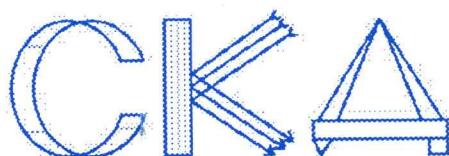


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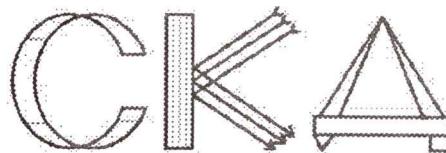


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PLENARY LECTURES
PLENARNA PREDAVANJA

COMPARATIVE STUDY OF STRUCTURAL CHARACTERISTICS IN TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS

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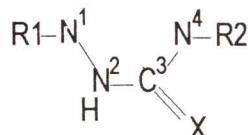
Introduction

Transition metal complexes with thiosemicarbazide-based ligands (TSC) have been studied for a long time because of their interesting structural properties, analytical applications and biological activities [1-7]. In Scheme 1, the atoms of thiosemicarbazide fragment are labeled in superscript which is in accordance with IUPAC rules. Thiosemicarbazide-based compounds belong to a more common class of molecules, which can be named by adding suffix "semicarbazone" (Scheme 1).

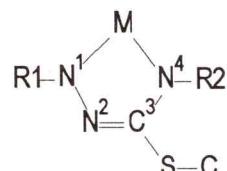
The most often, atom X is oxygen or sulphur but it also may be, for example, selenium [8]. Groups R1 and R2 originate from used carbonyl compound but they (R1 and R2) can also represent hydrogen atoms. This class of compounds (shown in Scheme 1) can be modified by placing substituents on the atom X, and thus S-alkyl derivatives of TSC compounds can be gained. This class of molecules is named isothiosemicarbazide-based compounds (ITSC).

ITSC-based compounds, especially metal complexes with this type of ligands, were thoroughly investigated by Leovac, Gerbeleu and coworkers [9]. Common coordination mode of ITSC-based ligands is shown in Scheme 2. Transition metal complexes with ITSC-based ligands show interesting molecular geometry [10-12], rare type of intermolecular interaction [13] and unusual coordination behavior [14]. In some of the cases, this molecules show possibility to grow 3D supramolecular structure [15]. The ligands of this type (S-substituted thiosemicarbazide-based ligands) can act as biologically active agents with antibacterial activity [16,17].

The objective of this talk is to present results of comparative analysis of some structural characteristics, which have not been systematically analyzed until now. Although some elements of structural behavior have been noted in the published papers, they have not been compared with all compounds from the same class (TSC or ITSC). And, what is more important, the reasons for observed characteristics have not been named or explained. Additionally, some interactions (mutual influences) between selected structural features (like dependence of *cis/trans* position of S-R group on the N² protonation) will be presented in this talk for the first time. Comparative study



Scheme 1

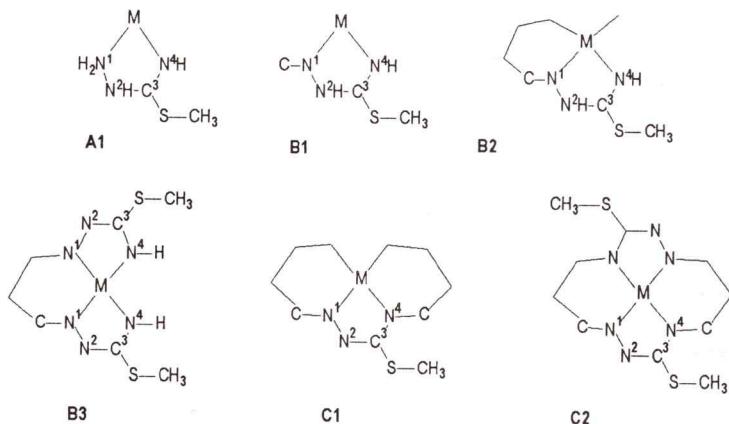


Scheme 2

is based on all X-ray crystal structures possessing TSC fragment, which were retrieved from Cambridge Structural Database (CSD) [18]. 1122 compounds possessing N-N-C(S)-N structural motif were extracted (664 of which being metal complexes).

1. Analysis of electron π delocalisation in ITSC fragment

The major part of comparative study is dedicated to the analysis of electron π delocalisation (EPD) in the ITSC fragment. For that purpose, X-ray crystal data were used for 172 ITSC-based compounds with 261 ITSC fragments. Crystal structures were classified in six groups so that all structures from one group possess the same structural motif defined for



Scheme 3

that group (shown in the scheme 3). Regarding that the N¹-N²-C³-N⁴ fragment is structurally very similar in all ITSC-compounds, one can observe that arrangement of electron π density surprisingly vary in rather high degree. For instance, the N²-C³ bond length (although both atoms always have the same adjacent atoms) can take values from 1.28 to 1.42 Å. Range of values for C³-N³ bond is mainly from 1.26 to 1.44 Å.

This interesting structural behaviour was studied through analysis of two structural characteristics of EPD: 1. electron π density arrangement within the N¹-N²-C³-N⁴ fragment and 2. quantity of electron p density in the fragment. Very good agreement of analysed bond distances inside of groups was observed, as well as regular relation of analysed parameters between groups. Also, main influences on both characteristics were detected. 1. Dominant factor acting on electron π density arrangement is protonation of the N² atom. Another important factor which acts on electron π density arrangement in different degree (depending on the group) is the type of the atoms bonded to the N¹ and N⁴ atoms and their ability to take part in the π delocalisation of the π electron density from ITSC fragment. 2. Dominant factor which acts on quantity of electron π density in the fragment is degree of ability of the atoms bonded to the N¹ and N⁴ atoms to receive part of electron p density from ITSC fragment (or to donate part of its own electron π density to the ITSC fragment). Influence of protonation of the N² atom on quantity of electron π density is significantly less but it also exists. All quoted factors have been quantitatively derived for each group with good approximation.

2. Structural behaviour of the sulphur atom

Structural behavior of the S atom could be one of the important factors for bioactivity of ITSC-based compounds (as well as TSC compounds), especially metal complexes with this type of ligand. For that reason different structural properties for S atom and S-alkyl group in ITSC-based compounds have been studied. It was established that the S atom could take part in weak C-H...S hydrogen bonds. Orientation of S-alkyl group to the rest of isothiosemicarbazide moiety was analyzed and it was identified that S-alkyl takes coplanar position to the rest of ITSC, while some rare exceptions from coplanar position could be explained by intermolecular interactions of S-alkyl. Direct relation (mutual dependence) between *cis/trans* orientation of S-alkyl group (including bond angle geometry) and protonation of the N² atom was established. Some exceptions are successfully explained with intermolecular interactions and hydrogen bonds.

3. Metal-TSC ligand distances

Metal-TSC ligand distances were analysed separately for metal complexes with TSC-based and ITSC-based ligands (Scheme 3). It was established that, (beside the type of metal atoms), coordination mode and hybridisation state of coordinated atoms are main influences which causes differences in the metal-ligand distances. The results of this analysis are demonstrated on the Ni complexes, which are the most numerous transition metal complexes with TSC- and ITSC-based ligands.

4. Chelate rings conformation

All metal complexes with tridentate ITSC-based ligands possess two fused chelate rings, one of which being six-membered. Metal complexes with tetradeinate ITSC ligands possess three fused chelate rings and two of them are six-membered. It is well known that six-membered rings are flexible and very often exist as non-planar. To analyse ring-planarity, a very simple rule was used: that summation of angles inside of ring is directly related to ring planarity. The use of this simple rule as a criteria for ring-planarity gives parameters which are in excellent agreement to Cromer-Pople parameter Qt (total puckering parameter).

All chelate rings are approximately planar. Some exceptions can be explained by square-pyramidal coordination. In those cases metal atom is somewhat displaced from ring plane due to requirements of coordination geometry. Generally it can be concluded that chelate rings show tendency toward planarity. Explanation for this behaviour is probably in the electron π delocalisation through the chelate rings and inter-relation of π systems from ITSC fragment and six-membered chelate rings if they are presented.

Conclusions

It is reasonable to expect that ITSC (or TSC) fragment takes part in the biological activity of the molecules which possess this structural part. In that case, it is of exceptional importance to recognise main influences which act on structural behaviour and to know how we can modify structural characteristics in thiosemicarbazide fragment. On the basis of the results quoted in this work, it is possible to predict basic characteristics, such as EPD for chosen ITSC-based compound even before it is synthesised. Also, composition of molecule for desired EPD could be predicted (or suggested). With previously established relation

between bioactivity (or some other feature) and EPD, it is possible to perform more selective molecule structure design. Analyses of other structural characteristic, like possible intermolecular interactions and conformational behaviour of S-alkyl group, as well as analysis of chelate ring conformation can also help better understanding of molecular structure of ITSC-based compounds and their structural modification.

This approach to analysis of structural characteristics based on the X-ray crystal data is also applicable to the other class of molecules (first of all SC- and TSC-based compounds) possessing conjugated π bonds and adequate number of known crystal structures.

