Q_2

TIME-OF-FLIGHT NEUTRON POWDER DIFFRACTION STUDY OF $ZnFe_2O_4$.

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The spinel group of minerals, with general formula AB_2O_4, has been the subject of investigations using many different experimental techniques. The apparent simplicity of these cubic structures gives way under close scrutiny to complex relationships among chemical composition, structural state, etc.

Their structure (Space group $Fd3m$) can be described as a cubic closest-packed array of O atoms, with one-eighth of the tetrahedral sites and one-half of the octahedral sites filled. The formula may be written as $^{[4]}(A_{1-x}B_x)^{[6]}(B_{2-x}A_x)O_4$ assuming stoichiometric spinel. The terms "normal" and "inverse" are used to denote spinels for which $x = 0$ and $x = 1$, respectively.

The present study is focused on structural differences of both bulk and nanosized $ZnFe_2O_4$ samples. Bulk $ZnFe_2O_4$ was prepared by ceramic procedure, using ZnO and Fe_2O_3 as a starting compounds. Nanosize $ZnFe_2O_4$ was obtained by co-precipitation method at low temperature using aqueous solutions of nitrate precursors [1]. The time of flight neutron powder diffraction data were collected using special environment powder diffractometer SEPD [2] at intense pulsed neutron source (IPNS), Argonne National Laboratory, USA at 5 and 295 K. Rietveld refinement was performed using the program FULLPROF [3].

The peak shape was defined as convolution of a pseudo-Voigt function with a pair of back-to-back exponentials. Preliminary results are indicating increase of the unit cell parameter a from 8.4396(2) for bulk sample to 8.464(4) Å for nanosized sample collected at room temperature. Besides obvious difference in microstructure, both bulk and nanosized $ZnFe_2O_4$ are structurally close to normal spinels with x values 0.04(2) and 0.17(8), respectively. This is confirmed with no significant difference in A-O and B-O bond distances of tetrahedraly and octahedraly coordinated cations. Bulk data collected at 5 K are characterized with the presence of magnetic structure.

[1] M. Maletin, Z. Cvejic, S. Rakic, Lj. M. Nikoliv, V. V. Srdic, Mat. Sci. Forum, 518 (2006) p.p. 91-94.
[2] J. D. Jorgensen *et al*, J. Appl. Cryst., 22 (1989), p.p. 321-333.
[3] J. Rodríguez-Carvajal, Commission on Powder Diffraction (IUCr). Newsletter 26 (2001), p.p. 12-19.

ISPITIVANJE $ZnFe_2O_4$ TOF NEUTRONSKOM DIFRAKCIJOM NA PRAHU.

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Grupa minerala spinela, opšte formule AB_2O_4, predmet je istraživanja različitim eksperimentalnim tehnikama. Očigledna jednostavnost ove teseralne strukture omogućava detaljno proučavanje složenih odnosa između hemijskog sastava, strukture, itd.

Struktura spinela (prostorna grupa $Fd3m$) može se opisati kao najgušće teseralno pakovanje O atoma gde je popunjena osmina tetraedarskih položaja i polovina oktaedarskih položaja. Formula se može napisati kao $^{[4]}(A_{1-x}B_x)^{[6]}(B_{2-x}A_x)O_4$, ako pretpostavimo stehiometrijski sastav spinela. Izrazi „normalan“ i „inverzan“ spinel koriste se u slučaju kada je $x = 0$ i $x = 1$.

Istraživanje u ovom radu usredsređeno je na strukturne razlike između voluminoznog i nano $ZnFe_2O_4$ uzorka. Voluminozan $ZnFe_2O_4$ je pripremljen keramičkom procedurom, pri čemu su ZnO i Fe_2O_3 korišćeni kao polazne hemijske supstance. Nano $ZnFe_2O_4$ je dobijen metodom koprecipitacije vodenih rastvora nitratnih prekursora na sobnoj temperaturi [1]. Podaci TOF neutronske difrakcije na prahu prikupljeni su na difraktometru za prah SEPD [2] u okviru intenzivnog pulsnog neutronskog izvora (IPNS) Nacionalne laboratorije Argonne, SAD. Podaci su prikupljeni na temperaturi od 5 i 295 K. Za utačnjavanje Ritveldovom metodom korišćen je program FULLPROF [3].

Oblik pika definisan je konvolucijom pseudo-fojktove funkcije sa parom eksponencijalnih članova. Početna istraživanja podataka skupljenih na sobnoj temperaturi ukazuju na povećanje parametra jedinične ćelije a od 8,4396(2) za voluminozan uzorak do 8,464(4) Å za nano uzorak. I pored očigledne razlike u mikrostrukturi oba uzorka (voluminozan i nano), odgovarajućih x vrednosti 0,04(2) i 0,17(8), su strukturno bliska normalnim spinelima. Ovaj zaključak je potvrđen osustvom značajne razlike u dužinama veza A-O i B-O tetraedarski i oktaedarski koordinisanih katjona. Za podatke prikupljene na 5 K za voluminozan uzorak karakteristično je postojanje magnetne strukture.

[1] M. Maletin, Z. Cvejic, S. Rakic, Lj. M. Nikoliv, V. V. Srdic, Mat. Sci. Forum, 518 (2006) s.s. 91-94.
[2] J. D. Jorgensen *et al*, J. Appl. Cryst., 22 (1989), s.s. 321-333.
[3] J. Rodríguez-Carvajal, Commission on Powder Diffraction (IUCr). Newsletter 26 (2001), s.s. 12-19.

APPLICATION OF RIETVELD REFINEMENT IN COMPARATIVE ANALYSIS OF NANOCRYSTALLINE BIOMATERIALS BIORESORBABLE POLYMER/CALCIUM PHOSPHATE AND HUMAN ALVEOLAR BONE

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Human bone tissue contains biominerals dispersed in an organic matrix. The major inorganic component in the mammalian bones is a poorly crystalline calcium phosphate (abbreviation CP), *i.e.* hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (abbreviation HAp) with a variable Ca/P mole ratio. Therefore, HAp is of interest for biological application and bone tissue repair.

The aim of the present work was structural and microstructural characterization of human alveolar bone and two synthetic composite biomaterials based on calcium phosphate.

Composite biomaterials were prepared from CP coated with bioresorbable polymer poly(DL-lactide-co-glycolide), (abbreviation DLPLG). CP/DLPLG ratio is 80/20 wt. %. Inorganic part of sample *A* corresponds to the CP obtained by precipitation method and drying at room temperature. CP which is calcined at 1150 °C is ceramic component of the sample *B*. Sample *C* is deproteinized human alveolar bone [1, 2]. The X-ray powder diffraction patterns showed that sample which was not calcined as well as humane alveolar bone contained only HAp, while material which was calcined at 1150°C contained both HAp and β–tricalcium phosphate, $Ca_3(PO_4)_2$ (abbreviation β–TCP). Based on quantitative X-ray analysis we obtained HAp/β–TCP ratio 72.68/27.32 wt. %.

Determination of structural and microstructural parameters of mentioned samples was carried out using Rietveld refinement. The refinement was performed with the FullProf computing program [3]. Microstructure analysis shows elongated shapes of crystallites of investigated samples (anisotropic extension along the *00l* crystallographic direction). The obtained crystallite size values are as follow: sample *A* 50.57, sample *B* 63.7, and sample *C* 17.93 nm. R_{wp} values were 10.50, 10.00, and 12.1 % for samples *A*, *B* and *C*, respectively, which confirm good agreement between theoretical and experimental structural models.

[1] Lj. Kandić, M. Mitrić and N. Ignjatović, Mat. Sci. Forum 518 (2006), 507-512.
[2] N. Ignjatović, C. Z. Liu, J. T. Czernuszka, D. P. Uskoković, Acta Biomat. 3 (2007) 927-935.
[3] J. Rodriguez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) 127.

PRIMENA RITVELDOVE METODE U KOMPARATIVNOJ ANALIZI NANOKRISTALNOG KOMPOZITNOG BIOMATERIJALA BIORESORBILNI POLIMER / KALCIJUM FOSFAT I UZORKA VILIČNE KOSTI ČOVEKA

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Koštano tkivo čoveka predstavlja biomineral dispergovan u organskoj matrici. Osnovna neorganska komponenta koštanog tkiva sisara je slabo iskristalisao kalcijum fosfat (skraćenica CP) tj. hidroksiapatit, $Ca_{10}(PO_4)_6(OH)_2$ (skraćenica HAp) sa promenljivim molskim odnosom Ca/P. Zbog toga su hidroksiapatiti veoma interesantni za biološku primenu i reparaciju koštanog tkiva.

Cilj ovog rada bio je strukturna i mikrostrukturna karakterizacija uzorka vilične kosti čoveka kao i dva sintetički dobijena kompozitna biomaterijala koji u osnovi imaju CP.

Kompozitni biomaterijal je dobijen oblaganjem kalcijum fosfata bioresorbilnim polimerom, poli(DL-laktid-co-glikolidom), (skraćenica DLPLG). Odnos CP/DLPLG je 80/20 mas. %. Keramičku komponentu u uzorku *A* predstavlja CP dobijen metodom precipitacije na sobnoj temperaturi. CP kalcinisan na 1150 ^{o}C predstavlja keramičku komponentu uzorka *B*. Uzorak *C* je deprotonizovano koštano tkivo čoveka (vilična kost) [1, 2].

Na osnovu rendgenske difrakcione analize utvrđeno je da nekalcinisani uzorak kao i uzorak vilične kosti čoveka sadrže samo HAp, dok uzorak koji je kalcinisan na 1150 ^{o}C sadrži i HAp i β-trikalcijum fosfat, $Ca_3(PO_4)_2$, (skraćenica β–TCP) i to u odnosu 73/27 mas. %.

Strukturni i mikrostrukturni parametri pomenutih uzoraka dobijeni su na osnovu Ritveldove analize. U ovu svrhu korišćen je kompjuterski program FullProf [3]. Mikrostrukturna analiza pokazuje štapićastu formu kristalita hidroksiapatita (anizotropno izduženje duž kristalografskog pravca *00l*). Dobijene vrednosti za veličinu kristalita su sledeće: uzorak *A* 50,57, uzorak *B* 63,70 i uzorak *C* 17,93 nm.

Prikazani faktori slaganja R_{wp} = 10.50 (uzorak *A*), R_{wp} = 10.00 (uzorak *B*), R_{wp} = 12.1 (uzorak *C*) potvrđuju dobro slaganje između teorijskog i eksperimentalnog strukturnog modela.

[[1] Lj. Kandić, M. Mitrić and N. Ignjatović, Mat. Sci. Forum 518 (2006), 507-512.
[2] N. Ignjatović, C. Z. Liu, J. T. Czernuszka, D. P. Uskoković, Acta Biomat. 3 (2007) 927-935.
[3] J. Rodriguez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) 127.

HYDROPHOBIC INTERACTIONS OF PORPHYRINS IN PORPHYRIN CONTAINING PROTEINS

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Noncovalent interactions of porphyrin in porphyrin containing proteins are very important since in the majority of different types of porphyrin containing proteins, porphyrin is noncovalently bound. In our previous work it was shown that porphyrin in metal complexes and in proteins can be involved in specific noncovalent interactions, CH/π interactions between CH-groups and the π-system of porphyrin [1,2]. Searching structures of porphyrin containing proteins from the Protein Data Bank revealed that π-system of every porphyrin ring is involved in CH/π interactions, most of the porphyrins are making several interactions. The amino acids involved in the interactions show high conservation score indicating that CH/π interactions play an important role in the porphyrin-protein stability [2].

This study aims to systematically characterize hydrophobic interactions of porphyrins in porphyrin containing proteins. Structures of porphyrin containing proteins from the Protein Data Bank (PDB) Select January 2007, the list of non-redundant protein chains (25% threshold), were searched in order to find out hydrophobic interactions of porphyrins in proteins. The study has revealed that hydrophobic interactions are commonly found in porphyrin containing proteins and are widely present in different regions of the protein chain, such as the backbone or side chain. Examination of the highly cross-linked hydrophobic network points to a core of several residues with multiple contacts. These contacts cross-link the porphyrin ring in the proteins, essentially tying them together. Side-chains hydrophobic interactions are more frequent than those with backbone. The average conservation score for the amino acids making hydrophobic interactions with the porphyrin is statistically significantly higher than for the amino acids that are not involved in noncovalent interactions with porphyrin.

[1] Medaković V.B., Milčić M.K., Bogdanović G.A., Zarić S.D., J. Inorg. Biochem. 98 (2004), 1867-1873.
[2] Stojanović S.D., Medaković V.B., Predović G., Beljanski M., Zarić S.D., J. Biol. Inorg. Chem. 12 (2007), 1063-1071.

HIDROFOBNE INTERAKCIJE PORFIRINSKOG PRSTENA U PROTEINIMA KOJI SADRŽE PORFIRIN

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Nekovalentne interakcije porfirina u proteinima koji sadrže porfirin su veoma značajne, uglavnom je porfirin nekovalentno vezan u različitim tipovima proteina. U našem predhodnom radu je pokazano da porfirini u kompleksu sa metalima i proteinima mogu biti uljučeni u specifičnim nekovalentnim interakcijama, CH/π interakcijama između CH-grupa i π-sistema porfirina [1,2]. Pretražujući strukture proteina koji sadrže porfirin u PDB bazi otkriveno je da π-sistem svakog porfirinskog prstena učestvuje u CH/π interakcijama, mnogi od porfirina grade nekoliko interakcija. Aminokiseline uključene u interakcije pokazuju visok stepen konzervativnosti što ukazuje da CH/π interakcije imaju važnu ulogu u stabilnosti proteina u kompleksu sa porfirinima.