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KOMPARATIVANA STUDIJA STRUKTURNIH KARAKTERISTIKA KOMPLEKSA PRELAZNIH METALA SA LIGANDIMA NA BAZI TIOSEMIKARBAZIDA

Goran A. Bogdanović

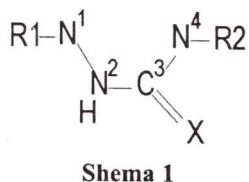
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Uvod

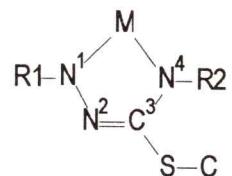
Kompleksi prelaznih metala sa ligandima na bazi tiosemikarbazida (TSC) proučavaju se već dugo vremena zbog njihovih interesantnih strukturnih osobina, primene u analitičke svrhe i biološke aktivnosti [1–7]. Na shemi 1 atomi iz tiosemikarbazidnog fragmenta su obeleženi oznakama u superskriptu koje su u skladu sa IUPAC-ovim pravilima. Jedinjenja na bazi tiosemikarbazida pripadaju opštijoj klasi molekula koji se imenuju dodavanjem sufiksa "semikarbazon" (shema 1). Atom X je najčešće kiseonik ili sumpor ali takođe može biti neki drugi atom kao naprimjer atom selena [8]. Grupe R1 i R2 potiču sa karbonilnih jedinja, ali R1 i R2 takođe mogu predstavljati i atome vodonika. Ova klasa jedinjenja (pričekana na shemi 1) može biti modifikovana postavljanjem supstituenta na atomu X i na takav način se može dobiti S-alkil derivat TSC jedinjenja pri cemu se ova klasa molekula naziva jedinjenjima na bazi izotiosemikarbazida (ITSC).

Jedinjenja na bazi ITSC a posebno kompleksi metala sa ovim tipom liganada intenzivno su pručavana od strane Leovca, Gerbeleua i njihovih saradnika [9]. Uobičajen način koordinacije liganada na bazi ITSC prikazan je na shemi 2. Kompleksi prelaznih metala sa ligandima na bazi ITSC pokazuju interesantnu geometriju molekula [10-12], redak tip intermolekulskih interakcija [13] i neobično koordinaciono ponašanje [14]. U nekim primerima ovi molekuli pokazuju mogućnost gradenja trodimenzionalnih supramolekulskih struktura [15]. Ligandi ovog tipa (S-supstituisani ligandi na bazi tiosemikarbazida) mogu delovati kao biološki aktivni agensi sa antibakterijskim dejstvom [16,17].

Cilj ovog predavanja jeste prezentacija rezultata komparativne analize strukturnih karakteristika koje do sada nisu sistematski proučavani. Naime, mada su u predhodno publikovanim radovima zabeleženi neki od elemenata struktornog ponašanja, oni nikad nisu upoređeni i analizirani za sva jedinjenja iz TSC i (ili) ITSC klase molekula. Dalje, što je još značajnije, uzroci opaženih karakteristika nisu do sada dati ili objašnjeni. Dodatno, neki od međusobnih uticaja između odabranih strukturnih karakteristika nisu do sada razvedeni.



Shema 1

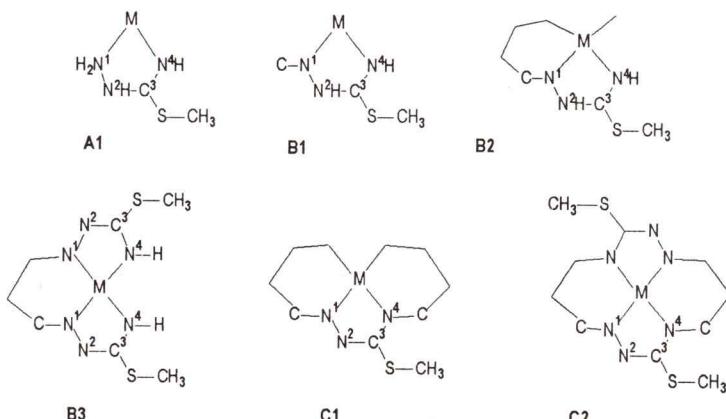


Shema 2

teristika (kao što je zavisnost *cis/trans* položaja S–R grupe od protonovanja N² atoma azota) biće prvi put izloženi na ovom predavanju. Komparativna studija obuhvata sve kristalne strukture koje poseduju TSC fragment a čiji su kristalografski podaci bili dostupni u CSD banci podataka [18]. Ukupno je bilo izdvojeno 1122 jedinjenja (od toga 664 kompleksa) koja poseduju N–N–C(S)–N strukturalni motiv.

1. Analiza delokalizacije π elektrona u ITSC fragmentu

Najveći deo komparativne analize posvećen je analizi delokalizacije π elektrona (EPD) u ITSC fragmentu. U cilju navedene analize korišćeni su kristalografski podaci za



Shema 3

172 jedinjenja na bazi ITSC koja ukupno sadrže 261 ITSC fragment. Kristalne strukture su klasifikovane u šest grupa tako da sve strukture iz jedne grupe sadrže isti strukturalni motiv definisan za tu grupu (grupe su predstavljene na shemi 3). Imajući u vidu da je N¹–N²–C³–N⁴ fragment strukturalno veoma sličan u svim ITSC jedinjenjima, iznenadjuće je da se može opaziti da raspored elektronske gustine varira u fragmentu u značajnoj meri. Na primer, dužina N²–C³ veze (iako oba atoma u svim strukturama imaju istu okolinu) može imati vrednosti u opsegu od 1.28 do 1.42 Å. Opseg vrednosti za C³–N³ vezu je približno od 1.26 do 1.44 Å.

Ovo interesantno strukturalno ponašanje je istraživano analizom dve strukturalne karakteristike EPD: 1. raspodele (rasporeda) π elektronske gustine u N¹–N²–C³–N⁴ fragmentu i 2. količine π elektronske gustine u fragmentu. Utvrđeno je veoma dobro slaganje dužina veza u okviru grupa kao i pravilnost odnosa analiziranih parametara između grupa. Za oba navedena karakteristike utvrđeni su glavni uticaji koji deluju na njih. 1. Dominantni faktor koji utiče na raspodelu π elektronske gustine je protonovanost N² atoma azota. Drugi značajan faktor koji u zavisnosti od grupe deluje u različitom stepenu jeste tip atoma vezanih za N¹ i N⁴ i njihova sposobnost da učestvuju u delokalizaciji π elektronske gustine iz ITSC fragmenta. 2. Dominantni uticaj koji deluje na količinu π elektronske gustine jeste sposobnost atoma vezanih za N¹ i N⁴ atome da prime deo π elektronske gustine iz ITSC fragmenta (ili, u drugom slučaju, da daju deo sopstvene π elektronske gustine ITSC fragmentu). Uticaj protonovanja N² atoma na količinu π elektronske gustine je značajno manji ali takođe postoji. Svi navedeni uticaji su kvantitativno opisani za svaku grupu posebno.

2. Struktурно ponašanje atoma sumpora

Struktурно ponašanje atoma sumpora može biti jedan od značajnijih uticaja na ispoljavanje biološke aktivnosti jedinjenja na bazi ITSC (kao i jedinjenja na bazi TSC), a posebno kompleksa metala sa ligandima ovog tipa. Iz navedenog razloga istražene su različite strukturne osobine atoma sumpora i S-alkil grupe u jedinjenjima na bazi ITSC. Utvrđeno je da atom sumpora može učestvovati u građenju slabih C–H...S vodoničnih veza. Analizirana je orijentacija S-alkil grupe prema ostatku ITSC fragmenta, pri čemu je utvrđeno da S-alkil grupa zauzima koplanaran položaj prema ostatku fragmenta, dok se retki izuzeci od ovog ponašanja mogu objasniti intermolekulskim interakcijama S-alkil grupe. Utvrđena je direktna međuzavisnost između *cis/trans* položaja S-alkil grupe (kao i deformisanosti uglova oko C³ atoma) i protonovanosti N² atoma. Izuzeci koji su nađeni su uspešno objašnjeni preko intermolekulskih interakcija i vodoničnih veza.

3. Metal-TSC ligand rastojanje

Analizirana su metal-TSC ligand rastojanja i to odvojeno za komplekse sa ligandima na bazi TSC i komplekse sa ligandima na bazi ITSC. Utvrđeno je da su pored vrste metala, koordinaciona geometrija i hibridizacija koordinovanih atoma najvažniji uticaji koji prouzrokuju razlike u rastojanjima između atoma metala i liganada. Rezultati ove analize su prezentovani na kompleksima nikla kao najbrojnijim kompleksima sa ligandima na bazi TSC i ITSC.

4. Konformacija helatnih prstenova

Svi kompleksi metala sa tridentatnim ligandima na bazi ITSC sadrže dva spojena helatna prstena od kojih je jedan šestočlani. Kompleksi metala sa tetradentatnim ligandima na bazi ITSC sadrže tri spojena helatna prstena od kojih su dva šestočlana. Poznato je da su šestočlani prstenovi fleksibilni i da često zauzimaju neplanarnu formu. U svrhu analize planarnosti šestočlanih prstenova korišćena je jednostavno pravilo da je zbir uglova u prstenu u direktnoj zavisnosti od planarnosti prstena. Korišćenje navedenog pravila kao kriterijuma planarnosti prstena je u odličnom slaganju sa Kromer–Poplovim parametrom Qt, ali je znatno jednostavnije i lakše za korišćenje.

Izračunato je da su helatni prstenovi približno planarni. Izuzeci od planarnosti koji postoje mogu se objasniti kvadratno-piramidalnom koordinacijom u tim slučajevima. U navedenim slučajevima atom metala je pomeren iz ravni prstena usled zahteva geometrije koordinacije oko metala. Uopšte rečeno može se zaključiti da helatni prstenovi pokazuju tendenciju zauzimanja planarne forme. Objašnjenje za ovakvo ponašanje je verovatno u delokalizaciji π elektrona preko prstenova i međuzavisnosti π sistema iz ITSC fragmenta i šestočlanih helatnih prstenova ako su oni prisutni.

Zaključci

Za očekivati je da ITSC (ili TSC) fragment učestvuje u ispoljavanju biološke aktivnosti molekula koji sadrže ovaj strukturalni deo. U tom slučaju od izvanredne važnosti je prepoznati glavne uticaje koji deluju na strukturalno ponašanje, kao i znati kako možemo modifikovati strukturne karakteristike u TSC fragmentu. Na osnovu rezultata koji su navedeni u ovom radu moguće je predvideti takve fundamentalne karakteristike kao što je EPD za odabranu jedinjenje na bazi ITSC, i to pre nego što ono bude sintetisano. U drugom slučaju moguće je predvideti (ili sugerisati) sastav molekula za željeni EPD. Uz predhodno utvrđen odnos

između stepena bioaktivnosti (ili neke druge osobine) i EPD moguće je primeniti selektivnije i efikasnije modifikacije molekulske strukture a u cilju postizanja željenih osobina. Analiza i drugih strukturalnih karakteristika, kao što su moguće intermolekulske interakcije i konformacija S-alkil grupe, kao i analiza konformacije helatnih prstenova takođe mogu biti od pomoći za bolje razumevanje molekulske strukture jedinjenja na bazi ITSC i njihovih strukturalnih razlika.

Ovakav pristup analizi strukturalnih karakteristika zasnovan na kristalografskim podacima je takođe primenljiv i na druge klase molekula (pre svega jedinjenja na bazi SC i TSC) koja poseduju konjugovane π veze i adekvatan broj poznatih kristalnih struktura.

Zahvalnost

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NEUTRON DIFFRACTION AND ITS APPLICATION TO MATERIALS SCIENCE RESEARCH

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X-ray and neutron diffraction is the basis for information and understanding of materials on the atomic level. X-ray diffraction is and has always been the main source. However for some special problems, neutrons can give important additional information or in some cases even new and unique information. This is especially true for magnetic materials. The lecture will point out the main differences between x-rays and neutrons and give examples of structural studies in materials science research where neutrons have contributed a lot to a better understanding of the structure and of the properties.

**ORAL PRESENTATIONS
SAOPŠTENJA**

ANALYSIS OF THE INTERMOLECULAR CONTACTS IN THE STRUCTURES OF THE 3,5-DIMETHYL-1-THIOPYRAZOLE AND TRIS(3,5- DIMETHYL-1-THIOPYRAZOLE)COBALT(III); COMPARISON WITH THE RESULTS OBTAINED FROM DATABASE STUDY

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Pyrazolyl moiety has been widely used for the complexation of transition metals. This is partly because the size and the rigidity of the ligand, associated with the presence of different substituents make it a promising target, in attempts to use the properties of the ligand and to control the way of association of molecules. This has stimulated research of the characteristics of the intermolecular contacts in both the organic and coordination compounds containing this fragment.

We will present here the main structural characteristics of the 3,5-dimethyl-1-thiocarboxamidepyrazole and the same compound coordinated to Co in the tris-(3,5-dimethyl-1-thiocarboxamidepyrazolato)Cobalt(III). The special attention is given to the analysis of the intermolecular contacts. Packing of organic compound is determined by the presence of strong -S....H and -N....H hydrogen bonds as was expected on the basis of the structure of the isolated molecule. However the mutual position of the pyrazole rings suggest the possibility for the interaction between two rings. This has prompted us to perform the analysis of the intermolecular geometry in the pyrazolyl containing compounds using the data stored in CDB (Cambridge Structure Data Bank). The characteristics of the intermolecular contacts between the pyrazole rings will be analysed. The influence of the coordination of the molecules on their capacities for the intermolecular contacts will be discussed by comparison of the relevant parameters in the structures of 3,5-dimethyl-1-thiocarboxamidepyrazole and tris-(3,5-dimethyl-1-thiocarboxamidepyrazolato)Cobalt(III).

ANALIZA INTERMOLEKULSKIH KONTAKATA U 3,5-DIMETIL-1-TIOKARBOKSAMID PIRAZOLU I TRIS(3,5-DIMETIL-1-TIOKARBOKSAMIDPIRAZOLATO) KOBALTA(III); POREDJENJE SA REZULTATIMA DOBIVENIM ANALIZOM REL-EVANTNIH PARAMETARA U STRUKTURAMA ORGANSKIH MOLEKULA KOJI SADRŽE PIRAZOLNI PRSTEN

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Jedinjenja koja sadrže pirazolni prsten se koriste za kompleksiranje prelaznih metala. Jedan od razloga za to je što kombinacija rigidnosti pirazolnog prstena i prisustva razlicitih substituenata čini ove molekule pogodnim za predviđanje načina njihove intermolekulske interakcije. Ove činjenice su stimulisale istraživanje načina uredjivanja ovih molekula u čvrstom stanju, kako u organskim tako i u koordinacionim jedinjenjima. Izložićemo osnovne karakteristike struktura 3,5-dimetil-1-tiokarboksamid pirazola i tris-(3,5-dimetil-1-tiokarboksamidpirazolato)kobalta(III) sa posebnim osvrtom na način njihove asocijacije u kristalu. Pakovanje molekula je određeno prisustvom jakih -S...H i -N...H vodoničnih veza što se i očekivalo na osnovu strukture slobodnih molekula.

Medjutim, međusobni položaji pirazolnih prstenova sugerisu mogućnost postojanja interakcije između njih. Radi provere koliko je opažena geometrija bitna za razumevanje intermolekulskih interakcija u sličnim strukturama izvršena je analiza odgovarajućih geometrijskih parametara na osnovu podataka koji se nalaze u Banci kristalnih struktura (Cambridge Structure Data Bank). U ovom radu će biti izloženi rezultati koji se odnose na postojanje i učestalost nevezivnih interakcija između pirazolnih prstenova kao i na njihovu prirodu. Uticaj koji koordinacija molekula ima na njegove intermolekulske kontakte analiziran je poređenjem odgovarajućih parametara u strukturama 3,5-dimetil-1-tiokarboksamid pirazola i tris-(3,5-dimetil-1-tiokarboksamidpirazolato)kobalta(III).

CRYSTAL STRUCTURE OF MAGNESIUM SALT OF 12-TUNGSTOPHOSPHORIC ACID, MGHPW₁₂O₄₀ · 10 H₂O

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Magnesium salts of 12-tungstophosphoric acid (MgHWPA-nH₂O) exhibit some specific features in relation to other earth-alkali salts of this acid. Salts of heteropolyacids are classified in two groups, "small-weak" and "big-strong" cations [1]. Mg²⁺ ion radius is very close to Li⁺, and therefore some of its characteristics are similar to the Li-salt, although it belongs to earth-alkaline elements. Therefore, it is interesting to investigate the crystal structure of MgHWPA.

Structure of MgHWPA · 10 H₂O has been solved from the monocrystal data obtained on a Bruker CCD diffractometer. Crystal data: MgHPW₁₂O₄₀ · 10H₂O, Mr = 3118.5, monoclinic P21/c, Z = 4, F(000) = 5421.5, ρ_X = 4.95 g cm⁻³, μ(Mo Kα) = 33.033 mm⁻¹, dimensions: 0.20 x 0.16 x 0.15 mm, T = 298 K, unit cell parameters: a = 9.868(2), b = 21.980(5), c = 19.289(2) Å, α = γ = 90°, β = 90.63(1)°, V = 4183.5(3) Å³, 122667 measured reflections, 12066 independent reflections, mean redundancy 6.4, R1 = 4.83 % for 10179 observed reflections with Fo > 4s(Fo), refinement on F² for all reflections and 583 refined parameters, GOF = 1.25. Structure is composed of Keggin's anions, Mg(OH₂)₆ complexes, water molecules, hydronium and dioxonium cations which are statistically distributed between Keggin's ions and Mg(OH₂)₆ complexes.

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KRISTALNA STRUKTURA MAGNEZIJUMOVE SOLI 12-VOLFRAMFOSFOROVE KISELINE, MGHPW₁₂O₄₀ · 10 H₂O

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Magnezijumove soli 12-volframfosforove kiseline (MgHWPA-nH₂O) pokazuju neke specifične osobine u odnosu na ostale zemnoalkalne soli ove kiseline. Soli heteropolikiseline su podeljene u dve grupe, "malih-slabih" i "velikih-jakih" katjona [1]. Jonski radijusi Mg²⁺ i Li⁺ su bliski, zbog čega su i neke od njihovih karakteristika slične, i pored toga što je Mg zemnoalkalni element. Zbog toga je interesantno ispitati kristalnu strukturu MgHWPA.

Struktura MgHWPA · 10 H₂O je rešena iz podataka sa monokristala dobijenih na Bruker CCD difraktometru. Kristalni podaci: MgHPW₁₂O₄₀ · 10H₂O, Mr = 3118.5, monokliničan P2₁/c, Z = 4, F(000) = 5421.5, ρ_X = 4.95 g cm⁻³, μ(Mo Kα) = 33.033 mm⁻¹, dimenzije: 0.20 x 0.16 x 0.15 mm, T = 298 K, parametri jedinicne celije: a = 9.868(2), b = 21.980(5), c = 19.289(2) Å, α = γ = 90°, β = 90.63(1)°, V = 4183.5(3) Å³, 122667 izmerenih refleksija, 12066 nezavisnih refleksija, srednji broj ponovljenih merenja 6.4, R1 = 4.83 % za 10179 izmerenih refleksija za koje je Fo > 4σ(Fo), utačnjavanje na osnovu F² za sve refleksije i 583 utaćenjenih parametara, GOF = 1.25. Struktura se sastoji od Keggin-ovih anjona, Mg(OH₂)₆ kompleksa, molekula vode, hidronijum i dioksonijum katjona koji su statistički raspodeljeni između Keggin-ovih jona i Mg(OH₂)₆ kompleksa.