Cilj ovih istraživanja je sistematska karakterizacija hidrofobnih interakcija porfirina u proteinima koji sadrže porfirin. Za ispitivanje pojave hidrofobnih interakcija smo koristili proteinsku bazu podataka (PDB Select, januar 2007), ne-redundantna lista (verzija 25%). Istraživanja pokazuju da su hidrofobne interakcije u proteinima koji sadrže porfirin prisutne u različitim regionima proteinskog lanca, kao što su polipeptidna kičma ili bočni ostaci. Ispitivanja visoko umrežene hidrofobne mreže pokazuju jezgro nekoliko aminokiselinskih ostataka sa višestrukim kontaktima. Ti kontakti povezuju porfirinski prsten u proteinima, držeći ih zajedno. Hidrofobne interakcije aminokiselinskih ostataka su učestalije od hidrofobnih interakcija peptidne kičme. Konzervacioni skor aminokiselina koje grade hidrofobne interakcije sa porfirinima je statistički značajno veći u odnosu na aminokiseline koje ne grade hidrofobne interakcije.

[1] Medaković V.B., Milčić M.K., Bogdanović G.A., Zarić S.D., J. Inorg. Biochem. 98 (2004), 1867-1873.
[2] Stojanović S.D., Medaković V.B., Predović G., Beljanski M., Zarić S.D., J. Biol. Inorg. Chem. 12 (2007), 1063-1071.

STRUCTURAL INVESTIGATIONS ON YTTRIUM SILICATES

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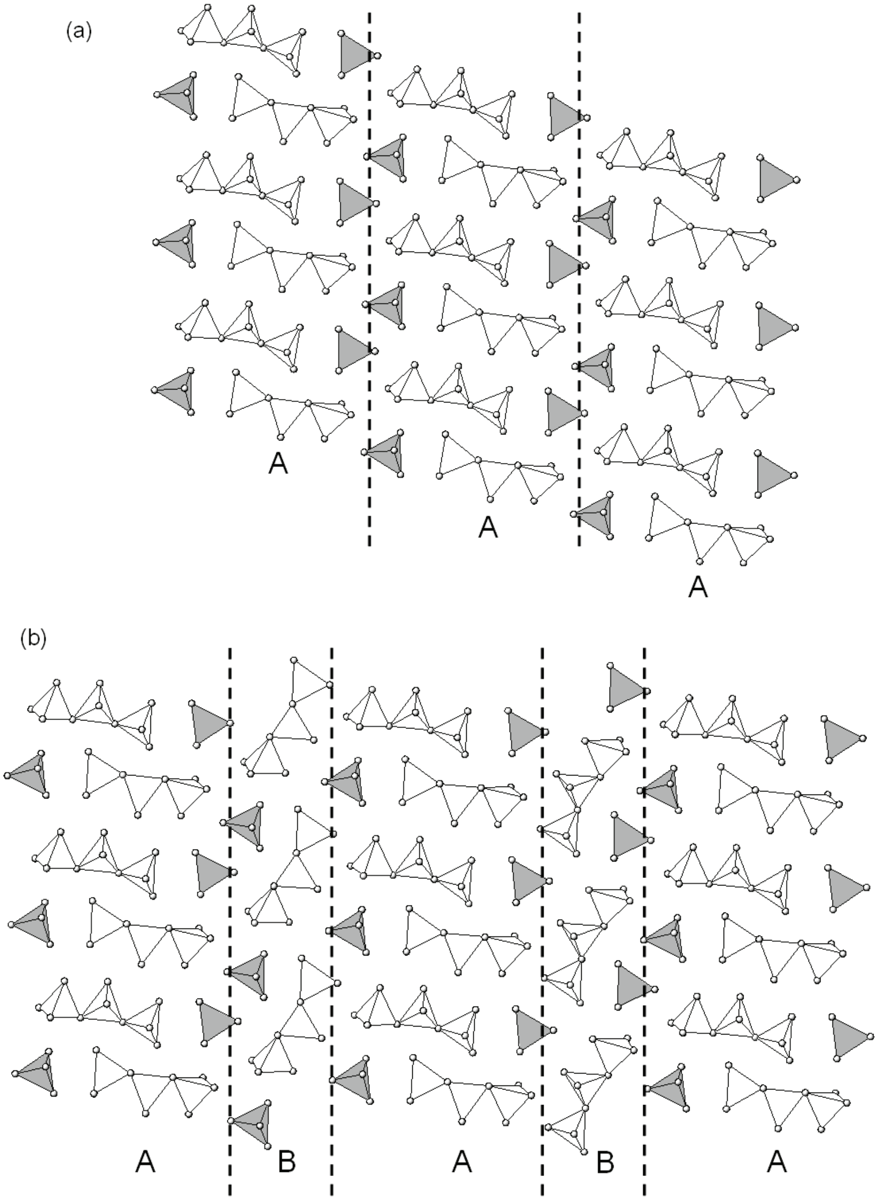
Yttrium silicates have been investigated in great detail, since the double oxides of the system Y_2O_3-SiO_2 are interesting materials in the field of applied inorganic chemistry. Up to now, two different yttrium silicates with composition $Y_2Si_2O_7$ and Y_2SiO_5 are known [1]. Originally, investigations on the technical applications of yttrium disilicate stemmed from its promising optical characteristics. After doping with rare earth elements (REE) the samples exhibited interesting optical properties making them potential candidates for the production of laser materials or high-energy phosphors [2-4]. In the field of advanced ceramics $Y_2Si_2O_7$ has been studied as a sintering aid for Si_3N_4 based materials or as an oxidation protective coating for SiC coated carbon/carbon composites [5-7]. On the other hand, $Y_2Si_2O_7$ has been also investigated due to its complex polymorphism. So far seven different modifications (α, β, γ, δ, y, ζ and η) have been reported. Ito and Johnson [8] established the following transition sequence of reconstructive transformations: $\alpha \xrightarrow{1225°C} \beta \xrightarrow{1445°C} \gamma \xrightarrow{1535°C} \delta$. These four modifications can be synthesized from appropriate reagents by solid state reactions in the respective stability range. The so-called y-phase corresponds to a “low-temperature” form that can be obtained by a hydrothermal approach at about 365 °C [9]. The existence of a further polymorph (ζ-$Y_2Si_2O_7$) was proofed as a by-product during attempts of preparing yttrium oxotellurates [10].

In the course of an excursion into the system Y_2O_3-SiO_2 polycrystalline material of α-$Y_2Si_2O_7$ has been obtained from the thermal decomposition of a precursor prepared by a sol-gel process and subsequently characterized by X-ray powder diffraction and Raman spectroscopy. The structure belongs to the so-called B-type of rare earth element disilicates and was refined using the Rietveld method. α-$Y_2Si_2O_7$ is triclinic with a = 6.58620(3), b = 6.62895(4), c = 12.02723(7) Å, α = 94.4706(4)°, β = 89.0681(4)°,γ = 88.2347(4)°, V = 523.166(5) Å^3, space group $P\bar{1}$, Z = 4 and D_x = 4.39 g/cm^3. The structure (R_{wp} = 4.7%, R_B = 2.9%) is built from triple tetrahedral [Si_3O_{10}]-groups and isolated [SiO_4]-units, i.e. from a structural point of view it belongs to the group of mixed anion silicates. The silicate anions are located in layers parallel to ($1\bar{1}1$). Linkage between the anionic groups is provided by Y cations having six and eight oxygen neighbours. The corresponding coordination polyhedra can be approximately described as distorted octahedra as well as bicapped trigonal prisms, respectively.

Including high pressure as an additional synthesis parameter experiments performed in the system Na_2O-Y_2O_3-SiO_2 revealed the existence of a novel polymorph of $Y_2Si_2O_7$ that was quenched from 6.0 GPa / 1350°C. Single crystal diffraction studies on the so-called η-form were performed at ambient conditions. Chemical composition was determined by electron probe microanalysis. The basic crystallographic data of η-$Y_2Si_2O_7$ are as follows: triclinic symmetry, space group *P*-1, *a* = 6.6290(12)Å, *b* = 6.5840(8)Å, *c* = 35.916(5)Å, α= 91.096(11)°, β= 94.534(13)°, γ = 91.730(13)°, V=1561.6(4)$Å^3$, Z=12, D_{calc}=4.415 g/cm^3. The structure is closely related to that of the α-modification. As can be seen from the comparison of Figures 1a and 1b the similarities are not restricted to the simultaneous occurrence of [Si_3O_{10}]- and [SiO_4]-units in both polymorphs. Both compounds have the same layer-like arrangement of sheets with silicate anions. Furthermore, within a single sheet the same type of ribbons (type *A*) can be identified. However, differences occur due to different arrangements of these ribbons. Whereas a single sheet of the α-form is exclusively build up from type *A* ribbons, the η-modification shows a more complex sheet structure involving an alternating sequence of two ribbon types (*A* and *B*).

Figure 1. Normal view of a single tetrahedral layer for (a) α-$Y_2Si_2O_7$ and (b) η-$Y_2Si_2O_7$. Insular (medium grey) and corner sharing (light grey) tetrahedra have been distinguished.



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CRYSTAL STRUCTURES OF TWO NOVEL STYRYL LACTONES RELATED TO GONIOFUFURONE

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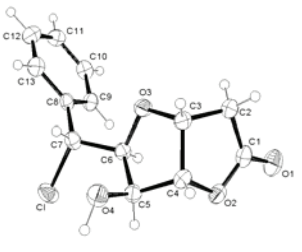
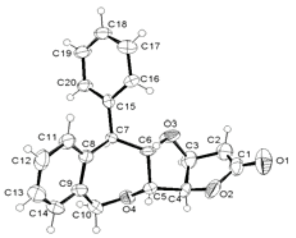
Goniofufurone is a dominant styryl lactone that was isolated from the plant *Goniothalamus giganteus*. It shows a significant cytotoxic activity against certain human tumour cells. As a part of our ongoing project directed to the search for new antitumour agents, two novel goniofufurone analogues (BS33 and BS33A) were synthesized starting from D-xylose [1]. In order to clarify the mechanism of the biological activity, crystal and molecular structure of both derivatives was determined. Recrystallization from CH_2Cl_2-hexane gave analytical samples. The X-ray diffraction data were collected on Xcalibur diffractometer equipped with a CCD area detector using monochromated Mo Kα radiation on 100,0(1) K for BS33 and 293(2) K for BS33A. The structures were solved by the direct methods and refined using the program SHELXS97 and SHELXL97.



BS33



BS33A

Basic crystallographic data and refinement results are the following:
BS33. $C_{13}H_{13}O_4Cl$, a=5.4188(2), b=13.6934(4), c=16.7257(5) Å, V=1241.08(7) Å^3, D_x=1.438 Mg m^{-3}, Z=4, $P2_12_12_1$, μ=0.311 mm^{-1}, F(000)=560, N=3477, I>2σ(I)=1778, N_p=168, R=0.0358, R_w=0.0968, S=0.994, $\Delta\rho_{max}$=0.242 e Å^{-3}, $\Delta\rho_{min}$=–0.347 e Å^{-3}.
BS33A. $C_{20}H_{18}O_4$, a=5.185(5), b=9.051(5), c=9.927(5) Å, α=63.16(5), β=81.27(5), γ=73.38(5)°, V=398.2(5) Å^3, D_x=1.344 Mg m^{-3}, Z=1, $P1$, μ=0.093 mm^{-1}, F(000)=170, N=1914, I>2σ(I)=1122, N_p=218, R=0.0831, R_w=0.1415, S=1.163, $\Delta\rho_{max}$=0.491 e Å^{-3}, $\Delta\rho_{min}$=–0.441 e Å^{-3}. Conformational analysis of the molecules confirms the *cis*-bonding of H atoms of the condensed five-membered rings and that π-electron system of the phenyl ring builds an angle of approximately 90° with the rest of the molecule. The biological activity analaysis has been shown that both compounds exhibit a potent cytotoxicity towards selected human tumour cell lines.

[1] B. Srećo, G. Benedeković, V. Kojić, G. Bogdanović, M. Popsavin, V. Popsavin, *45 Meeting of the Serbian Chemical Society*, Novi Sad, 25–26 January 2007. Proceedings, p. 126.

KRISTALNE STRUKTURE DVA NOVA STIRIL-LAKTONA TIPA GONIOFUFURONA

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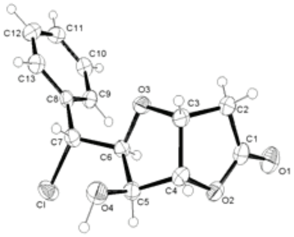
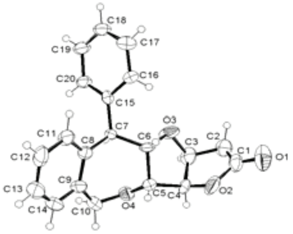
Goniofufuron je dominantni stiril-lakton izolovan iz biljne vrste *Goniothalamus giganteus*, koji pokazuje značajnu citotoksičnu aktivnost prema ćelijama izvesnih humanih tumora. U okviru istraživanja usmerenih na iznalaženje novih antitumorskih agenasa, sintetizovna su dva nova analoga goniofufurona (BS33 i BS33A), polazeći iz D-ksiloze [1]. U cilju rasvetljavanja mehanizma biološke aktivnosti određena je kristalna i molekulska struktura ova dva derivata. Ispitivani uzorci su iskristalisali iz rastvora metilen hlorida i heksana. Intenziteti difrakcionih refleksa izmereni su na automatskom difraktometru Xcalibur sa CCD area detektorom, korišćenjem Mo Kα zračenja na 100,0(1) K za BS33 i na 293(2) K za BS33A. Strukture su rešene direktnim metodama i utačnjene korišćenjem programa SHELXS97 i SHELXL97.



BS33



BS33A

Osnovni kristalografski podaci, kao i rezultati utačnjavanja su sledeći:

BS33. $C_{13}H_{13}O_4Cl$, a=5,4188(2), b=13,6934(4), c=16,7257(5) Å, V=1241,08(7) Å^3, D_x=1,438 Mg m^{-3}, Z=4, $P2_12_12_1$, μ=0,311 mm^{-1}, F(000)=560, N=3477, I>2σ(I)=1778, N_p=168, R=0,0358, R_w=0,0968, S=0,994, $\Delta\rho_{max}$=0,242 e Å^{-3}, $\Delta\rho_{min}$=–0,347 e Å^{-3}.