[1] E.Ukshe, L.S.Leonova, A.I.Korosteleva, Solid State Ionics, 36(1989)219.

SUPRAMOLECULAR STRUCTURE OF AQUANITRATO(PYRIDOXAL 3-METHYLISOTHOSEMICARBAZONE)COPPER(II)-NITRATE

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In the title complex, $[\text{Cu}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{NO}_3]\text{NO}_3$ (H_2L = pyridoxal 3-methylisothiosemicarbazone), the copper ion is in a square-pyramidal environment, with the basal plane being defined by the tridentate ONN isothiosemicarbazone and one H_2O molecule. Apical coordination site is occupied by the NO_3^- group with bond between Cu and the O atom significantly longer than the other bonds in the coordination sphere. The Cu atom is displaced from the equatorial plane towards the apically coordinated NO_3^- group by 0.202(1) Å. All non-hydrogen atoms from the equatorial H_2L ligand are approximately coplanar except for the OH group from the -CH₂-OH group, which is almost orthogonally directed out of the coordination plane.

The existence of numerous strong intermolecular hydrogen bonds, weak C-H...O and C-H...π interactions leads to a 3D supramolecular structure. Intermolecular C-H...π interaction exists between neighbouring layers of molecules in such way that each pyridine ring takes part in the interaction as a π-acceptor. The distance between the hydrogen atom directed to the pyridine and the center of the aromatic ring is 2.69(3) Å. The crystal packing consists of layers which are oriented in the direction of equatorial plane of the complex or in other words they are parallel to the y axis.

X-ray single-crystal data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. A gaussian-type absorption correction based on the crystal morphology was applied. The structure was solved by heavy-atom and difference-Fourier methods, and refined by full matrix least-squares using SHELXL97 program to a final R = 0.0335 for 2853 reflections with I > 2σI.

Crystallographic data: C₁₀H₁₆CuN₆O₉S, triclinic, space group P-1, a = 7.945(3) Å, b = 9.262(3) Å, c = 11.701(3) Å, α = 85.13(2) °, β = 89.34(3) °, γ = 80.35(3) °, V = 845.8(5) Å³, Z = 2, D_c = 1.806 Mg.m⁻³, μ(MoKa) = 1.477 mm⁻¹, Mo Kα radiation, λ = 0.71073 Å.

SUPRAMOLEKULSKA STRUKTURA AKVANITRATO(PIRIDOKSAL 3-METILIZOTIOSEMIKARBAZON)BAKAR(II)-NITRATA

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U navedenom kompleksu, $[\text{Cu}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{NO}_3]\text{NO}_3$ (H_2L = piridoksal 3-metilizotiosemikarbazon), ion bakra se nalazi u kvadratno-piramidalnom okruženju sa baznom ravni definisanom tridentatnim ONN izotiosemikarbazonom i jednim molekulom vode. Apikalno koordinaciono mesto je zauzeto jednom NO_3^- grupom sa vezom između Cu i O atoma koja je značajno duža od ostalih veza u koordinacionoj sferi. Atom bakra je pomeren iz ekvatorijalne ravni prema apikalno koordinovanoj NO_3^- grupi za $0.202(1)$ Å. Svi nevodonični atomi iz ekvatorijalnog H_2L liganda su približno u istoj ravni osim hidroksilne grupe iz $-\text{CH}_2-\text{OH}$ fragmenta koja je skoro u normalnom položaju u odnosu na koordinacionu ravan.

Prisustvo velikog broja intermolekulske vodoničnih veza, slabih C-H \cdots O i C-H \cdots π interakcija dovelo je do građenja 3D supramolekulske strukture. Intermolekulska C-H \cdots π interakcije ostvaruju se između molekula u susednim slojevima na takav način da svaki piridinski prsten učestvuje u interakciji kao π -akceptor. Rastojanje između atoma vodonika koji je usmeren prema píridinu i centra ovog aromatičnog prstena iznosi $2.69(3)$ Å. Kristalno pakovanje se sastoji od slojeva koji su orijentisani kao i ekvatorijalne ravni kompleksa ili drugačije opisano pružaju se paralelno prema y osi.

Kristalografski podaci prikupljeni su na Enraf-Nonius CAD-4 difraktometru uz korišćenje monohromatskog Mo-Kα zračenja. Primenjen je tip korekcije apsorpcije zasnovan na morfolografiji kristala. Struktura je rešena metodom teškog atoma i diferentnom Furijeovom sintezom, a utačnjena je metodom najmanjih kvadrata pune matrice korišćenjem programa SHELXL97 do finalnog $R = 0.0335$ za 2853 refleksija koje zadovoljavaju uslov $I > 2\sigma I$.

Kristalografski podaci: $\text{C}_{10}\text{H}_{16}\text{CuN}_6\text{O}_9\text{S}$, triklinični sistem, prostorna grupa P-1, $a = 7.945(3)$ Å, $b = 9.262(3)$ Å, $c = 11.701(3)$ Å, $\alpha = 85.13(2)$ °, $\beta = 89.34(3)$ °, $\gamma = 80.35(3)$ °, $V = 845.8(5)$ Å 3 , $Z = 2$, $D_c = 1.806 \text{ Mg.m}^{-3}$, $m(\text{MoKa}) = 1.477 \text{ mm}^{-1}$, Mo Kα zračenje, $\lambda = 0.71073$ Å.

CRYSTAL AND MOLECULAR STRUCTURE OF Z-FORM OF UNSATURATED ESTERS OF C-GLYCOSIDES AT 173 K

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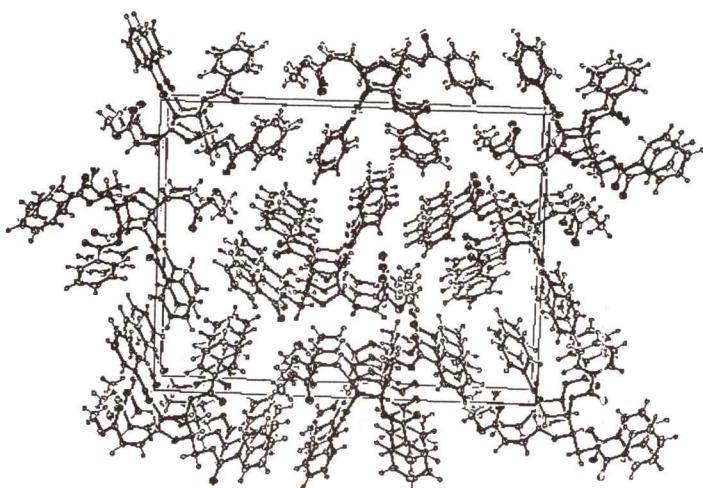
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The critical problem in the synthesis of all pyrazole-related C-nucleosides was the confirmation of the existence of β -configuration at the anomeric position (atom C4). As the intermediate in the process of the syntheses, the mixture of the corresponding Z and E unsaturated esters in 85 % combined yield was prepared. Z-isomer crystallize from CH_2Cl_2 - hexane to give white crystalline needles (m.p. 114–115 °C).

The compound $\text{C}_{30}\text{H}_{27}\text{NO}_8$ titled: Methyl Z-4,7-anhydro-5-benzamido-6,8-di-O-benzoyl-2,3,5-trideoxy-D-allo-oct-2-enate crystallize in the orthorhombic system, acentric space group $P2_12_12_1$, with the unit cell parameters $a=5.1297(13)$ Å, $b=19.667(5)$ Å, $c=25.871(6)$ Å, $V=2610.08(5)$ Å³, $Z=4$, $M_r=529.53$, $D_x=1.348 \text{ Mg}\cdot\text{m}^{-3}$, $\mu=0.10 \text{ mm}^{-1}$. 14271 independent reflections were collected with CCD detector on STOE diffractometer (MoK α) at $T=173$ K. The crystal structure was solved by the direct methods, on the basis of 2727 reflections using program SHELXS86 and refined by SHELXL98 to the final R factor $R = 0.0435$ for 1993 ($I > \sigma(I)$) independent reflections and 423 parameters. The X-ray diffraction analysis, unambiguously confirmed its structure providing a proof that all intermediates generated by the multistep sequences retained required β -configuration at the anomeric position.



KRISTALNA I MOLEKULSKA STRUKTURA Z-FORME NEZASIĆENOG ESTRA C-GLUKOZIDA NA 173 K

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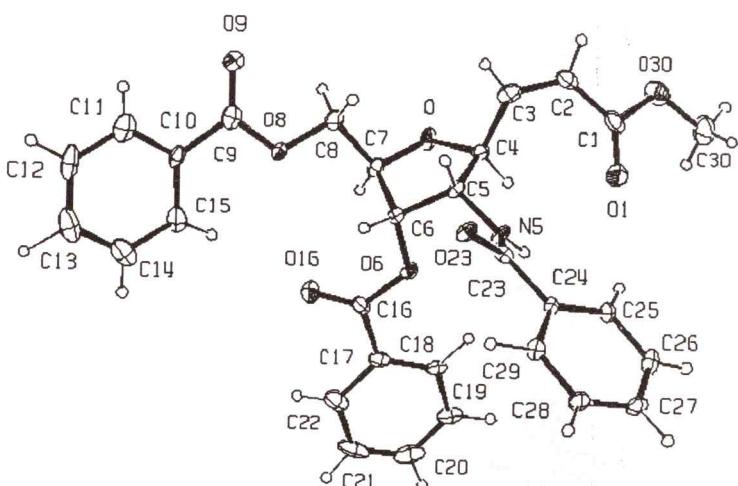
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Suštinski problem u sintezi pirazolskih derivata C-nukleozida je bilo potvđivanje postojanja β -konfiguracije na atomu C4. Kao međuprodot pri preparaciji dobijena je mešavina Z i E-forme odgovarajućeg nezasićenog estra u odnosu 2:1, a u prinosu 85 %. Z-izomer kristališe iz CH_2Cl_2 – heksana i daje beli kristalni talog. Prekristalizacijom su dobijene sitne bele iglice (m.p. 114–115 °C) od kojih je izdvojen monokristal dimenzija 0,09x0,15x0,05 mm.