BS33A. $C_{20}H_{18}O_4$, a=5,185(5), b=9,051(5), c=9,927(5) Å, α=63,16(5), β=81,27(5), γ=73,38(5)°, V=398,2(5) Å^3, D_x=1,344 Mg m^{-3}, Z=1, $P1$, μ=0,093 mm^{-1}, F(000)=170, N=1914, I>2σ(I)=1122, N_p=218, R=0,0831, R_w=0,1415, S=1,163, $\Delta\rho_{max}$=0,491 e Å^{-3}, $\Delta\rho_{min}$=–0,441 e Å^{-3}. Konformaciona analiza molekula potvrđuje *cis*-vezu H-atoma kondenzovanih petočlanih prstenova, kao i da π-elektronski sistem fenilnog prstena zaklapa ugao od približno 90° sa ostatkom molekula. Analize biološke aktivnosti pokazala je da oba jedinjenja ispoljavaju snažnu *in vitro* citotoksičnost prema ćelijskim linijama odabranih humanih tumora.

[1] B. Srećo, G. Benedeković, V. Kojić, G. Bogdanović, M. Popsavin, V. Popsavin, *XLV Savetovanje Srpskog hemijskog društva*, Novi Sad, 25–26. januar 2007. Izvodi radova, str. 126.

SYNTHESIS, STRUCTURE AND BIOLOGICAL EVALUATION OF SOME NEW *A,B*-RING MODIFIED STEROIDAL *D*-LACTONES

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Over the past two decades, substantial effort has been directed toward developing potent inhibitors of aromatase. Formestane (4-hydroxyandrostenedione) was used widely during the early 1990's, but it is not used frequently nowadays because of the need to administer it by intramuscular injection. In view of the above facts, we set as a goal to prepare some new lactones by combining 4-hydroxy-4-en-3-one system A ring of the potent aromatase inhibitor formestane and 17-oxa-D-homo ring. Also, we have synthesized the D-homo lactones with the 1,2-, 4,5-, 5,6-, and 6,7-epoxy function.

Structures of three of these epoxy steroidal compaunds: 4β,5β-epoxy-17-oxa-D-homoandrosta-3,16-dione (1), 6α,7α-epoxy-17-oxa-D-homoandrosta-1,4-diene-3,16-dione (2) and 1α,2α-epoxy-17-oxa-D-homoandrosta-4,6-diene-3,16-dione (3) were confirmed by X-ray structural analysis. The crystallograpiic data for compounds **1** and **2** were presented before [1]. Crystallographic data for compound **3** were collected at 183(2) K on an Oxford Diffraction Xcalibur system using Mo Kα radiation (λ = 0.7107 Å). The program suite CrysAlis^{Pro} [2] was used for data collection, semi-empirical absorption correction and data reduction. Structure was solved with direct methods using SIR97 [3] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97 [4]. The compound **3** ($C_{19}H_{22}O_4$) crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=8.353(2), b=12.214 (2), c=15.566 (3) Å, and Z=4, D_x=1.315 Mgm^{-3}, μ=0.09 mm^{-1}. The final R factor is 0.055 for 2626 independent reflections with $I > 2\sigma(I)$.

Compound **2** was tested in the denucleated ovarian fraction from PMSG pretreated female rats [1]. The well-known aromatase inhibitor formestane, with an inhibitory capacity of 99.2% at 1μM, was used as a reference compound. Other two compounds (1,2) were evaluated for their cytotoxic activity against MCF-7, human breast adenocarcinoma ER+,MDA-MB-231, human breast adenocarcinoma ER-, PC3, prostate cancer, and MRC-5, normal fetal lung fibroblasts [1].

[1] E. Đurendić, M. Sakač, M. Zaviš, A. Gaković, J. Čanadi, S. Andrić, O. Klisurić, V. Kojić, G. Bogdanović, K.P. Gaši, Steroids 73 (2008), 681–688.

[2] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.

[3] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 1999, 32, 115-119.

[4] G.M. Sheldrick, (1997). SHELX97. University of Göttingrn, Germany

SINTEZA, STRUKTURA I BIOLOŠKA EVALUACIJA NOVIH *A,B* MODIFIKOVANIH STEROIDNIH *D*-LAKTONA

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Tokom protekle dve decenije istraživanja na polju razvoja inhibitora aromataze su intezivirana. U ranim devedesetim godinama prošlog veka formestan (4-hidroksiandrostendion), druga generacija inhibitora aromataze, je široko upotrebljavan, dok danas to nije slučaj zbog toga što se on administrira isključivo intramišićno. Imajući u vidu sve ove probleme, sintetizovan je niz laktona sa kombinacijom 4-hidroksi-4-en-3-onskog sistema A prstena potentnog inhibitora aromataze formestana i 17-onskog-D-homo prstena. Takođe su sintetisati laktoni sa 1,2- 4,5- 5,6 i 6,7- epoksi funkcijom.
Strukture tri od ovih epoksi steroidnih jedinjenja: 4β,5β-epoksi-17-oksa-D-homoandrosta-3,16-dion (1), 6α,7α-epoksi-17-oksa-D-homoandrosta-1,4-dien-3,16-dion (2) and 1α,2α-epoksy-17-oksa-D-homoandrosta-4,6-dien-3,16-dion (3) su potvrđene rendgenskom strukturnom analizom. Kristalografski podaci za jedinjenja **1** i **2** predhodno su objavljeni [1]. Kristalografski podaci za jedinjenje **3** su prikupljeni na temperaturi od 182(2) K na Oxford Diffraction Xcalibur difraktometru uz upotrebu Mo Kα zračenja (λ = 0.7107 Å). Programski paket CrysAlis^{Pro} [2] upotrebljen je za prikupljanje, semi-empirijsku korekciju na apsorpciju i redukciju podataka. Struktura je rešena uz pomoć direktnih metoda upotrebom SIR97 [3] programa i utačnjena upotrebom SHELXL-97 programa [4]. Jedinjenje **3** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije: a=8,353(2), b=12,214 (2), c=15,566 (3) Å, and Z=4, D_x=1,315 Mgm^{-3}, μ=0,09 mm^{-1}. Konačna vrednost R faktora je 0,055 za 2626 nezavisnih refleksija sa $I > 2\sigma(I)$.

Jedinjenje **2** je testirano na potentnost inhibicije aromataze, a kao referenca je upotrebljen poznati inhibitor aromataze formestan sa inhibitornim kapacitetom od 99,2% na 1 μM. Ostala dva jedinjenja (1,2) testirana su na moguću citotoksičnu aktivnost na MCF-7, humani adenoma karcinom dojke, ER+, MDA-MB-231, humani adenoma karcinom dojke, PC3, kancer prostate i MRC-5, normalni fetalni plućni fibroblast [1].

[1] E. Đurendić, M. Sakač, M. Zaviš, A. Gaković, J. Čanadi, S. Andrić, O. Klisurić, V. Kojić, G. Bogdanović, K.P. Gaši, Steroids 73 (2008), 681–688.
[2] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.
[3] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 1999, 32, 115-119.
[4] G.M. Sheldrick, (1997). SHELX97. University of Göttingrn, Germany

STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF $Ti_xFe_{(1-x)}O_2$ RUTILE SOLID SOLUTIONS

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The nanoparticle samples of TiO_2 and $Ti_xFe_{(1-x)}O_2$ ($x = 0.075$, 0.95 and 0.90) solid solutions of rutile structure type were investigated from the structural, microstructural and magnetic point of view. TEM microscopy and x-ray powder diffraction (synchrotron radiation, wavelength $\lambda = 0.12$ Å) were used for determination of nanocrystal morphology, structure and microstructure.

The TEM analysis showed that particles adopt needle-like or arrow shape with the thickness of 4-5 nm, while the x-ray diffraction confirmed that the samples were of rutile structure type, without visible presence of other structure forms or impurities. This was also confirmed by Raman scattering.

Based on results of the x-ray powder analysis from synchrotron data (FullProf program), it was found that Rietveld method does not provide proper determination of microstructural parameters, which is ascribed to the issues originating from specific particle morphology (shape). In the different approach, using profile matching mode (LeBail fitting), by the analysis of peak broadening and profiles it was possible to obtain the mean values of microstrain, particle size and the direction of their preferential growth, which are in good overall agreement with TEM observations.

STRUKTURNE I MIKROSTRUKTURNE KARAKTERISTIKE ČVRSTIH RASTVORA $Ti_xFe_{(1-x)}O_2$ U FORMI RUTILA

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[a]Laboratorija za fiziku kondenzovane materije, Institut za nuklearne nauke «Vinča», Mike Petrovića Alasa 12-14, 11001 Beograd, Srbija; [b]Rudarsko-geološki fakultet, Laboratorija za kristalografiju, Đušina 7, 11000 Beolgad, Srbija; [c]Laboratorija za radijacionu hemiju i fiziku, Institut za nuklearne nauke «Vinča», Mike Petrovića Alasa 12-14, 11001 Beograd, Srbija; [d]Physics and Astronomy, 4250 Biomedical Physical Sciences, Michigan State University, East Lansing, MI 48824-2320 USA.
e-mail: blanusa@vin.bg.ac.yu

Uzorci nanočestičnih TiO_2 i čvrstih rastvora $Ti_xFe_{(1-x)}O_2$ (x = 0,075, 0,95 i 0,90) sa strukturom rutila ispitivani su sa stanovišta strukturnih, mikrostrukturnih i magnetnih osobina. U ispitivanju morfologije, kristalne strukture i mikrostrukture korišćeni su TEM mikroskopija i rendgenska difrakcija na polikristalnom materijalu (sinhrotronsko zračenje talasne dužine 0,12 Å).

Mikroskopska analiza pokazala je anizotropni rast čestica koje poprimaju oblik tankih štapića ili strelica debljine 4-5 nm, dok je na osnovu rendgenske difrakcije na polikristalnom materijalu potvrđeno da je u uzorcima prisutan samo rutil, bez vidljivog prisustva drugih kristalnih faza ili nečistoća. Ovo je potvrđeno i analizom Ramanovog rasejanja.

Na osnovu rendgenoske analize polikristalnog uzorka (program FullProf), utvrđeno je da primena Ritveldove metode ne omogućava korektno određivanje svih mikrostrukturnih parametara, što je pripisano problemima koji nastaju usled specifične morfologije čestica. U drugačijem pristupu, korišćenjem LeBail-ovog (profilnog) utačnjavanja, analizom poluširina i profila refleksija određene su srednje vrednosti veličine čestica, koje se u velikoj meri slažu sa rezultatima TEM mikroskopske analize i pravci njihovog preferentnog rasta, kao i srednje vrednosti parametara mikronaprezanja.

MONOCLINIC TRINEPHELINE: CRYSTAL STRUCTURE AND BEHAVIOUR AT ELEVATED TEMPERATURES.

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A new structural variety of nepheline with composition $Na_{7.85}Al_{7.85}Si_{8.15}O_{32}$ was obtained by single crystal growth experiments using a cryolite flux. The crystal structure (Fig. 1) has been solved from X-ray single crystal diffraction data (Mo $K\alpha$ radiation, Stoe IPDS-2 diffractometer, T = 302 K) and refined in S. G. $P112_1$, R_1 = 0.0294 [1] (a = 9.9897(6) Å, b = 9.9622(6) Å, c = 24.979(2) Å, γ = 119.788(4)°, V = 2157.4(2) Å^3). A monoclinic "trinepheline" has c-lattice constant three times the corresponding unit cell parameter observed in natural nepheline [2]. The crystal structure of monoclinic trinepheline can be explained as a stacking sequence of a conventional nepheline unit cell (composed of two layers) and one additional layer containing exclusively elliptical rings, similar to those observed in a related structure reported by [3].

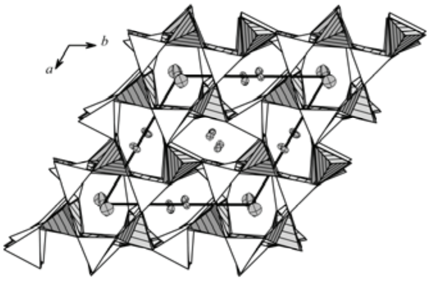

Figure 1. Crystal structure of monoclinic trinepheline in a projection parallel to c. Sodium ions are represented by thermal ellipsoids (50% probability level).

Upon heating to 373(5) K, monoclinic trinepheline transforms to hexagonal symmetry (S. G. $P6_1$, a = 9.969(1) Å, c = 25.056(2) Å, V = 2156.4(4) Å^3). The tripling of the c unit cell parameter is retained with very weak superlattice reflections, while the average structure of this phase corresponds to conventional pure sodium nepheline with $P6_3$-symmetry [4]. Superstructure reflections are due to disorder phenomena of one apical oxygen and one sodium ion situated in a ditrigonal ring. Upon further heating the disorder is averaged and at 473(5) K the crystal structure corresponds to that of conventional nepheline (S. G. $P6_3$, a = 9.977(2) Å, c = 8.354(2) Å, V = 720.2(2) Å^3).

[1] P. Vulić, V. Kahlenberg and J. Konzett, Am. Min., 93 (2008), accepted for publication.
[2] T. Hahn & M. J. Buerger, Z. Kristall., 106 (1955), 308-338.
[3] V. Kahlenberg & H. Böhm, Am. Min., 83 (1998), 631-637.
[4] B. Hippler & H. Böhm, Z. Kristall., 187 (1989), 39-53.

МОНОКЛИНИЧНИ ТРИНЕФЕЛИН: КРИСТАЛНА СТРУКТУРА И ПОНАШАЊЕ НА ПОВИШЕНИМ ТЕМПЕРАТУРАМА.

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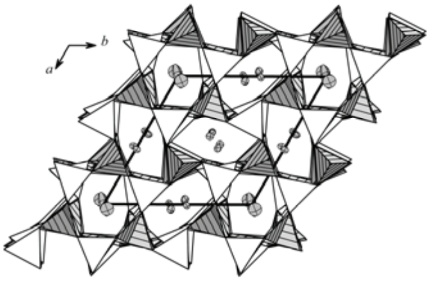
Нови варијетет нефелина састава $Na_{7,85}Al_{7,85}Si_{8,15}O_{32}$ је добијен растом кристала у криолитском флуксу. Кристална структура (Сл. 1) је решена из података добијених дифракцијом на монокристалу (Mo $K\alpha$ зрачење, Stoe IPDS-2 дифрактометар, T = 302 K) и утачњена у П. Г. $P112_1$, R_1 = 0,0294 [1] (a = 9,9897(6) Å, b = 9,9622(6) Å, c = 24,979(2) Å, γ = 119,788(4)°, V = 2157,4(2) $Å^3$). Параметар јединичне ћелије c моноклиничног тринефелина је троструко већи него одговарајући параметар природног нефелина [2]. Кристална структура моноклиничног тринефелина може се добити узастопним слагањем јединичне ћелије нефелина (која се састоји из два слоја) и додатног слоја изграђеног искључиво од елиптичних шесточланих тетраедарских прстенова [3] у правцу нормално на c осу.



Слика 1. Кристална структура моноклиничног тринефелина посматрана у правцу *c*. Јони натријума су представљени термалним елипсоидима.

Загревањем до 373(5) K моноклинични тринефелин се трансформише у хексагоналну симетрију (П. Г. $P6_1$, a = 9,969(1) Å, c = 25,056(2) Å, V = 2156,4(4) $Å^3$). Троструко већи c параметар је очуван, али су одговарајуће рефлексије суперструктуре веома слабе. Средња структура слична је структури Na нефелина $P6_3$ симетрије [4]. Рефлексије суперструктуре последица су неуређености једног од апикалних кисеоника и натријума који се налази у дитригоналном прстену. Даљим загревањем до 473(5) K структура прелази у нефелин (П. Г. $P6_3$, a = 9,977(2) Å, c = 8,354(2) Å, V = 720,2(2) $Å^3$).

[1] P. Vulić, V. Kahlenberg and J. Konzett, Am. Min., 93 (2008), прихваћен рад.
[2] T. Hahn & M. J. Buerger, Z. Kristall., 106 (1955), 308-338.
[3] V. Kahlenberg & H. Böhm, Am. Min., 83 (1998), 631-637.
[4] B. Hippler & H. Böhm, Z. Kristall., 187 (1989), 39-53.

HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF $Cd_2Cu(PO_4)_2$

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Using hydrothermal method (Teflon-lined steel autoclave, T = 473 K, 192 hours) title compound crystallised as blue prismatic crystals up to 100 μm in length from an aqueous mixture of $Cd(OH)_2$, $(NH_4)_2HPO_4$ and $CuCl_2{\bullet}2H_2O$. Green prismatic crystals of $Cu_2(PO_4)OH$ and colourless NH_4Cl crystallised in a similar amount. The qualitative EDX analysis confirmed the presence of Cd, Cu and P. The crystal structure was refined using single-crystal X-ray diffraction data (CCD detector, Mo $K\alpha$ radiation, 298 K, $2\theta_{\max} = 60°$). The refinement on F^2 (62 free parameters) yielded $R_1 = 0.0206$, $wR_2 = 0.0434$ using 803 unique reflections; for 745 observed reflections with $I \geq 2\sigma(I)$, $R_1 = 0.0176$. *Crystal data*: space group $P\,\bar{1}$, $a = 4.7982(3)$, $b = 5.5801(3)$, $c = 6.7217(3)$ Å, $\alpha = 74.266(3)$, $\beta = 86.330(3)$, $\gamma = 69.924(3)$ °, $V = 162.62(2)$ Å^3, $Z = 1$. The crystal structure is very similar to several published phosphates $Cu_3(PO_4)_2$, $Co_3(PO_4)_2$ [1], $(Mg_{0.21},Cu_{0.79})_3(PO_4)_2$ [2], and arsenate $Zn_2Cu(AsO_4)_2$ – mineral stranskiite [3], but not with monoclinic $Cd_{1.35}Cu_{1.65}(PO_4)_2$, which has very similar chemical composition [4].

The crystal structure of the $Cd_2Cu(PO_4)_2$ is built up of CdO_6, CuO_4, and PO_4 coordination polyhedra. The cadmium atom is surrounded by six O atoms forming a 5+1 (the sixth atom is at a longer distance of 2.716 Å) coordination polyhedron, which can be described as an extremely distorted octahedron (<Cd—O> = 2.336 Å). Two CdO_6 polyhedra, sharing the O4—O4^i (i = -x,-y,-z) edge, form Cd_2O_{10} dimmers, which are further polymerized in a double chains along *a*-axis. The copper atom, located on an inversion centre, is coordinated by four O atoms with an average Cu—O bond distance of 1.941 Å forming slightly distorted square-planar coordination (O2—Cu—O3 bond angles are 91.6(1) and 88.4(2) °). The phosphorus atom exhibits an usual tetrahedral coordination by four O (<P–O> = 1.541 Å). The PO_4 tetrahedra are connected to both, CdO_6 and CuO_4 polyhedra, and with CuO_4 polyhedra generate $Cu(PO_4)_2$ chains extending along the same [100] direction.

The second author gratefully acknowledges the financial support of the Austrian Science Foundation (FWF) (Grant T300-N19).

[1] J.B. Forsyth, C. Wilkinson, S. Paster, and H. Effenberger, J. Phys.-Condens. Mat., 2 (1990) 1609-1617;
[2] A. Moqine, A. Boukhari, E.M. Holt, J. Solid State Chem., 108 (1994) 193-197;
[3] P. Keller, H. Hess, P.J. Dunn, TMPM, 26 (1979) 167-174;
[4] H. Mueller-Buschbaum, S. Muenchau, Z. Naturforsch., 51 (1996) 229-232.

ХИДРОТЕРМАЛНА СИНТЕЗА И КРИСТАЛНА СТРУКТУРА $Cd_2Cu(PO_4)_2$

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Плави призматични кристали величине до 0,10 mm добијени су као производ реакције између компонената $Cd(OH)_2$, $(NH_4)_2HPO_4$ и $CuCl_2•2H_2O$ уз додатак дестиловане воде. Кристали су синтетисани хидротермалном методом у тефлонским судовима у аутоклавима Морејевог типа (473 K, 192 h). Квалитативна SEM (EDX) анализа потврдила је присуство Cd, Cu и P. Прикупљени су дифракциони подаци на монокристалу (Mo Kα рендгенско зрачење, CCD равни детектор, 298 K, $2\theta_{max} = 60$ °) и утачњена је структура. Утачњавањем 62 параметра добијени су следећи R-параметри*:* $R_1 = 0,0206$*,* $wR_2 = 0,0434$ за укупно 803 рефлексије и $R_1 = 0,0176$ за 745 рефлексија са $I \geq 2\sigma(I)$. Кристалографски подаци*:* просторна група $P\bar{1}$, a = 4,7982(3), b = 5,5801(3), c = 6,7217(3) Å, α = 74,266(3), β = 86,330(3), γ = 69,924(3) °, V = 162,62(2) Å^3, Z = 1. Структура је веома слична структурама фосфата $Cu_3(PO_4)_2$, $Co_3(PO_4)_2$ [1], $(Mg_{0.21},Cu_{0.79})_3(PO_4)_2$ [2], и арсената $Zn_2Cu(AsO_4)_2$ – минерал странскиит [3], али не и моноклиничном $Cd_{1,35}Cu_{1,65}(PO_4)_2$ једињењу које има врло сличан хемијски састав [4].

Структура $Cd_2Cu(PO_4)_2$ је изграђена од CdO_6, CuO_4, и PO_4 координационих полиедара. Кадмијум је окружен са шест O атома који формирају 5+1 (шести атом O је на дужем растојању од 2.716 Å) координациони полиедар, који се може описати као екстремно деформисани октаедар (<Cd—O> = 2.336 Å). Два CdO_6 полиедра, који деле заједничку ивицу O4—O4^i (i = -x,-y,-z), формирају Cd_2O_{10} димере, који се даље полимеризују у двоструке ланце дуж a-осе. Бакар лежи у центру симетрије и окружен је са 4 O на просечном растојању Cu—O од 1.941 Å, који формирају мало деформисану квадратно-планарну координацију (O2—Cu—O3 углови су 91.6(1) и 88.4(2) °). Фосфор је у уобичајеној тетраедарској координацији (<P–O> = 1.541 Å). PO_4-тетраедри су повезани са CdO_6 и CuO_4 полиедрима, а са CuO_4 полиедрима граде $Cu(PO_4)_2$ ланце који се такође пружају дуж правца [100].

Другопотписани аутор овог рада захваљује Научном Фонду Републике Аустрије (FWF) (Пројекат T300-N19).

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[3] P. Keller, H. Hess, P.J. Dunn, TMPM, 26 (1979) 167-174;
[4] H. Mueller-Buschbaum, S. Muenchau, Z. Naturforsch., 51 (1996) 229-232.

CLASSIFICATION OF AMINO ACIDS BASED ON THE PROPENSITIES TOWARDS A PARTICULAR SECONDARY STRUCTURE: CONNECTION WITH THEIR CHEMICAL STRUCTURE

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Conformational preferences of amino acids are very important for understanding conformational interactions in proteins. Moreover, when used as propensities they can be helpful in predicting secondary and tertiary structures of proteins. There are many methods that consider protein folding and many of them use some information about the protein secondary structure. Preferences of amino acids were introduced and calculated long time ago and it is known that different amino acids have distinct preferences for the adoption of helical, strand, and random coil conformation. Levitt observed [1] that 19 of 20 naturally occurring amino acids have preferences for only one of the several types of secondary structure, leading to a very clear classification of amino acids by their preferences. It was shown that the preferences and classification correlate with the chemical structure of amino acids.

The correlations of primary and secondary structures of proteins were analyzed using large data set from the Protein Data Bank [2]. Clear preferences of amino acids towards certain secondary structures classify amino acids into four groups: α-helix preferrers, strand preferrers, turn and bend preferrers, and *His* and *Cys* (the latter two amino acids do not show clear preference for any secondary structure). Amino acids in the same group have similar structural characteristics at their Cβ and Cγ atoms that predicts their preference for a particular secondary structure. All α-helix preferrers have neither polar heteroatoms on Cβ and Cγ atoms nor, branching nor aromatic group on the Cβ atom. All strand preferrers have aromatic groups or branching on the Cβ atom. All turn and bend preferrers have polar heteroatom on Cβ or Cγ atoms or do not have a Cβ atom at all. These new rules can be helpful in making predictions about non-natural amino acids.

[1] Levitt M (1978) Biochemistry 17:4277-4285
[2] S. N. Malkov, M. V. Živković, M.V. Beljanski, M. B. Hall, S. D. Zarić, Journal of Molecular Modeling, in press

КЛАСИФИКОВАЊЕ АМИНО КИСЕЛИНА НА ОСНОВУ НАКЛОНОСТИ ПРЕМА РАЗЛИЧИТИМ СЕКУНДАРНИМ СТРУКТУРАМА: ПОВЕЗАНОСТ СА ЊИХОВОМ ХЕМИЈСКОМ СТРУКТУРОМ

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Тенденције амино киселина да граде различите секундарне структуре су веома важне за разумевање просторних интеракција у протеинима. Штавише, оне могу бити од помоћи при предвиђању секундарне и терцијалне структуре протеина. Постоји више метода који разматрају увијање протеина и многи од њих користе неке информације о секундарној структури протеина. Склоности амино киселина су уочене и израчунаване релативно давно и познато је да различите амино киселине имају различите склоности према одређеним типовима секундарних структура. Levitt је уочио [1] да 19 од 20 амино киселина имају јасне склоности према само по једном типу секундарних структура, што је водило веома јасној класификацији амино киселина. Показано је да су склоности и класификација повезани са хемијском структуром АК.

Корелације између примарне и секундарне структуре протеина су анализиране на ширем скупу протеина из Протеинске банке података [2]. На основу јасних склоности амино киселина према грађењу одређених секундарних структура, оне се класификују у четири групе: амино киселине склоне α-хеликсима, амино киселине склоне β-структурама, амино киселине склоне завојима и амино киселине без јасних склоности (*His* и *Cys*). Амино киселине које чине исту групу имају исте структурне карактеристике на атомима Cβ и Cγ, које одређују њихову склоност према одговарајућој секундарној структури. Све амино киселине склоне грађењу α-хеликса немају ни поларне хетеро-атоме на Cβ и Cγ, ни гранање нити ароматичну групу на атому Cβ. Све амино киселине склоне грађењу β-структура имају ароматичне групе или гранање на атому Cβ. Све АК склоне грађењу завоја имају поларне хетероатоме на атому Cβ или атому Cγ, или уопште немају атом Cβ.

[1] Levitt M (1978) Biochemistry 17:4277-4285

[2] S. N. Malkov, M. V. Živković, M.V. Beljanski, M. B. Hall, S. D. Zarić, Journal of Molecular Modeling, у штампи

POSTER PRESENTATIONS
ПОСТЕРСКА СЕКЦИЈА

CRYSTAL STRUCTURE OF POLYMERIC (2,2'-BIPYRIDINE)(μ-ISOPHTHALATO)COBALT(II), $[Co(C_8H_4O_4)(C_{10}H_8N_2)]_\infty$

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In the title compound, the formula of asymmetric unit is $[Co_2(bipy)_2(ipht)_2]$, where bipy = 2,2'-bipyridine and ipht = isophthalate ion. The structure can be described as built of two different $Co(bipy)^{2+}$ ions bridged by two ipht anions in a complex manner. One ipht ion bridges two Co atoms acting as bis-chelate ligand. Another ipht ion bridges three Co atoms with one bridging and one chelating COO group. In this way centrosymmetric double chains extending along *b*-axis are formed (Fig. 1). Both Co atoms are in highly distorted octahedral environment. The shortest intrachain Co–Co distance is 4.31 Å. There are π-π and numerous C–H···O interactions in the structure.