Jedinjenje $\text{C}_{30}\text{H}_{27}\text{NO}_8$: Metil Z-4,7-anhidro-5-benzamido-6,8-di-O-benzoil-2,3,5-trideoksi-D-alo-okta-2-enat kristališe u ortorombičnom kristalnom sistemu, prostorna grupa $\text{P}2_1\text{2}_1\text{2}_1$ sa parametrima jedinične celije: $a=5,1297(13)$ Å, $b=19,667(5)$ Å, $c=25,871(6)$ Å, $V=2610,08(5)$ Å³, $Z=4$, $\text{Mr}=529,53$, $D_x=1,348 \text{ Mg m}^{-3}$, $\mu=0,10 \text{ mm}^{-1}$. Intenzitet 14271 refleksije je izmeren CCD kamerom na difraktometru STOE (MoK α) na $T=173$ K. Kristalna struktura je rešena direktnim metodama na osnovu 2727 refleksija korišćenjem programa SHELXS86 i utačnjena programom SHELXL98 do konačnog R faktora $R = 0,0435$ za 1993 ($I > 2\sigma(I)$) nezavisnih refleksija i 423 parametra. Analiza geometrije je potvrdila da međuprodot dobijen u procesu višefazne sinteze novih derivata zadržava β -konfiguraciju na anomernoj poziciji na atomu C4.



AN ANALYSIS OF THE STRUCTURE-ACTIVITY RELATIONSHIPS IN SOME ANDROSTANES AND ANDROSTENES

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In the study of some synthetic estranes and androstanes with potential antiestrogenic and antiandrogenic properties a number of androgenic compounds were synthesized, structurally analysed and tested for biologic effects.

As a part of our study, the influence of molecule flexibility and substituents on the structure-activity relationships were examined.

In this paper our attention was directed toward the influence of the structure differences in the $3\beta,17\beta$ -dihydroxy-5-androstenes and $3\beta,17\beta$ -dihydroxy-androstanes with different 16- and 17-substituents on their biolocal activity.

The crystal structures of the compounds were determined by the single crystal X-ray diffraction methods. The energy minimum structures were obtained by the molecular-mechanics calculations.

ANALIZA VEZE IZMEĐU STRUKTURE I BIOLOŠKE AKTIVNOSTI U NEKIM ANDROSTENIMA I ANDROSTANIMA

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U cilju proučavanja nekih sintetičkih estrana i androstana sa potencijalnim antiestrogenim i antiandrogenim osobinama, brojna androgena jedinjenja su sintetizovana, strukturalno analizirana i testirana na biološku aktivnost.

Deo našeg istraživanja odnosio se na uticaj fleksibilnosti molekula i substituenata na vezu između strukture i biološke aktivnosti ovih jedinjenja.

U ovom radu je naša pažnja bila usmerena na $3\beta,17\beta$ -dihidroksi-5-androstene i $3\beta,17\beta$ -dihidroksi-androstane sa različitim 16- and 17-substituenata na njihovu biološku aktivnost.

Kristalne strukture jedinjenja su određene difrakcijom X-zraka na monokristalu. Strukture molekula u energetskom minimumu su dobijene pomoću molekularno-mehaničkih proračuna.

POLYMERIC COPPER (II) COMPLEX WITH 1,10-PHENANTROLINE AND TEREPHTHALATE IONS

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This work presents continuation of our studies on synthesis and characterisation of ternary transition metal complexes with terephthalate ion (tpht^{2-}) and some aromatic diamines, as 1,10-phenanthroline (phen). Although some mononuclear tpht-complexes are known [1], polymeric complexes, with tpht ion acting as bridging ligand, are more encountered [2,3]. The obtained complex is isostructural with previously described compounds with the general formula $[\text{M}(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$, M=Co, Zn, [2,3]. In the title compound, two crystallographically different, but chemically identical tpht ions with monodentately coordinated COO groups exist, and both of them act as bridging ligands forming zigzag chains. Cu(II) ions are in deformed trigonal bipyramidal environment consisting of two N atoms from phen, two O atoms from different tpht ligands and one O atom from coordinated H_2O molecule. In the series of isostructural Co, Cu and Zn complexes, the mean bond distances in the coordination polyhedra increase in the order: Cu < Co ≈ Zn. This is accompanied by the similar changes in the unit cell volumes, which increase as follows: Cu < Co < Zn.

Crystal data: $\text{C}_{20}\text{H}_{14}\text{CuN}_2\text{O}_5$, Mr = 425.87, triclinic system, space group P-1, $a=9.0073(5)$, $b=10.5572(6)$, $c=11.5540(6)\text{\AA}$, $\alpha=114.343(1)$, $\beta=92.942(1)$, $\gamma=114.516(1)^\circ$, $V=877.38(8)\text{ \AA}^3$, $Z=2$, $F(000)=434$, $\rho_x=1.612\text{ g cm}^{-3}$, $\mu=1.281\text{ mm}^{-1}$, 5108 measured reflections, $R_1=0.0286$ for 4357 reflections with $I>2\sigma(I)$, $wR2=0.0839$ (refinement on F^2) for all reflections and 309 refined parameters, with $(\text{Dr})_{\text{max}}=0.390$, $(\text{Dr})_{\text{min}}=-0.348\text{ e \AA}^{-3}$. Since the crystal has a regular shape, it was possible to index its faces and to search different ways of correction for adsorption and its influence on the results of the structure analysis. It was obtained that agreement factors decrease in the order: no correction > correction for lamina " SADABS > 'face indexing'+SADABS ≈ ellipsoid ≈ 'face indexing'. However, none correction had a significant influence on atomic coordinates and its displacement parameters, or on precision of the results, probably because of small μ value.

- [1] J. Rogan, D. Poleti, Lj. Karanović, G. Bogdanović, A. Spasojević-de Bire, D. M. Petrović, Polyhedron, 19, (2000), 1415-1421.
- [2] D. Sun, R. Cao, Y. Liang, Q. Shi, W. So, M. Hong, J. Chem. Soc., Dalton Trans., (2001), 2335-2340.
- [3] Lj. Karanović, D. Poleti, J. Rogan, G. A. Bogdanović, A. Spasojević-de Bire, Acta Cryst., C58, (2002), 275-279.

POLIMERNI BAKAR(II) KOMPLEKS SA 1,10-FENANTROLINOM I TEREFALAT-JONIMA

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Ovaj rad predstavlja nastavak istraživanja iz oblasti sinteze i karakterizacije ternarnih kompleksa prelaznih metala sa tereftalat-jonom (tpht^{2-}) i nekim aromatičnim diaminima, kao što je 1,10-fenantrolin (phen). Iako su poznati neki mononuklearni tpht–kompleksi [1], mnogo je više polimernih supstanci, gde se tpht–jon ponaša kao mostovni ligand [2,3]. Dobijeni kompleks je izostrukturiran sa ranije opisanim jedinjenjima formule $[\text{M(tpht)(phen)}(\text{H}_2\text{O})]_n$, $\text{M} = \text{Co}, \text{Zn}$, [2,3]. U jedinjenju postoje dva kristalografski nezavisna, ali hemijski identična tpht–jona i oba imaju ulogu mosta sa monodentatno koordiniranim COO–grupama, tako da nastaju cik–cak lanci. Cu(II)–joni se nalaze u veoma deformisanim trigonalno–bipiramidalnom okruženju koje čine dva atoma N iz phen, dva atoma O iz razlicitih tpht–liganada i jedan atom O iz koordiniranog molekula H_2O . U pomenutom nizu izostrukturnih kompleksa Co, Cu i Zn prosečna dužina veza u koordinacionom poliedru raste sledećim redom: $\text{Cu} < \text{Co} \approx \text{Zn}$, što je praćeno i sličnom promenom zapremine jedinične celije, koja raste u nizu $\text{Cu} < \text{Co} < \text{Zn}$. Kristalografski podaci: $\text{C}_{20}\text{H}_{14}\text{CuN}_2\text{O}_5$, $\text{Mr} = 425,87$, triklinični sistem, prostorna grupa P–1, $a=9,0073(5)$, $b=10,5572(6)$, $c=11,5540(6)\text{\AA}$, $\alpha=114,343(1)$, $\beta=92,942(1)$, $\gamma=114,516(1)$ °, $V=877,38(8)\text{\AA}^3$, $Z=2$, $F(000)=434$, $\rho_X=1,612 \text{ g cm}^{-3}$, $\mu=1,281 \text{ mm}^{-1}$, 5108 izmerenih refleksija, $R1=0,0286$ za 4357 refleksija sa $I>2\sigma(I)$, $wR2=0,0839$ (učenjavanje pomoću F^2) za sve refleksije i 309 utaćnjavanih parametara; $(\text{Dr})_{\text{max}}=0,390$, $(\text{Dr})_{\text{min}}=-0,348 \text{ e \AA}^{-3}$. Pošto je kristal bio pravilnog oblika, bilo je moguće indicirati njegove pljosni, tako da su ispitane različite mogućnosti korekcije za apsorpciju i njihov uticaj na rezultate strukturne analize. Dobijeno je da faktori slaganja opadaju u nizu: bez korekcije $>>$ korekcija za pločicu \approx SADABS $>$ 'face indexing'+SADABS \approx elipsoid \approx 'face indexing'. Međutim, nijedna korekcija nije imala značajniji uticaj na koordinate atoma i njihove parametre pomeranja niti na preciznost dobijenih rezultata. Moguće objasnjenje leži u maloj vrednosti μ .