The compound was prepared by hydrothermal method (a Teflon-lined steel autoclave, heating temperature: 140 ºC, heating time: 3 days) starting from an aqueous solution containing $Co(NO_3)_2$, 2,2'-bipyridine and sodium isophthalate. The structure was refined using single-crystal X-ray diffraction data (Oxford diffractometer, CCD detector, Mo*K*α radiation, $\theta_{max} = 25.7$ °, 13024 measured reflections, $R_{int} = 0.023$, $T = 293$ K).

Crystal data: space group $P\bar{1}$, $a = 9.3376(5)$, $b = 11.2636(5)$, $c = 16.7560(8)$ Å, $\alpha = 98.701(4)$, $\beta = 94.538(4)$, $\gamma = 112.325(4)$ °, $V = 1593.4(1)$ Å^3, $Z = 2$, $\rho_x = 1.581$ g cm^{-3}, $\mu = 1.10$ mm^{-1}. The refinement on F^2 (451 parameters) yielded $R_1 = 0.051$, $wR_2 = 0.067$, $S = 1.01$ for all data, and $R_1 = 0.031$ for 4471 observed reflections with $I \geq 2\sigma(I)$.

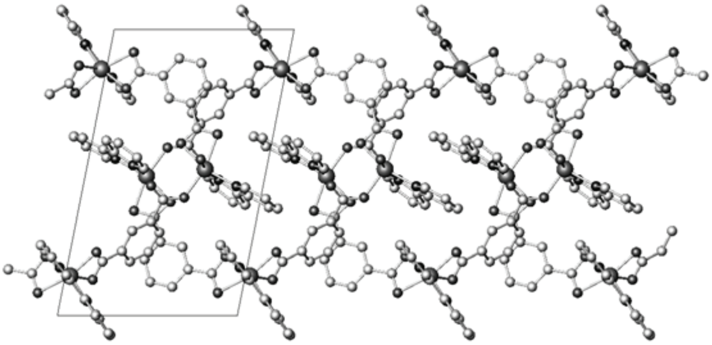

Fig. 1. Centrosymmetric double chains extending along *b*-axis (*c*-axis down).

KRISTALNA STRUKTURA POLIMERNOG (2,2’-BIPIRIDIN)(μ-IZOFTALATO)KOBALTA(II), $[Co(C_8H_4O_4)(C_{10}H_8N_2)]_\infty$

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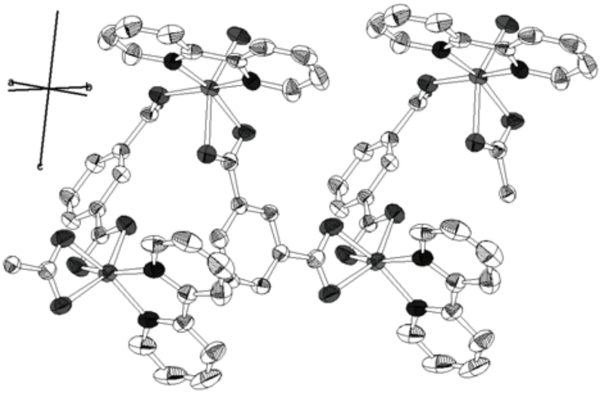
Asimetrična jedinica jedinjenja opisanog u ovom radu ima formulu $[Co_2(bipy)_2(ipht)_2]$, gde je bipy = 2,2’-bipiridin, a ipht = izoftalat-jon. Strukturu je najlakše zamisliti kao da je sastavljena od dva nezavisna $Co(bipy)^{2+}$-jona, koji su premošćeni složenom mrežom dva različita ipht-anjona (slika 1). Jedan ipht-jon premošćava dva atoma Co i ponaša se kao bis-helatni ligand. Drugi ipht-jon sadrži jednu mostovnu i jednu helatnu COO-grupu i premošćava tri atoma Co. Na taj način nastaju centrosimetrični dvostruki lanci koji se protežu duž *b*-ose. Oba atoma Co nalaze se u veoma deformisanom oktaedarskom okruženju. Najkraće Co–Co rastojanje unutar lanaca iznosi 4,31 Å. U strukturi postoje π-π i brojne C–H···O interakcije.

Jedinjenje je dobijeno hidrotermalnim postupkom (čelični autoklav obložen teflonom, temperatura zagrevanja: 140 ºC, vreme zagrevanja: 3 dana) polazeći od vodenog rastvora $Co(NO_3)_2$, 2,2’-bipiridina i natrijum-izoftalata. Struktura je rešena i utačnjenja na osnovu podataka dobijenih rendgenskom difrakcijom na monokristalu (Oxford difraktometar, CCD detektor, Mo*K*α zračenje, $\theta_{max} = 25{,}7$ °, 13024 izmerene refleksije, $R_{int} = 0{,}023$, $T = 293$ K).

Kristalografski podaci: prostorna grupa $P\bar{1}$, $a = 9{,}3376(5)$, $b = 11{,}2636(5)$, $c = 16{,}7560(8)$ Å, $\alpha = 98{,}701(4)$, $\beta = 94{,}538(4)$, $\gamma = 112{,}325(4)$ °, $V = 1593{,}4(1)$ Å^3, $Z = 2$, $\rho_x = 1{,}581$ g cm^{-3}, $\mu = 1{,}10$ mm^{-1}. Utačnjavanje sa F^2 (451 parametar) dalo je $R_1 = 0{,}051$, $wR_2 = 0{,}067$, $S = 1{,}01$ za sve podatke, i $R_1 = 0{,}031$ za 4471 refleksiju sa $I \geq 2\sigma(I)$.



Slika 1. Način koordinacije izoftalat-jona.

CRYSTAL STRUCTURE OF *O,O'*-DICYCLOPENTYL-(*S,S*)--ETHYLENEDIAMMONIUM-*N,N'*-DI-2-PROPANOATE CHLORIDE DICHLOROFORM SOLVATE

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O,O'-dicyclopentyl-(*S,S*)-ethylenediammonium-*N,N'*-di-2-propanoate chloride dichloroform solvate, $[(S,S)\text{-}H_2Cp_2eddp]Cl_2{\cdot}2CHCl_3$ ($Cp = C_5H_9$) was synthesized by analog method described for similar compounds [1]. A small quantity of the product was disolved in a cyclopentyl alcohol containing small volume of $CHCl_3$ and from this solution after a few days crystals suitable for X-ray analysis were obtained.

Crystallographic data: $C_{20}H_{36}Cl_8N_2O_4$, orthorhombic system, chiral space group $P2_12_12$, $a = 14.5059(5)$ Å , $b = 20.0906(1)$ Å, $c = 5.2876(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1540.98(1)$ Å^3, $Z = 2$, $D_c = 1.405$ Mg/m^3, $\mu(\mathrm{Mo}K_\alpha) = 0.759$ mm^{-1}, F(000) = 676. Data collection: $2.81 < \theta < 25.68°$, no. of parameters: 174, $R = 0.056$, $wR2 = 0.1108$ for 2929 reflections with $I > 2\sigma(I)$.

In the measured crystals there are one dicationic specie $[(S,S)\text{-}H_2Cp_2eddp]^{2+}$, two Cl^- anions and two chloroform molecules. The most significant hydrogen bonds for the way of packing are N–H1N···Cl, 3.120(4) Å, 168(5)° and N–H2N···Cl, 3.095(4) Å, 159(4)° as shown in Figure 1.

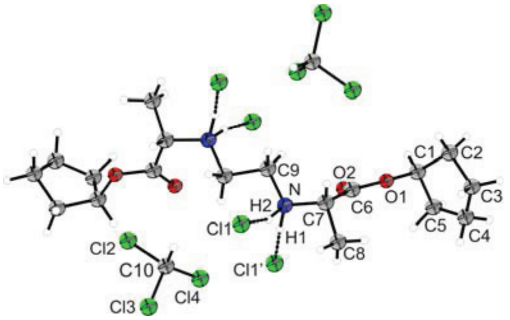

Figure 1. Crystal structure of $[(S,S)\text{-}H_2Cp_2eddp]Cl_2{\cdot}2CHCl_3$ (H-bonds shown by dashed lines)

[1] B. B. Krajčinović, G. N. Kaluđerović, D. Steinborn, H. Schmidt, Ch. Wagner, Ž. Žižak, Z. D. Juranić, S. R. Trifunović and T. J. Sabo, J. Inorg. Biochem., 102 (2008) 892–900.

KRISTALNA STRUKTURA (*O,O'*-DICIKLOPENTIL-(*S,S*)-ETILENDIAMMONIUM-*N,N'*-DI-2-PROPANOAT)-HLORIDA DIHLOROFORM SOLVATA

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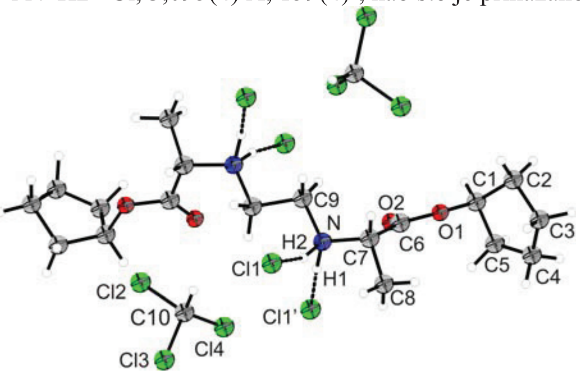
(*O,O'*-diciklopentil-(*S,S*)-etilendiammonium-*N,N'*-di-2-propanoat)-hlorid dihloroform solvat, $[(S,S)\text{-}H_2Cp_2eddp]Cl_2{\cdot}2CHCl_3$ ($Cp = C_5H_9$) sintetisan je na sličan način kao i srodna jedinjenja opisana u literaturi [1]. Deo proizvoda rastvoren je u ciklopentanolu i maloj količini hloroforma i iz tog rastvora dobijeni su kristali pogodni za rendgensku strukturnu analizu.

Kristalografski podaci: $C_{20}H_{36}Cl_8N_2O_4$, ortorombičan sistem, prostorna grupa $P2_12_12$, $a = 14{,}5059(5)$ Å , $b = 20{,}0906(1)$ Å, $c = 5{,}2876(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1540{,}98(1)$ Å^3, $Z = 2$, $D_c = 1.405$ Mg/m^3, μ(Mo$K\alpha$) = 0.759 mm^{-1}, F(000) = 676. Opseg: $2{,}81 < \theta < 25{,}68°$, broj parametara: 174, $R = 0{,}056$, $wR2 = 0{,}1108$ za 2929 refleksija sa $I > 2\sigma(I)$.

Dobijeni monokristali se sastoje iz dikatjona $[(S,S)\text{-}H_2Cp_2eddp]^{2+}$, dva anjona Cl^- i dva molekula hloroforma. Najznačajnije vodonične veze za način pakovanja su N–H1···Cl, 3,120(4) Å, 168(5)º i N–H2···Cl, 3,095(4) Å, 159(4)º, kao što je prikazano na Slici 1.



Slika 1. Kristalna struktura $[(S,S)\text{-}H_2Cp_2eddp]Cl_2{\cdot}2CHCl_3$ (prikazane H-veze)

[1] B. B. Krajčinović, G. N. Kaluđerović, D. Steinborn, H. Schmidt, Ch. Wagner, Ž. Žižak, Z. D. Juranić, S. R. Trifunović and T. J. Sabo, J. Inorg. Biochem., 102 (2008) 892–900.

CRYSTALLOGRAPHIC AND THEORETICAL INVESTIGATION OF OH···π (ARYL) INTERACTIONS OF WATER MOLECULE

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The conformations and functions of crystal structures depend importantly on the interactions with the surrounding solvent, in particular with water molecules. The interactions of water molecule with the π-electrons of aromatic groups play important roles [1]. The investigation of OH/π interactions between water molecule and the aromatic groups of amino acids in crystal structures of proteins confirmed relatively frequent occurence of aromatic interactions [2].

In this paper an analysis of crystal structures from the Cambridge Structural Database (CSD) involving aryl rings and water molecules is presented. The crystal structures satisfying the geometric criteria were selected and screened for short intermolecular contacts between the water molecule and the aryl group. Three regions of the C_6-aromatic ring are inspected [3,4]: the ring centar, the C-atom, and the C-C bond. The analysis of data shows that there is substantial number of interactions with short distances (around 3.0 Å). We found in total 308 contacts where the hydrogen atom of the water molecule is donor and the C_6–aromatic ring is acceptor. *Ab initio* calculations on selected geometries of water-benzene dimers are performed and the interaction energies are obtained using different methods and basis sets. The obtained results are compared with the observations from the CSD search.

Figure 1. The examples of the aryl containing compounds where OH/π interactions with water molecule are observed.

[1] M.Milčić, S.D.Zarić, Eur. J. Inorg.Chem., (2001) 2143-2150
[2] T. Steiner, Biophys.Chem., 95, (2002), 195-201
[3] J.F.Malone, C.M.Murray, M.H.Charlton, R.Docherty, A.J.Lavery, J.Chem.Soc.,Farad. Trans., 93, (1997), 3429-3436
[4] S.Tsuzuki, K.Honda, T.Uchimaru, M.Mikami, K. Tanabe, J.Am.Chem.Soc., 122, (2000), 11450-11458

КРИСТАЛОГРАФСКО И ТЕОРИЈСКО ИСТРАЖИВАЊЕ OH···π (ARYL) ИНТЕРАКЦИЈА МОЛЕКУЛА ВОДЕ

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Конформације и функције кристалних структура зависе много од интеракција са растварачем, посебно са молекулима воде. Интеракције молекула воде са π електронима ароматичних група играју значајну улогу [1]. Истраживања OH/π интеракција између молекула воде и ароматичних група амино киселина у кристалним структурама протеинима показала су да се ароматичне интеракције јављају релативно често [2].

У овом раду представљена је анализа кристалних структура Кембричке базе података (Cambridge Structural Database (CSD)) које укључују aryl прстенове и молекул воде. Издвојене су кристалне структуре које задовољавају одређене геометријске критеријуме и лоцирана су кратка интермолекулска растојања између молекула воде и арил групе. Посматране су три области C_6-ароматичног прстена [3,4]: центар прстена, C-атом и C-C веза. Анализа података показује да постоји знатан број интеракција на кратким растојањима (око 3 Å). Пронађено је 308 интеракција у којима учествује молекул воде као донор и C_6-ароматични прстен као акцептор. Урађена су *ab initio* израчунавања на одабраним геометријама димера бензен-вода и добијене су вредности енергија интеракције разним методама и базисним сетовима. Добијени подаци су упоређени са резултатима претраге кристалографске базе података.

Слика 1. Примери кристалних структура у којима су примећене OH/π интеракције између молекула воде и ароматичних прстенова aryl група

[1] M.Milčić, S.D.Zarić, Eur. J. Inorg.Chem., (2001) 2143-2150
[2] T. Steiner, Biophys.Chem., 95, (2002), 195-201
[3] J.F.Malone, C.M.Murray, M.H.Charlton, R.Docherty, A.J.Lavery, J.Chem.Soc.,Farad. Trans., 93, (1997), 3429-3436
[4] S.Tsuzuki, K.Honda, T.Uchimaru, M.Mikami, K. Tanabe, J.Am.Chem.Soc., 122, (2000), 11450-11458

NONCOVALENT INTERACTIONS BETWEEN BIPYRIDYL LIGANDS IN CRYSTAL STRUCTURES IN SQUARE-PLANAR, TETRAHEDRAL AND OCTAHEDRAL METAL COMLEXES

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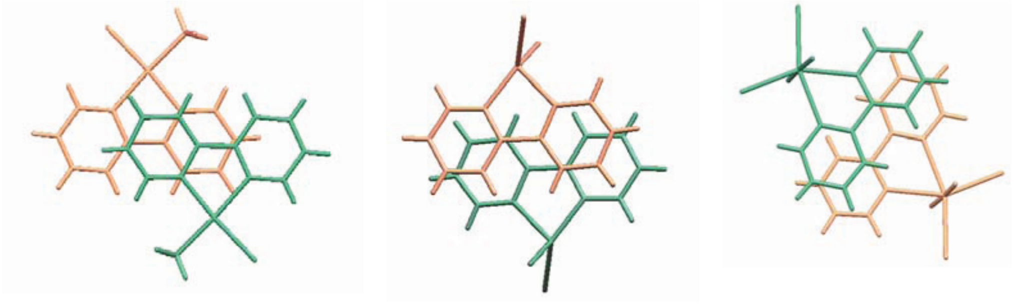
Stacking interactions are important noncovalent forces occurring between organic aromatic rings. In some transition metal complexes there are planar chelate rings with delocalized bonds that can be also involved in specific types of stacking interactions. Bipyridyl ligand has two organic aromatic rings, and by coordinating to a metal forms planar chelate ring, therefore coordinated bipyridyl ligand forms large planar delocalized system suitable for staking interactions.

We studied stacking interactions between bipyridyl ligands in crystal structures of square-planar, tetrahedral and octahedral metal complexes. By searching Cambridge Structural Database (CSD), all crystal structures of square-planar, tetrahedral, and octahedral metal complexes with bipyrydil ligand were found (Figure). Analyzing geometrical parameters in these crystal structures indicate stacking interactions between bipyridyl ligands and showed mutual orientation of bipyridyl ligands and whole complexes. The stacking interactions can orient square-planar, tetrahedral and octahedral metal complexes in a few different ways.



НЕКОВАЛЕНТНЕ ИНТЕРАКЦИЈЕ ИЗМЕЂУ БИПИРИДИНСКИХ ЛИГАНАДА У КРИСТАЛНИМ СТРУКТУРАМА КВАДРАТНО-ПЛАНАРНИХ, ТЕТРАЕДАРСКИХ И ОКТАЕДАРСКИХ КОМПЛЕКСА МЕТАЛА

Ивица Д. Миловановић[а], Милица В. Букоровић[а], Горан В. Јањић[б], Снежана Д. Зарић[а]

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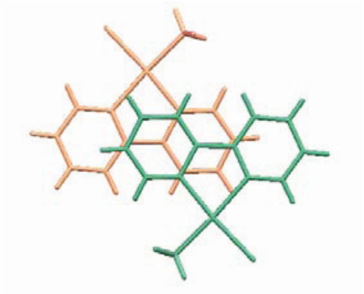
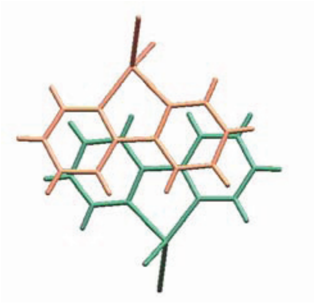
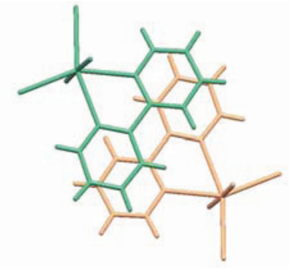
"Стекинг" интеракције су важне нековалентне силе које се јављају између органских ароматичних прстенова. У комплексима прелазних метала, који садрже планарне хелатне прстенове са делокализованим везама, јављају се специфични типови "стекинг" интеракција. Бипиридински лиганд садржи два органска ароматична прстена који координовањем са металом граде планарни хелатни прстен, при чему долази до повећања делокализације система погодног за "стекинг" интеракције.

Ми смо проучавали "стекинг" интеракције између бипиридинских лиганада у кристалним структурама квадратно-планарних, тетраедарских и октаедарских комплекса метала. Претражујући Кембричку банку података (CSD) издвојили смо све структуре квадратно-планарних, тетраедарских и октаедарских комплекса прелазних метала са бипиридинским лигандом (Слика). Анализом геометријских параметара у издвојеним кристалним структурама примећене су "стекинг" интеракције између бипиридинских лиганада и показане су међусобне оријентације бипиридинских лиганада и читавих комплекса. Ове интеракције оријентишу квадратно-планарне, тетраедарске и октаедарске комплексе на неколико различитих начина.







STUDY OF STACKING INERACTIONS IN CRYSTAL STRUCTURES IN SQUARE-PLANAR AND TETHRAEDRAL METAL COMLEXES WITH PHENANTHROLINE LIGANDS

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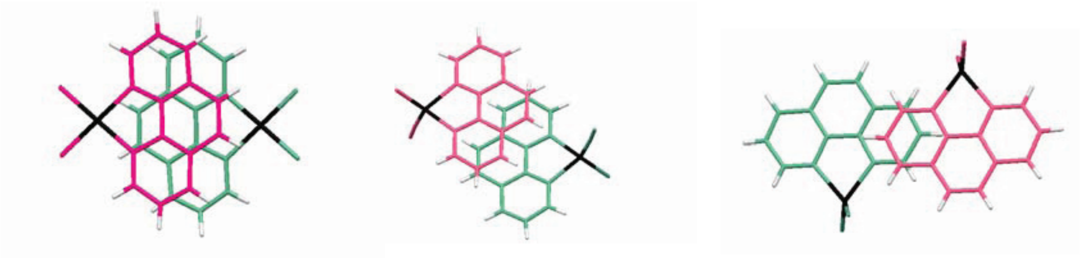
Studies of noncovalent interactions, including π systems, in many areas of chemistry, biochemistry and molecular biology indicate importance of these interactions. Ligands with aromatic rings coordinated to a metal can be involved in stacking interactions. 1,10-phenanthroline molecule consists of three organic aromatic rings, and by coordination to a metal forms the chelate ring that also can be involved in stacking interactions.

Crystal structures of all metal complexes with coordination number four (square-planar and tetrahedral complexes), containing 1,10-phenanthroline ligand, were found in Cambridge Structural Database (CSD). Geometrical criteria were used to study intermolecular interaction in crystal structures. In most of the crystal structures of square-planar complexes 1,10-phenanthroline ligands are completely overlapped, while in most of the crystal structures of tetrahedral complexes there is a partial overlapping of 1,10-phenanthroline ligands (Figure).



ПРОУЧАВАЊЕ "СТЕКИНГ" ИНТЕРАКЦИЈА У КРИСТАЛНИМ СТРУКТУРАМА КВАДРАТНО-ПЛАНАРНИХ И ТЕТРАЕДАРСКИХ КОМПЛЕКСА МЕТАЛА СА ФЕНАНТРОЛИНСКИМ ЛИГАНДИМА

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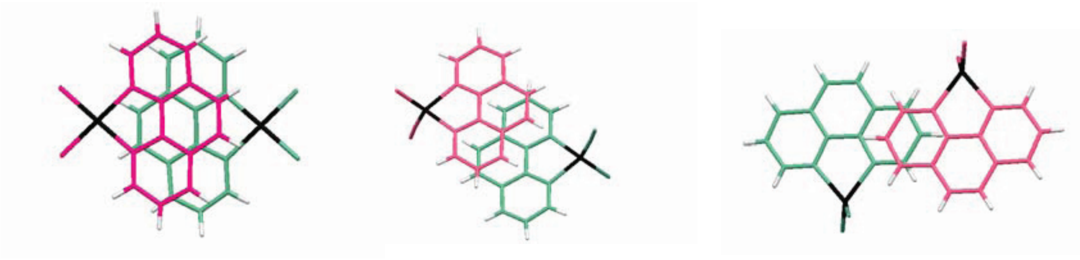
Проучавање нековалентних интеракција, укључујучи и π системе, у многим областима хемије, биохемије и молекуларне биологије показује значај ових интеракција. Лиганди са ароматичним прстеновима координованим за метал могу учествовати у "стекинг" интеракцијама. 1,10-фенантролин садржи три органска ароматична прстена, а његовим координовањем за метал формира се хелатни прстен који такође учествује у "стекинг" интеракцијама.

У Кембричкој банци података (CSD) пронађене су кристалне структуре свих комплекса метала са координационим бројем четири (квадратно-планарни и тетраедарски), који садрже 1,10-фенантролин. За проучавање интеракција у кристалним структурама коришћени су геометријски параметри. У већини структура квадратно-планарних комлекса, 1,10-фенантролински лиганди се преклапају у потпуности, док се код тетраедарских комлекса фенантролински лиганди преклапају само једним делом (Слика).



STRUCTURAL INVESTIGATION OF SOME Ag AND Au - BASED LEAD-FREE SOLDER ALLOYS

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Lead-free solder alloys, which supstituted classic lead-based solders from July 2006 due to the ecological reasons, present the subject of wide interest of experts in materials science recently. Silver and gold-based alloys are specially interesting for the application in electronics, and therefore the results of structural investigations of some lead-free solder alloys in Ag-In-Sb, Ag-In-Sn, Au-In-Sb and Au-Bi-Sb systems are presented in this paper. Mentioned alloys were experimentally analyzed using DTA, DSC, XRD, SEM-EDX and LOM, and phase equilibria in these systems have been determined based on the obtained results.

STRUKTURNA ISPITIVANJA NEKIH BEZOLOVNIH LEMNIH LEGURA NA BAZI SREBRA I ZLATA

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Bezolovne lemne legure koje su iz ekoloških razloga od jula 2006. godine zamenile klasične lemove na bazi olova, predstavljaju predmet širokog interesovanja stručnjaka u oblasti materijala poslednjih godina. Za primenu u elektronici, posebno su interesantne legure na bazi srebra i zlata, te su iz tog razloga u ovom radu predstavljeni rezultati strukturnih ispitivanja nekih bezolovnih lemnih legura ovog tipa u sistemima Ag-In-Sb, Ag-In-Sn, Au-In-Sb i Au-Bi-Sb. Navedene legure su eksperimentalno analizirane korišćenjem metoda DTA, DSC, XRD, SEM-EDX i LOM i na osnovu dobijenih rezultata određene su fazne ravnoteže u datim sistemima.

PHYSICO-CHEMICAL CHANGES IN COPPER CONCENTRATE PROCESSING WITH HIGHER AS CONTENT

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Copper concentrates contain numerous sulphide minerals, about 80-92% of the total concentrate mass. The most importants among them are: Cu_2S, CuS, $CuFeS_2$, FeS_2, FeS, then NiS, ZnS, PbS, as well as Cu_3AsS_4, As_2S_3, Sb_2S_3 in certain quantities, and rare and noble metals.

In our copper concentrates As content varies between 0,01-0,5%. In the pyrometallurgical process of copper concentrate processing, As behaves differently, depending on applied technological process. During roasting process, great part of As content (even more then 50%) goes to the gaseous phase, and the rest goes to the melting with the roasted material. Therefore, during processing of the copper concentrate with higher As content, it is necessary to remove As from copper concentrate during roasting.

The results of experimental investigation of roasting process of copper concentrate with higher As content are presented in this paper. The chemism of the process has been determined based on the data of XRD, ICP-OES, EDXRF and SEM analysis, as well as previous thermodynamic and kinetic analysis.

[1] P. Balaž, M. Achmovičova, Z. Bastl, T. Ohtani, M. Sanches, , Influence of mechanical activation on the alkaline leaching of enargite concentrate, Hydrometallurgy, 54 (2000), 205-216.

[2] J. Vinals, A. Roca, M.C. Hernandez, O. Benevente, Topochemical transformation of copper oxide by hypochlorite leaching. Hydrometallurgy 68 (2003), 183-193.

[3] V.I. Smirnov, A.I. Tihonov, Roasting of copper ores and concentrates (In Russian), Metallurgy, Moscow, 1966.

FIZIČKO-HEMIJSKE PROMENE KOD PRERADE KONCENTRATA BAKRA SA POVIŠENIM SADRŽAJEM ARSENA

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Koncentrati bakra se sastoje od većeg broja sulfidnih minerala, koji čine 80-92% od mase koncentrata. Najvažniji od njih su: Cu_2S, CuS, $CuFeS_2$, FeS_2, FeS, zatim NiS, ZnS, PbS i u određenim količinama Cu_3AsS_4, As_2S_3, Sb_2S_3, kao i retki i plemeniti metali.