- [1] J. Rogan, D. Poleti, Lj. Karanović, G. Bogdanović, A. Spasojević–de Bire, D. M. Petrović, Polyhedron, 19, (2000), 1415–1421.
- [2] D. Sun, R. Cao, Y. Liang, Q. Shi, W. So, M. Hong, J. Chem. Soc., Dalton Trans., (2001), 2335–2340.
- [3] Lj. Karanović, D. Poleti, J. Rogan, G. A. Bogdanović, A. Spasojević–de Bire, Acta Cryst., C58, (2002), 275–279.

**CRYSTAL STRUCTURE OF [Fe(TSCP_x-H)(TSCP_x-2H)]·4H₂O
(TSCP_x = PYRIDOXAL THIOSEMICARBAZONE)**

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The monocrystals of the title compound were obtained in the reaction of the metanolic solution of [Fe(TSCP_x-H)₂]Cl·5H₂O and water solution of NH₃. The crystal structure consists of neutral complex molecules and water molecules. The coordination around Fe(III) is distorted octahedral. The both ligands are tridentate and bonded to the metal ion through sulfur, nitrogen and oxygen atoms. One of the ligands is coordinated as a monoanion, while the other one is dianione. The crystal structure is stabilized by hydrogen bonds and π-stacking interactions.

Crystallographic data: C₁₈H₂₉FeN₈O₈S₂, triclinic crystal system, space group P -1, a = 11.117(4) Å, b = 11.191(4) Å, c = 12.164(4) Å, α = 115.71(2)°, β = 102.72(4)°, γ = 99.76(4)°, V = 1268.2(7) Å³, Z = 2, D_c = 1586 Mg/m³, MoKα - radiation, μ(MoKα) = 0.819 mm⁻¹, λ = 0.71073 Å, Enraf-Nonius CAD-4 diffractometer. The structure was solved using SIR92 program and refined using SHELXL97 program to final R = 0.0728 for 3195 (I > 4σI) independent reflections.

KRISTALNA STRUKTURA [Fe(TSCP_x-H)(TSCP_x-2H)]·4H₂O (TSCP_x = TIOSEMIKARBAZON PIRIDOKSALA)

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Monokristali naslovljenog kompleksa su dobijeni reakcijom metanolnog rastvora [Fe(TSCP_x-H)₂]Cl·5H₂O i vodenog rastvora NH₃. Kristalna struktura se sastoji od neutralnih molekula kompleksa i molekula vode. Fe(III) ion se nalazi u deformisanom oktaedarskom okruženju. Tridentatni ligandi su koordinovani za atom gvožđa posredstvom atoma kiseonika, sumpora i azota. Jedan od molekula liganda je koordinovan kao monoanjon dok je drugi u dianjonskom obliku. Kristalna struktura je stabilizovana vodoničnim vezama i "π - stacking" interakcijama.

Kristalografski podaci: C₁₈H₂₉Fe N₈O₈S₂, triklinički kristalni sistem, prostorna grupa P ̄-1, a = 11.117(4) Å, b = 11.191(4) Å, c = 12.164(4) Å, α = 115.71(2)°, β = 102.72(4)°, γ = 99.76(4)°, V = 1268.2(7) Å³, Z = 2, D_c = 1586 Mg/m³, MoKα zračenje, μ(MoKα) = 0.819 mm⁻¹, l = 0.71073 Å, Enraf–Nonius CAD–4 difraktometar. Struktura je rešena programom SIR92 i utaćnjena programom SHELLXL97 do konačnog R = 0.0728 za 3195 (I > 4σI) nezavisnih refleksija.

CRYSTAL STRUCTURE OF NOBLEITE, $\text{CaB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, FROM PISKANJA

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Nobleite is a hydrous calcium hexaborate. It was first described in 1958 from borate deposit in the Death Valley area, California. Some crystallographic data were published in 1961 [1], but crystal structure was not known yet.

The plate-like single crystal (average size: 0.183 mm) was selected for the structure analysis. Data were collected at room temperature (25 °C) on a Bruker AXS four-circle diffractometer equipped with CCD 1000K area detector ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by Patterson method and refined by full-matrix least-squares on F^2 . Hydrogen atoms were found in difference Fourier maps and were refined isotropically. In the nobleite structure (Fig. 1), Ca is surrounded by three H_2O molecules and six O atoms from hexaborate polyanion with formula $[\text{B}_6\text{O}_9(\text{OH})_2]^{2-}$, which consists of three BO_4 -tetrahedra and three BO_3 -coordination triangles. The H_2O molecules coordinate Ca making a planar coordination triangle. Six additional O atoms are situated in the plane nearly perpendicular to the triangle and they are a part of BO_4 -tetrahedra and BO_3 -triangles. Those BO_4 -tetrahedra and BO_3 -triangles form puckered layers parallel to (001). The layers are linked by normal to weak hydrogen bonds.

Table 1. Crystal data and some details of the structure refinement for nobleite.

Tabela 1. Kristalni podaci i neki detalji utvrđivanja strukture nobleita

| Crystal system, space group (No.) | Monoclinic, P21/n (14) |
|-----------------------------------|--------------------------|
| A (\AA) | 9.8486(8) |
| B (\AA) | 8.0240(7) |
| c (\AA) | 14.244(1) |
| β (o) | 108.136(2) |
| V (\AA^3) | 1069.7(2) |
| Z | 4 |
| D_x (g cm^{-3}) | 2.092 |
| m (mm^{-1}) | 0.669 |
| Goodness-of-fit, S | 0.938 |
| R indices [$I > 2\sigma(I)$] | R1 = 0.0324 wR2 = 0.0604 |
| R indices (all data) | R1 = 0.0540 wR2 = 0.0645 |

[1] R. C. Erd, J. F. McAllister, A. C. Vlasisidis, Am. Mineral., 46 (1961), 560-571.

KRISTALNA STRUKTURA NOBLEITA, $\text{CaB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ IZ PISKANJE

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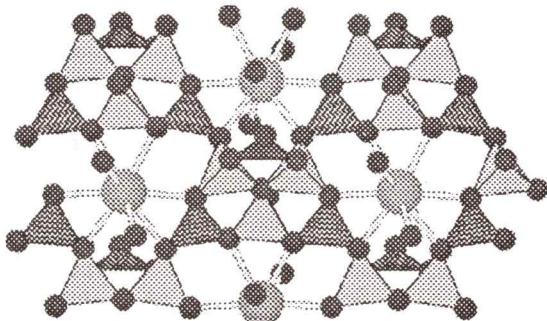
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Nobleit je mineral iz grupe hidratisanih heksaborata kalcijuma. Prvi put je opisan još 1958. godine iz ležišta u Dolini smrti u Kaliforniji. Osnovni kristalografski podaci o nobleitu objavljeni su 1961. [1], ali do sada nije bila poznata njegova kristalna struktura.

Za analizu je odabran tabličast monokristal veličine $0,34 \times 0,18 \times 0,04$ mm. Podaci su sakupljeni na četvorokružnom difraktometru Bruker AXS sa CCD 1000K detektorom (25°C ; $\lambda = 0.71073$ Å). Struktura je rešena Patersonovom metodom i utvrđena metodom najmanjeg kvadrata F². Atomi vodonika nadjeni su na diferentnoj Furijeovoj mapi i utvrđeni izotropno. Kristalni i eksperimentalni podaci, kao i rezultati utvrđivanja, prikazani su u tabeli 1.

U strukturi nobleita (slika 1) atom Ca je okružen sa tri molekula H₂O i šest atoma O iz heksaboratnog polianjona $[\text{B}_6\text{O}_9(\text{OH})_2]^{2-}$, koji se sastoji od tri BO₄⁻ tetraedra i tri BO₃-trougla. Molekuli vode formiraju sa kalcijumom planarni trougao. Preostalih šest atoma O smešteno je u ravni skoro normalnoj na taj trougao i deo su BO₄⁻-tetraedra i BO₃-trouglova koji formiraju nabrane slojeve paralelne ravni (001). Slojevi su međusobno vezani vodoničnim vezama.



Slika 1. Struktura nobleita (BO₃-trouglovi su šrafirani)

Fig. 1. Nobleite structure (BO₃-triangles are shaded)

TETRAHEDRAL DISTORTION INDUCED BY MAGNETIC ORDERING IN $\text{Co}_x\text{Zn}_{1-x}\text{O}$ ($x=1, 0.9, 0.83, 0.75$)

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$\text{Co}_x\text{Zn}_{1-x}\text{O}$ samples were synthesized by sintering of the appropriate mixtures of CoO and ZnO in the inert atmosphere, at temperature of 1650 K during 8 hours. Neutron diffraction patterns were taken within 4 -140° 2θ range with neutron wavelength of 1.2 Å, at the research reactor R-2, in Studsvik, Sweden. The measurements were done at seven different temperatures between 10 K and 295 K. The diffraction patterns were refined with the Rietveld profile method using the Fullprof program.

Above 300 K, CoO has the cubic crystal structure of NaCl type [1]. At lower temperatures, the antiferromagnetic ordering is established, causing the tetragonal distortion of the cubic cell [2], which becomes quite significant at low temperatures. The tetragonal unit cell was refined within the P4/mmm space group, while the magnetic structure was described and the reflections were generated from P1. The magnetic moment of cobalt ion was refined as a function of temperature and concentration. It was also found that the magnetic moment make an angle of about 20° with c-axes.

- [1] R. Walline, J. Chem. Phys., 41 (1964) 3285.
- [2] U. R. Daniel, A. P. Cracknell, Phys. Rev. 177 (1969) 932.