U domaćim koncentratima bakra sadržaj arsena varira od 0,01-0,5%. U procesu pirometalurške prerade koncentrata bakra, arsen se različito ponaša, što pre svega zavisi od primenjenog tehnološkog procesa. U procesu prženja veliki deo arsena (često i više od 50%) prelazi u gasnu fazu, a ostatak prelazi u prženac i odlazi na topljenje. Iz tih razloga, pri preradi koncentrata sa visokim sadržajem arsena neophodno je da se pre topljenja, izvrši detaljno uklanjanje arsena iz koncentrata u procesu prženja.

U radu su prikazani rezultati eksperimentalnih ispitivanja procesa prženja koncentrata bakra sa povišenim sadržajem arsena. Eksperimentima, XRD, ICP–OES, EDXRF i SEM, potvrdjen je hemizam ispitivanog procesa koji je odredjen prethodnom termodinamičkom i kinetičkom analizom.

[1] P. Balaž, M. Achmovičova, Z. Bastl, T. Ohtani, M. Sanches, , Influence of mechanical activation on the alkaline leaching of enargite concentrate, Hydrometallurgy, 54 (2000), 205-216.

[2] J. Vinals, A. Roca, M.C. Hernandez, O. Benevente, Topochemical transformation of copper oxide by hypochlorite leaching. Hydrometallurgy 68 (2003), 183-193.

[3] V.I. Smirnov, A.I. Tihonov, Roasting of copper ores and concentrates (In Russian), Metallurgy, Moscow, 1966.

MEASURES OF MINERALS STECHIOMETRIC COMPOSITION ACCORDANCE DETERMINED BY RDA AND CHEMICAL ANALYSIS

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Roasting process of sulphide copper concentrates in fluo-solid reactor is an oxidation process and presents the first stage in a chain of copper concentrate treatment in Bor, so the importance of accurate and quality process control is understandable precondition for correct treatment in the following stages, and at least also for quality cathode copper. Pyrite and a part of chalcopyrite from charge dissociate during the roasting process to more stable copper and iron sulphides: bornite, pyrrhotite and magnetite, while a part of chalcopyrite stays unchanged. RDA and chemical analysis are usually used for the reliable monitoring of the process, so the measures of minerals stechiometric composition accordance determined by RDA and chemical analysis using statistical method “variance analysis” are presented in this paper.

[1] M. Cocić, Quantitative determination of transformation products in the copper concentrate roasting process in fluo-solid reactor, Ms. Thesis, Bor 2004, pp. 34-45.
[2] M.M.Ćirković, “The study of roasting process sulphide concentrate in a reactor with fluidized layer by air enriched on oxygen”, Ms. Thesis, Bor, 1998, pp. 3-88.
[3] Janjić S., Crystallographic and Mineralogical Investigation of Copper Sulphides Minerals and Products of Pirometallurgic Processing in Bor Copper Smelter, Doctoral thesis, Belgrade, 1978, pp. 101-110.

MERE SAGLASNOSTI STEHIOMETRIJSKOG SASTAVA MINERALA ODREĐENIH RENDGENSKOM DIFRAKCIONOM I HEMIJSKOM ANALIZOM

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Proces prženja sulfidnih koncetrata bakra u reaktoru sa fluidizacionim slojem je oksidacioni proces i predstavlja prvu fazu u lancu prerade koncetrata bakra u Boru, te je i razumljiv značaj pravilnog i kvalitetnog vođenja procesa kao preduslov za korektnu preradu u fazama koje slede, a u krajnjem i za kvalitetan katodni bakar. U procesu prženja prisutni pirit i deo halkopirita disusosuju i prelaze u stabilnije sulfide bakra i gvožđa: bornit, pirotin i magnetit, a deo halkopirita ostaje nepromenjen. Za pouzdano praćenje ovog procesa najčešće se koriste rendgensko-difrakciona i hemijska analiza, te su u ovom radu predstavljene mere saglasnosti stehiometrijskog sastava minerala određenih rendgenskom difrakcionom i hemijskom analizom primenom statističke metode "analiza varijanse".

[1] M. Cocić, Mineralne transformacije pri prženju koncentrata bakra u fluo-solid reaktoru, Magistarska teza, Bor, 2004, 34-45.
[2] M.M. Ćirković, Teorijska i eksperimentalna proučavanja procesa prženja sulfidnih bakarnih koncetrata u reaktoru sa fluidizacionim slojem primenom vazduha obogaćenog kiseonikom, Magistarska teza Bor, (1999)3-88.
[3] S. Janjić, Kristalografska i mineralo{ka proušavanja sulfidnih minerala rudnika bakra u Boru i produkata pirometalur{ke prerade bakra borske topionice, Beograd, (1978),101-110.

STRUCTURE AND SIZE-STRAIN MICROSTRUCTURE ANALYSIS OF PARTIAL EXCHANGE HEXACELSIAN AND ITS FELDSPAR PHASE

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The hexacelsian ($BaAl_2Si_2O_8$), prepared from Ba_{LTA} zeolite in the process of thermally induced transformation, has been partially exchange with Ca^{2+} cation. The partial Ca^{2+} for Ba^{2+}cation substitution process has been performed in the 0.21M solution of $CaCl_2$ in autoclave and constant temperature of 180°C/7 days. The partially ion exchanged hexagonal diphyllosilicate has a composition of $(Ba_{0.6},Ca_{0.4})Al_2Si_2O_8$. During prolonged heating it transformed to Ba,Ca celsian feldspar. Crystal structure of these two compounds and the X-ray line-broadenings was analyzed by using the FULLPROF software. The background intensity of each pattern was refined using linear interpolation between selected points. Initially, the position of the peaks was corrected by successive refinements of zero-shift. The obtained profiles were fitted by the TCH-pV (Thompson Cox Hastings–pseudo Voight) function. Hexagonal unit-cell parameters of hexacelsian yielded the best refinement agreement factors (R_w=13.0, R_p=9.73, R_B=5.54, R_F=4.93) and for monoclinic celsian unit-cell parameters factors was (R_w=12.1, R_p=9.15, R_B=3.20, R_F=3.95). From the X-ray line broadening analysis, the apparent crystallite sizes and strains were calculated for the all reflections. Both β_{size} and β_{strain} is obtained from the size parameters contributing to the FWHM parameters.

СТРУКТУРНИ И МИКРОСТРУКТУРНИ ПАРАМЕТРИ ДЕЛИМИЧНО ИЗМЕЊЕНОГ ХЕКСАЦЕЛЗИЈАНА И ЦЕЛЗИЈАНА

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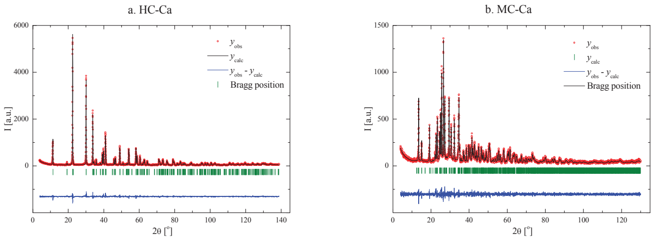
Хексацелзијан добијен методом индукованог термиичког третмана $\mathrm{Ba}_{\mathrm{LTA}}$ зеолита, измењиван је Ca^{2+} јонима, у 0,21M раствору CaCl_2 у аутоклавима при константној температри од 170°C/7дана. Кристалохемијска формула делимично измењеног хексацелзијан је $(\mathrm{Ba}_{0.6},\mathrm{Ca}_{0.4})\mathrm{Al}_2\mathrm{Si}_2\mathrm{O}_8$. У продуженом термичком третману добијена је фаза Ba,Ca-фелдспата. Кристална структура ове две фазе, као и анализа ширина дифракционих максимума, испитивана је помоћу кристалографског програма FULLPROF. Посматрани профили утачњавани су помоћу функције TCH-pV (Thompson Cox Hastings–pseudo Voight). Квалитет утачњавања фаза даје следеће вредности за конвенционалне факторе; хексацелзијан (R_w=13,0; R_p=9,73; R_B=5,54; R_F=4,93) и целзијан (R_w=12,1; R_p=9,15; R_B=3,20; R_F=3,95). Из посматраних профила, односно вредности FWHM, одређивани су микроструктурни параметри β_{size} и β_{strain}. Слике утачњених фаза представљене су на слици 1а и 1б.



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Слика 1. Утачњени рендгенски дијаграми посматраних фаза:(а)хексацелзијан (б) целзијан

SYNTHESIS AND HIGH-TEMPERATURE CHARACTERIZATION OF CERIA NANOPOWDERS

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Nanometric size ceria powder particles with fluorite-type structure were obtained by applying self-propagating room temperature methods. Powder properties such as specific surface area, crystallite and particle size and lattice parameters have been studied. High temperature behaviour was studied using a Theta-Theta diffractometer "X-Pert MPD" from PANALYTICAL with a heating chamber "HTK-1200" from ANTON PAAR. The instrument is built in Bragg-Brentano geometry, the Anode was Co under 40 kV and 40 mA. Prim. Soller-slit: 0,04 rad. Divergence-slit: 0,5°, Antiscatter-slit: 1°, Sek. Soller-slit: 0,04 rad, Recieving-slit: 0,4mm in hight. Secundary monochromator: Graphite, Detector: Gas filled proportional counter. For the measurements from RT up to 600 °C we used a step width of 0.08° in 2 θ and a time per step of 90 s, for 800° and the final RT-measurement we switched to 0.04° in 2 θ and 45 s/step. After the heating with a temperature slope of 20°C/min we held the sample for 20 min at the desired temperature and then started measurements. Regular interval was 200° C, in static air. Particle size is determined using the Scherrer equation $d = 0.9\lambda/B \cos \theta_B$, where λ is the wavelength, B is the FWHM of the Bragg peak corrected using the corresponding peak in micron-sized powder, and θ_B is the Brgg angle. It was found that the peaks are broad, suggesting presence of small crystalline size. However, these peaks gradually sharpen with increasing heat temperature, indicating an increasing of crystalline size. For all heated samples small shifts of XRD peaks position toward lower angle side were observed. This behaviour can be explained by a thermal expansion property of lattice parameters with elevating temperature. Fig 1. shows an evolution of the (hkl) peak of the ceria.

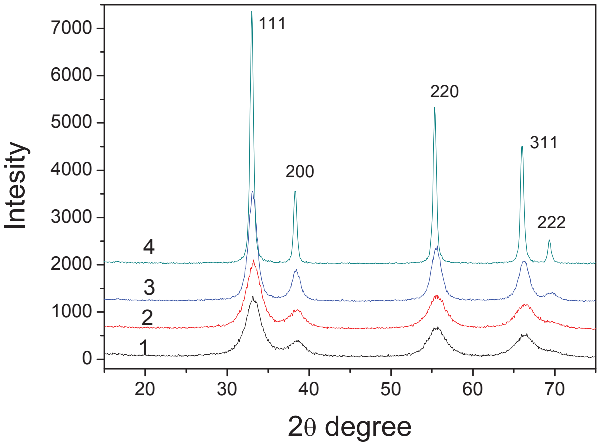

Fig. 1. High-temperature XRD measurement of ceria (1: 25°C, 2: 200°C, 3: 400°C, 4: 600°C).

СИНТЕЗА И ВИСОКОТЕМПЕРАТУРНА КАРАКТЕРИЗАЦИЈА НАНОЧЕСТИЧНЕ ЦЕРИЈЕ

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Реакцијом самопропагирајуће синтезе добијен је наночестични прах церије: Његове особине као величина кристалита, параметар решетке, специфична површина су проучаване у фукцији температуре. Такође је високотемпературном комором испитивано понашање прахова до 800 степени са кораком од 2000 степени. утврђено је да кристалити раст са температуром док се се њихов специфична површина драстично опада.

STRUCTURAL PROPERTIES OF $Ba_{1-x}Sr_xTiO_3$ POWDER PREPARED BY SPRAY PYROLYSIS

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Barium titanate ($BaTiO_3$) and its related compounds have been used in the preparation of high dielectric capacitors, PTC resistors, ferroelectric memories, etc. Solid solution, ternary $Ba_{1-x}Sr_xTiO_3$, is ferroelectric, with tetragonal structure at room temperature for $x < 0.3$. Curie temperature could be easily adjusted by changing of $SrTiO_3$ content in solid solution. The traditional method of preparation of barium strontium titanate (BST) by solid state reaction, from $BaCO_3$ or BaO, SrO, and TiO_2, is not suitable for preparation of ceramics for high performance application because the material shows large particle size, nonhomogeneity and presence of impurities.

In our work spray pyrolysis has been applied for the production of the BST powders. It is very difficult to prepare stoichiometric compounds of titanium because titanium salts are mainly unstable; for example $TiCl_4$, that is unstable at room temperature and could be already decomposed in atomizer before atomization, or Ti-isopropoxide, that hydrolyzes in air atmosphere. For that reason we prepared Ti-citrate as the precursor for the Ti ions. Other precursors were strontium acetate and barium acetate. The processing parameters, such as flux of aerosol and temperature profile inside the furnace, were optimized to obtain single phase BST. The powders were characterized by the methods of X-ray diffraction analysis, SEM, EDS and HRTEM.

The obtained powders were submicronic, consisting of spherical, polycrystalline particles, with internal nanocrystalline structure. Crystallite size of 10 nm, calculated using Rietveld refinement, is in a good agreement with results of HRTEM. Based on all results it is possible to conclude that the obtained powder is consisted of polycrystalline particles, with hollow structure, and with significant amount of amorphous phase. This is a consequence of high heating rate, which was inevitable to suppress formation of carbonates. According to XRD analysis with internal standard the obtained powder contains $Ba_{0.8}Sr_{0.2}TiO_3$ phase (space group *P*4*mm*) and small quantity (~1.5 wt. %) of $BaCO_3$ (space group *Pmcn*). Also, it contains approximately 42 wt. % of amorphous phase. Final values of lattice parameters, volume and density of BST powder, calculated by Rietveld refinement were the following: $a = b = 3.9897(3)$ Å, $c = 4.0282(7)$ Å, $\alpha = 90^o$; $V = 64.12(1)$ $Å^3$; $d = 5.783$ g/cm^3. Crystallites size of BST were $<t>_{//axis-c} = 9.8$ nm and $<t>_{\perp axis-c} = 10.8$ nm. EDS analysis was performed at different points of the TEM figure to compare dark and bright parts at figure, parts with and without crystal planes, as well as particle boundaries. The spectra were almost identical at all observed points. This means that both, crystalline and amorphous parts, contain the same, single phase BST.

STRUKTURNA SVOJSTVA PRAHA $Ba_{0,7}Sr_{0,3}TiO_3$ DOBIJENOG ULTRAZVUČNIM RASPRŠIVANJEM

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Materijali na bazi $BaTiO_3$ se koriste za proizvodnju dielektričnih kondenzatora visoke kapacitivnosti, PTC rezistora, feroelektričnih memorija, i drugih elektronskih komponenti. Čvrsti rastvor $Ba_{1-x}Sr_xTiO_3$ (za $x < 0,3$) je na sobnoj temperaturi feroelektrik tetragonalne strukture. Promenom udela $SrTiO_3$ u čvrstom rastvoru lako se podešava vrednost Kiri temperature materijala. Tradicionalna metoda sinteze $Ba_{1-x}Sr_xTiO_3$ (BST) reakcijom u čvrstoj fazi polazeći od smeše $BaCO_3$ ili BaO, SrO i TiO_2, nije pogodna za dobijanje visokokvalitetne keramike zbog prisustva aglomerata, nehomogenosti, nečistoća i drugih defekata.

U našem radu metoda ultrazvučnog raspršivanja je primenjena kao moguće rešenje za dobijanje kvalitetnih prahova BST-a. Treba napomenuti da u sintezi BST-a iz rastvora postoji ozbiljan problem izbora odgovarajućeg prekursora titana i da je vrlo teško pripremiti stehiometrijska jedinjenja titana zbog nestabilnosti njegovih soli. Na primer, $TiCl_4$ je nestabilan na sobnoj temperaturi i moglo bi da dodje do njegovog raspadanja i pre atomizacije, a Ti-izopropoksid hidrolizuje na vazduhu. Zbog toga je pripremljen rastvor Ti-citrata, a kao drugi prekursori korišćeni su acetati stroncijuma i barijuma. Parametri procesiranja, kao što su protok aerosola i temperaturni profil peći, optimizirani su tako da se dobije jednofazni BST. Prahovi su karakterisani sledećim metodama: rendgenska difrakcciona analiza, SEM, EDS i HRTEM.

Pod optimalnim uslovima sinteze dobijeni su submikronski prahovi koji su se sastojali od sfernih polikristalnih čestica. Veličina kristalita izračunata Rietveld-ovom metodom iznosila je 10 nm i u saglasnosti je sa razultatima dobijenim metodom HRTEM. Na osnovu svih izvršenih analiza može se zaključiti da su dobijene polikristalne čestice šuplje i da sadrže visok procenat amorfne faze. To je posledica velike brzine zagrevanja, koja je s druge strane bila neophodna da bi se izbeglo formiranje karbonata. Prema rezultatima XRD analize sa unutrašnjim standardom dobijeni prah sadrži BST fazu (prostorna grupa *P*4*mm*) i malu količinu (~1.5 wt. %) $BaCO_3$ (prostorna grupa *Pmcn*). Takođe, prah sadrži približno 42 wt. % amorfne faze. Vrednosti parametara rešetke, zapremine i gustine, izračunate Rietveld-ovom metodom bile su sledeće: $a = b = 3,9897(3)$ Å, $c = 4,0282(7)$ Å, $\alpha = 90^o$; $V = 64,12(1)$ Å^3; $d = 5,783$ g/cm^3. Veličina kristalita bila je $<t>_{//axis\text{-}c} = 9,8$ nm i $<t>_{\perp axis\text{-}c} = 10,8$ nm. EDS analiza je urađena u različitim tačkama na TEM mikrografiji, da bi se uporedio sastav svetlih i tamnih delova na slici, delova sa i bez uočljivih kristalnih ravni, kao i na granicama zrna. Spektar je bio skoro identičan u svim posmatranim tačkama. To znači da su kristalna i amorfna faza istog hemijskog sastava, odnosno da sadrže jednofazni BST.

X-RAY LINE BROADENING ANALYSIS IN NANOSIZE SAMPLES USING FULLPROF PROGRAM

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Microstructure parameters, crystallite size and microstrain, in nanosize oxides, were obtained from X-ray powder diffraction data with the Fullprof program. Nanoparticle Yb_2O_3 and Y_2O_3/Gd_2O_3 were synthesised by thermal decomposition of acetylacetonato complexes. X-ray powder diffraction data were collected on a Stoe STADI MP diffractometer (CuKα1), Ge monochromator and PSD detector. Sample Y_2O_3/Gd_2O_3 was annealed on different temperatures and XRPD were collected on PANalytical Xpert PRO MD diffractometer.

X-ray line broadening analysis was used to obtain information on XRPD line broadening due to crystallite size and strain effects. The X-ray line broadening was analyzed through the refinement of regular TCH-pV function parameters (isotropic effects) and the refinement of multipolar functions, i.e. symmetrised cubic harmonics (anisotropic effects) [1, 2]. An average apparent size and average maximum strains of Yb_2O_3 were found to be 13(2) nm and $5.7(1)\cdot 10^{-4}$. Microstructure analysis of XRPD for Yb_2O_3 sample was also performed with MarqX computer program.

Cation distribution for all Y_2O_3/Gd_2O_3 samples was found to be metastable. Crystallite size decreases while microstrain increases with the annealing temperature increase for Y_2O_3/Gd_2O_3. The particle size and morphology of Y_2O_3/Gd_2O_3 were characterized by transmission electron microscopy (HRTEM). The mean particle size is approximately same as crystallite size, (5 nm), indicating that the most grains are composed of one crystallite.

[1] Honkimäki V.; Surotti P. *Effects of instrument function, crystallite size and strain on reflection profiles* in: Snyder R. L.; Fiala J.; Bunge H. J. (Eds) *Defect and Microstructure Analysis by Diffraction*; IUCR book series; Oxford Univer. Press Inc.: New York, 1999.
[2] Stephens P. W. *J. Appl. Crystallog.*. 1999, 32,281.

ANALIZA ŠIRENJA DIFRAKCIONIH MAKSIMUMA KOD NANOČESTIČNIH UZORAKA KORIŠĆENJEM FULLPROF PROGRAMA

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Mikrostrukurni parametri, veličina kristalita i mikronaprezanja, kod nanočestičnih oksida određeni su koristeći podatke difrakcije x-zraka i Fullprof program. Nanočestični Yb_2O_3 i Y_2O_3/Gd_2O_3 sintetisani su termičkom dekompozicijom acetilacetonato kompleksa. Difrakcioni podaci za Yb_2O_3 dobijeni su koristeći Stoe STADI MP difraktometar (CuKα1), Ge monohromator i PSD brojač. Uzorak Y_2O_3/Gd_2O_3 je odgrejan na različitim temperaturama i sniman na difraktometru PANalytical Xpert PRO MD.

Analiza širenja difrakcionih linija rađena je u cilju dobijanja podataka o veličini kristalita i mikronaprezanju. Širenje difrakcionih linija analizirano je utačnjavanjem parametara TCH-pV profilne funkcije (izotropan efekat) kao i utačnjavanjem multipolarnih funkcija (anizotropni efekat) [1, 2]. Na ovaj način dobijena, srednja vidljiva veličina kristalita i srednje maksimalno naprezanje za Yb_2O_3 iznose 13(2) nm i $5.7(1)\cdot 10^{-4}$. Mikrostruckurna analaliza difrakcionih podataka za Yb_2O_3 uzorak je urađena i pomoću programa MarqX.

Raspodela katjona u mešovitom oksidu Y_2O_3/Gd_2O_3 je metastabilna i ostaje takva nakon odgrevanja uzorka. Veličina kristalita Y_2O_3/Gd_2O_3 opada a mikronaprezanje raste sa odgrevanjem. Veličina kao i morfologija česica Y_2O_3/Gd_2O_3 određena je pomoću transmisionog elektronskog mikroskopa (HRTEM). Srednja veličina čestica je oko 5 nm kao i vrednosti kristalita, što ukazuje da je najveći broj zrna monokristalitan.

[1] Honkimäki V.; Surotti P. *Effects of instrument function, crystallite size and strain on reflection profiles* in: Snyder R. L.; Fiala J.; Bunge H. J. (Eds) *Defect and Microstructure Analysis by Diffraction*; IUCR book series; Oxford Univer. Press Inc.: New York, 1999.
[2] Stephens P. W. *J. Appl. Crystallog.*. 1999, 32,281.

THE DETERMINING OF THE AVERAGE CRYSTALLITE SIZE OF NANOCRYSTALLINE ZINC FERRITE DOPED WITH INDIUM

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Following the method of Chantrell et al [1] , for the weakly-interacting systems (the method, firstly, has been applied to ferofluids), the average crystallite size of the powdered samples of $In_xZn_{1-x}Fe_2O_4$, $x \leq 0.3$, were determined from the hysteresis curve at room temperature. Also, using the Scherrer formula relating the crystallite size to the FWHM, the average crystallite size were determined from the obtained diffraction profiles.

The investigated powders were scanned by difractometer described in [2]. Hysteresis loops were measured at 300 K after zero-field-cooling using an SQUID magnetometer with accuracy of 10^{-7} emu. The measurements were made from -60 up to 60 kOe, and vice versa.

The obtained values of the crystallite size by using the equation:

$$D_V = \left[\frac{18 \cdot kT}{\pi M_{SB}} \cdot \sqrt{\frac{\chi_i}{3 \cdot M_S} \cdot \frac{1}{H_0}} \right]^{\frac{1}{3}}$$

where: M_{SB} the value of saturation magnetisation of the balk sample at ambient temperature [3], χ_i initial susceptibility, M_S saturation magnetisation of the sample, $1/H_0$ the value obtained by intersection of the curve $M(1/H)$ on $M=0$ and the values of the crystallite size obtained by the analyzing diffraction date are given in *Table 1.*

Sastav	D_V [nm]	D_V [nm]
$ZnFe_2O_4$	2.17	2.10 (*Scherr.eq.*)
$In_{0.15}Zn_{0.85}Fe_2O_4$	3.60	3.00 (*Scherr.eq.*)
$In_{0.2}Zn_{0.8}Fe_2O_4$	3.86	2.40 (*Scherr.eq.*)
$In_{0.3}Zn_{0.7}Fe_2O_4$	2.86	2.00 (*Scherr.eq.*)

Table 1.

The observed values of the crystallite size are in the good agreement and indicate that in the investigated samples the interparticle intaraction can be ignored.

[1] R.W. Chanttrell, J. Popplewell, S. W. Charles, IEEE trans. Magn. MAG-14, 975 (1978)
[2] Ž. Cvejić, S. Rakić, S. Jankov, S. Skuban, A. Kapor, V. Srdić, XIV Conf. of the Serbian Crystallographic Society, Book of Abstracts, p.48 (2007)
[3] E. P. Wohlfarth (Ed.) Handbook of Ferromagnetic Materials Vol. 2, p.285 1982 (1962)

ODREĐIVANJE VELIČINE KRISTALITA NANOKRISTALNOG CINK FERITA DOPIRANOG INDIJUMOM

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Koristeći metod razvijen od strane Šantrela i drugih [1], za slabointeragujuće sisteme (prvobitno razvijen za ferofluide), iz histerezisne petlje na sobnoj temperaturi, izračunata je usrednjena veličina kristalita za praškaste uzorke sastava $In_xZn_{1-x}Fe_2O_4$, $x \leq 0.3$. Usrednjena veličina kristalita ispitivanih uzoraka izračunata je i iz širine difrakcionih linija korišćenjem Šererove jednačine.

Ispitivani prahovi su snimani pomoću difraktometra opisanog u [2]. Merenje magnetne susceptibilnosti izvršeno je na SQUID magnetometru čija je preciznost merenja 10^{-7} emu.

Izračunate vrednosti veličine kristalita korišćenjem jednačine:

$$D_V = \left[\frac{18 \cdot kT}{\pi M_{SB}} \cdot \sqrt{\frac{\chi_i}{3 \cdot M_S} \cdot \frac{1}{H_0}} \right]^{\frac{1}{3}}$$

gde su: M_{SB} vrednost saturacione magnetizacije balk uzorka na sobnoj temperaturi [3], χ_i vrednost početne susceptibilnosti, M_S vrednost saturacione magnetizacije uzorka, $1/H_0$ vrednost dobijena presekom krive $M(1/H)$ pri vrednosti $M=0$ i veličine kristalite dobijene analizom podataka iz difrakcije X-zraka date su u *Tabeli 1.*

Sastav	D_V [nm]	D_V [nm]
$ZnFe_2O_4$	2.17	2.10 (*Šerer.jedn.*)
$In_{0.15}Zn_{0.85}Fe_2O_4$	3.60	3.00 (*Šerer.jedn.*)
$In_{0.2}Zn_{0.8}Fe_2O_4$	3.86	2.40 (*Šerer.jedn.*)
$In_{0.3}Zn_{0.7}Fe_2O_4$	2.86	2.00 (*Šerer.jedn.*)

Tabela 1.

Uočeno dobro slaganje izračunatih veličina kristalita, implicira da se međučestična interakcija može zanemariti kod ispitivanih uzoraka.

[1] R.W. Chanttrell, J. Popplewell, S. W. Charles, IEEE trans. Magn. MAG-14, 975 (1978)
[2] Ž. Cvejić, S. Rakić, S. Jankov, S. Skuban, A. Kapor, V. Srdić, XIV Conf. of the Serbian Crystallographic Society, Book of Abstracts, p.48 (2007)
[3] E. P. Wohlfarth (Ed.) Handbook of Ferromagnetic Materials Vol. 2, p.285 1982 (1962)