TETRAGONALNA DISTORZIJA INDUKOVANA MAGNETNIM UREĐENJEM U $\text{Co}_x\text{Zn}_{1-x}\text{O}$ ($x=1; 0,9; 0,83; 0,75$)

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Uzorci $\text{Co}_x\text{Zn}_{1-x}\text{O}$ sintetisani su žarenjem odgovarajućih mešavina CoO i ZnO u inertnoj atmosferi, na temperaturi od 1650 K u trajanju od 8 časova. Neutronski difraktogrami svih uzoraka snimljeni su na istraživačkom reaktoru R-2 u Štucviku u intervalu $4 - 140^\circ 2\theta$, neutronima talasne dužine 1.2 Å. Snimanja su obavljena na sedam različitih temperatura u intervalu od 10 K do 295 K. Difraktogrami su analizirani Ritveldovom profilnom metodom korisćenjem programa Fullprof.

Iznad temperature magnetnog faznog prelaza od oko 300 K, CoO ima kubnu kristalnu strukturu tipa natrijum hlorida [1]. Sa sniženjem temperature uspostavlja se antiferomagnetsko uredjenje praćeno tetragonalnom distorzijom kubne celije [2], koja postaje izrazita na niskim temperaturama. Prisustvo cinka snižava temperaturu magnetnog faznog prelaza, što omogućava postojanje nedeformisane kubne faze na sobnoj temperaturi. Tetragonalna jedinična celija je opisana u prostornoj grupi $P4/mmm$, dok je magnetna struktura opisana u prostornoj grupi $P1$. Utačnjavanjem su dobijene zavisnosti magnetnih momentata kobalta od temperature i koncentracije cinka. Nađeno je takođe i da je magnetski moment kobalta otklonjen od c-ose za ugao od oko 20° .

- [1] R. Walline, J. Chem. Phys., 41 (1964) 3285.
- [2] U. R. Daniel, A. P. Cracknell, Phys. Rev. 177 (1969) 932.

A STUDY OF STRUCTURAL PHASE TRANSITION (P4₃32-Fd-3m) AND CATION DISTRIBUTION INFLUENCE ON THE MAGNETIC PROPERTIES OF Li_{1.33x}Co_{2-2x}Ti_{1+0.67x}O₄

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The Li_{1.33x}Co_{2-2x}Ti_{1+0.67x}O₄ ($0 \leq x \leq 1$) samples crystallize in the spinel structure type. At room temperature, the $0 \leq x \leq 0.40$ and $x = 1$ samples have disorder spinel phase (s.g. Fd-3m), but samples with $x = 0.50$, 0.75 and 0.875 are ordered spinels (s.g. P4₃32). Only sample with $x = 0.75$ is fully ordered spinel with cation ordering of 1:3 type at octahedral 4b and 12d sites.

By increasing the temperature from 972 K to 1253 K, order/disorder phase transition were studied *in situ* by x-ray diffraction. The lattice parameters and thermal expansion coefficients of the samples are determined. In the $x = 0.50$ sample temperature dependence of lattice constant was linear up to the phase transition temperature. At the higher temperatures, sample has been in the Fd-3m space group and the temperature dependence of $a(T)$ has been approximated by a polynom of the third degree. The lattice parameter a versus temperature for the $x = 0.75$ and $x = 0.875$ samples have been linear in the temperature region of the experiment. The corresponding linear coefficients of thermal expansion are: $\alpha|_{x=0.50} = 13.5 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha|_{x=0.75} = 13.67 \cdot 10^{-6} \text{ K}^{-1}$ and $\alpha|_{x=0.875} = 14.88 \cdot 10^{-6} \text{ K}^{-1}$. In the $x = 0.50$ sample the phase transition has been observed at the temperature $T = 1083 \pm 10$ K. In the sample with $x = 0.875$ phase transition was at $T < 973$ K, but the sample with $x = 0.75$ have been in the ordered phase up to $T = 1133$ K.

Samples of Li_{1.33x}Co_{2-2x}Ti_{1+0.67x}O₄ have different magnetic behaviour due to a variation in the distribution of magnetic Co²⁺ ions. Sample with $x = 0.50$ have complex dependance of the inverse magnetic susceptibility versus temperature because Co²⁺ ions occupy three different crystallographic sites: 8c, 4b and 12d (s.g. P4₃32) and many different superexchange paths are possible. The samples with $x = 0.75$ and $x = 0.875$ have paramagnetic behaviour down to the temperature of $T = 1.9$ K. In these samples Co²⁺ ions are placed only in tetrahedral 8c sites and superexchange interactions are very weak because they occur via more than one anion, *i.e.* via the 8c-O(2)-12d-O(2)-8c path. In disordered spinels with $x = 0.25$ and $x = 0.40$ (s.g. Fd-3m) paramagnetic \rightarrow magnetic ordered phase transitions have been observed. Co²⁺ ions occupy both tetrahedral (8a) and octahedral (16d) sublattices and the most intense superexchange interactions for spinel structure type occur between these sublattices.

[1] N. Jović, B. Antić, A. Kremenović, A. Spasojević-de Bire and V. Spasojević, submitted to *Physica Status Solidi (A)*.

PRAĆENJE STRUKTURNOG FAZNOG PRELAZA (P4₃32-Fd-3m) DIFRAKCIJOM X-ZRAKA I UTICAJ KATJONSKE RASPODELE NA MAGNETNE OSOBINE Li_{1,33x}Co_{2-2x}Ti_{1+0,67x}O₄

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Serija uzoraka Li_{1,33x}Co_{2-2x}Ti_{1+0,67x}O₄ ($0 \leq x \leq 1$) kristališe u spinelnom tipu strukture. Na sobnoj temperaturi, u uzorcima sa $0 \leq x \leq 0.40$ i $x = 1$ pokazano je prisustvo neuredjene spinelne faze (Fd-3m), a u uzorcima $x = 0,50, 0,75$ i $0,875$ javlja se delimično uređena spinelna faza (P4₃32). Jedino uzorak sa $x = 0,75$ ima potpuno uređenje katjona na oktaedarskim mestima tipa 1: 3 [1].

Difracijom x-zraka *in situ* povećavajući temperaturu uzorka u opsegu od 973 K do 1253 K, tražen je fazni prelaz uredena \rightarrow neuredena faza tj. P4₃32 \rightarrow Fd-3m. Određeni su parametri rešetke i koeficijenti termalne ekspanzije uzorka. U uzorku $x = 0,50$ zavisnost parametra rešetke a od temperature je linearna funkcija do temperature faznog prelaza. Po prelasku u prostornu grupu Fd-3m zavisnost a(T) aproksimirana je polinomom trećeg stepena. Zavisnost parametra rešetke od temperature je linearna u slučaju uzorka sa $x = 0,75$ i $x = 0,875$ u datom temperaturskom opsegu. Odgovarajući linearni koeficijenti termalnog širenja su: $\alpha|_{x=0,50} = 13.5 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha|_{x=0,75} = 13.67 \cdot 10^{-6} \text{ K}^{-1}$ i $\alpha|_{x=0,875} = 14.88 \cdot 10^{-6} \text{ K}^{-1}$. U uzorku sa $x = 0,75$ fazni prelaz se javlja na $T = 1083 \pm 10 \text{ K}$. U uzorku sa $x = 0,875$ fazni prelaz se desio na $T < 973 \text{ K}$, dok uzorak sa $x = 0,75$ ostaje u uredenoj fazi do $T = 1133 \text{ K}$.

Temperaturska zavisnost magnetizacije uzorka merena je na SQUID magnetometru u temperaturskom opsegu od 1,9 K do 300K i u magnetnom polju od 0,1 T. Uzorci Li_{1,33x}Co_{2-2x}Ti_{1+0,67x}O₄ pokazuju različito magnetno ponašanje u zavisnosti od kristalografske raspodele magnetnog Co²⁺ jona. Tako uzorak sa $x = 0,50$ pokazuje kompleksnu zavisnost inverzne magnetne susceptibilnosti od temperature jer joni Co²⁺ sva tri kristalografska mesta: 8c, 4b i 12d (P4₃32), pa su moguće razne kombinacije superizmenskih interakcija. Uzorci sa $x = 0,75$ i $x = 0,875$ pokazuju paramagnetno ponašanje do temperature $T = 1,9 \text{ K}$. U njima joni Co²⁺ popunjavaju samo tetraedarsko 8c mesto, a superizmenska interakcija se odvija preko više od jednog anjona, tj. 8c – O(2)-12d-O(2)-8c, i vrlo je slaba.

Kod uzorka sa $x = 0,25$ i $x = 0,40$ (Fd-3m) primećen je magnetni fazni prelaz paramagnetik \rightarrow magnetno uredena faza. Joni Co²⁺ su prisutni i u tetraedarskoj (8a) i u oktaedarskoj (16d) podrešetki, a najjače superizmenske interakcije u spinelnom tipu strukture se odvijaju upravo između ove dve podrešetke

[1] N. Jović, B. Antić, A. Kremenović, A. Spasojević- de Bire and V. Spasojević, submitted to Physica Status Solidi (A)

NEW NANOSIZED $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ SPINEL

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Li-ferrite has been prepared by different methods and crystal structures were described in the space groups Fd-3m and P4₃32 [1, 2]. We have synthesized for the first time $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ with another crystal structure.

Samples of nanosized $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{La}_x\text{O}_4$ ($x=0.00, 0.05$ and 0.10) were synthesized by thermal decomposition of the appropriate mixture of acetil-acetates $[\text{M}(\text{AA})_x]$ ($\text{M}=\text{Fe}, \text{Li}, \text{La}$) at 500°C in nitrogen atmosphere. Basic complexes $[\text{Fe}(\text{AA})_3]$, $[\text{La}(\text{AA})_3]$ and $[\text{Li}(\text{AA})]$ were obtained by following previously described method [3]. Cooling and heating velocities were $10^\circ\text{C}/\text{min}$ and $20^\circ\text{C}/\text{min}$, respectively. Samples were hold 1 minute at $T=500^\circ\text{C}$. Bulk $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ was prepared by clasical ceramic technolo gy at $T=650^\circ\text{C}$ in oxygen atmosphere, starting from Li_2CO_3 and Fe_2O_3 .

Diffraction data were collected at room temperature at a Philips PW 1830 diffractometer ($\text{CuK}\alpha$) from $10-120^\circ$ in 2θ range, with the step of 0.02° and exposition time of 10 s. The structural phase transition was studied in situ by x-ray diffraction technique in a $700-950^\circ\text{C}$ temperature range.

We have noticed a splitting of (400) and (440) reflections at the diffraction pattern of nanosized Li-ferrite, which indicated a possibility of a spinel lattice distortion. With annealing at higher temperatures, the mentioned splitting becomes more pronounced and also a splitting of a few more reflections appear. From the crystal structure point of view, we have looked for a structure model in a group-subgroup relation. The description of the crystal structure of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (at room temperature) in orthorombic space group P4₁2₁2 is sug gested, as a subgroup of cubic P4₃32 group.

Change of the characteristic reflections intensity of the spinel phase (210) and (211) with the temperature was studied in order to find an order-disorder phase transition. We have unveiled the existence of the reversible phase transition in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ at $835 \pm 5^\circ\text{C}$.

Crystal structures of Li-ferrite obtained by different methods were compared. Crystal structure of the sample prepared by ceramic method (bulk sample) was refined by the Rietveld method in the space group P4₃32. In nanosized sample a change of cubic symmetry from a cubic into orthorombic one is caused by a distortion of a lattice. This effect is probably influenced by a sample preparation method. Thus, preparation method influences structure properties as well as other physical properties.

- [1] S. J. Marin, M. O'Keeffe, D. E. Partin, *J. Sol. St. Chem.*, 113 (1994) 413
- [2] P. B. Braun, *Nature*, 27 (1952) 1123.
- [3] R. G. Charles, M. A. Pawlikowski, *J. Phys. Chem.*, 62 (1958) 440

NOVI NANOČESTIČNI $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ SPINEL

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Litijum–ferit je dobijan različitim postupcima, a struktura je opisivana u prostornim grupama Fd–3m i P4₃32 [1, 2]. Prvi put je sintetisan $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ sa drugačijom strukturom.

Nanočestični spineli $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{La}_x\text{O}_4$ ($x=0.00, 0.05$ i 0.10) sintetisani su termalnom dekompozicijom odgovarajuće mešavine acetil-acetata $[\text{M}(\text{AA})_x]$ ($\text{M}=\text{Fe, La, Li}$) na $500\text{ }^{\circ}\text{C}$ u atmosferi azota. Osnovni kompleksi $[\text{Fe}(\text{AA})_3]$, $[\text{La}(\text{AA})_3]$ i $[\text{Li}(\text{AA})]$ dobijeni su prema ranije opisanom metodu [3]. Brzine grejanja i hladjenja bili su $10\text{ }^{\circ}\text{C}/\text{min}$ i $20\text{ }^{\circ}\text{C}/\text{min}$. Uzorci su držani 1 minut na $500\text{ }^{\circ}\text{C}$. Voluminozni $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ dobijen je klasičnim keramičkim postupkom na $650\text{ }^{\circ}\text{C}$ u atmosferi kiseonika, polazeći od Li_2CO_3 i Fe_2O_3 .

Uzorci su snimani na difraktometru Philips PW 1830 ($\text{CuK}\alpha$) u ugaonom opsegu $10\text{--}90\text{ }^{\circ}$ (2θ), sa korakom 0.02 ° i ekspozicijom od 5 s. Promena kristalne strukture praćena je difrakcijom rendgenskih zraka na prahu u temperaturskom opsegu $700\text{--}950\text{ }^{\circ}\text{C}$.

Na difraktogramu nanočestičnog Li–ferita uočava se značajno razdvajanje (400) i (440) refleksija što ukazuje na mogućnost distorzije spinelne rešetke. Uzorak žaren na $700\text{ }^{\circ}\text{C}$ takođe pokazuje jasno razdvajanje nekoliko refleksija (posebno (400) i (440)) što je još izraženije na višim temperaturama. Sa stanovišta kristalne strukture tražili smo strukturni model iz relacija grupa – podgrupa. Predložen je opis strukture $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (na sobnoj temperaturi) u ortorombičnoj prostornoj grupi P4₁2₁2, koja je podgrupa kubične P4₃32.

Praćena je promena intenziteta karakterističnih refleksija uredjene spinelne faze ((210) i (211)) sa temperaturom. Nadjeno je da dolazi do reverzibilnog strukturnog faznog prelaza tipa "uredjeno" – "neuredjeno" u $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ na $835 \pm 5\text{ }^{\circ}\text{C}$. Uporedjene su strukture Li–ferita dobijene različitim postupcima. Struktura uzorka dobijenog keramičkim postupkom utvrđena je Ritveldovim metodom u prostornoj grupi P4₃32.

Nanočestični uzorak $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ pokazuje sniženje simetrije, $\text{P}4_332 \rightarrow \text{P}4_12_12$. Otuda postupak pripreme Li–ferita ima uticaj na strukturne, a samim tim i druge osobine materijala.

- [1] S. J. Marin, M. O'Keeffe, D. E. Partin, *J. Sol. St. Chem.*, 113 (1994) 413
- [2] P. B. Braun, *Nature*, 27 (1952) 1123.
- [3] R. G. Charles, M. A. Pawlikowski, *J. Phys. Chem.*, 62 (1958) 440

HYDROXYAPATITE AND FLUOROAPATITE MECHANOCHEMICAL SYNTHESIS AND CHARACTERIZATION

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Powder mixtures of $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ and $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5\text{-CaF}_2$ were milled in planetary ball mill. A single phase of HA, hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, was formed from first powder mixture after 4 hours of grinding and the single phase of FHA, fluoroapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ was formed from second powder mixture after 5 hours of grinding. The various experimental techniques like x-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectroscopy (IR) and scanning electron microscopy (SEM) were used to characterize the synthesized powders. The single phase of HA milled for 6h exhibits an average crystallite size of approximately 10 nm and the single phase of FHA milled for 6 hours exhibits an average crystallite size of approximately 22 nm.

HIDROKSIAPATIT I FLUOROAPATIT: MEHANOHEMIJSKA SINTEZA I KRISTALIZACIJA

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Suvim mlevenjem smeša $\text{Ca}(\text{OH})_2\text{--P}_2\text{O}_5$ i $\text{Ca}(\text{OH})_2\text{--P}_2\text{O}_5\text{--CaF}_2$ u planetarnom mlinu sintetisani su hidroksiapatit $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA i fluoroapatit $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FHA. Monofazni HA je dobijen nakon 4 sata mlevenja, a monofazni FHA je dobijen nakon 5 sata mlevenja. Različite eksperimentalne tehnike, kao što su rendgenostruktturna analiza (XRD), diferencijalna termijska analiza (DTA), infracrvena spektroskopija (IR) i skanirajuća elektronska mikroskopija (SEM), su korištene za karakterizaciju sintetizovanih prahova. Rezultujući HA pokazuje veličinu kristalita oko 10 nm, a FHA oko 22 nm.

MECHANOCHEMICAL TREATMENT OF Bi_2O_3 - TiO_2 SYSTEM

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Mechanochemical treatment has been recognised as a powerful technique for the synthesis of a wide range of materials. Thus, complex, multi-component metallic and ceramic materials that may be otherwise difficult to prepare by conventional high temperature treatment, has been successfully prepared by milling. Mechanochemical treatment is non-equilibrium solid-state process whereby final product retains the very fine, typically nanocrystalline or amorphous structure. Therefore, such powders may be used as a precursor for later solid-state reactions and potentially, for the preparation of thin or thick solid films.

Polycrystalline ferroelectrics with perovskite structure are one of the most important materials for electronics and are frequently applied for the preparation of high-dielectric-constant capacitors, piezoelectric transducers, sensors as well as high-density dynamic random access memories and non-volatile memories.

This work presents some of the results of our current research on the synthesis and properties of ferroelectric materials with perovskite or layer perovskite structure. The mechanochemical treatment of either powder mixture of Bi_2O_3 and TiO_2 in stoichiometric composition or pulverised $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound previously prepared by reactive sintering was done in planetary ball mill. Structural changes occurred during milling was followed by X-ray diffraction. In the powder mixture, mechanochemical reaction between Bi_2O_3 and TiO_2 takes place during milling leading to the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound. On the other hand, mechanochemical treatment of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder induces gradual deformation of crystal lattice and distortion of perovskite structure. However, in both cases, after some milling times, steady state was reached characterised by very disordered, amorphous-like structure. Thus, for given milling conditions systems evolve towards non-equilibrium stationary state regardless of different initial thermodynamic states.

MEHANOHEMIJSKI TRETMAN Bi_2O_3 - TiO_2 SISTEMA

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Prihvaćeno je da je mehanohemijski tretman efikasana tehnika za sintezu različitih klasa materijala. Tako se kompleksni, višekomponentni metalni i keramički materijali, koji se inače teško dobijaju uobičajenim visokotemperaturnim tretmanom, uspešno dobijaju mlevenjem. Mehanohemijski tretman je neravnotežni proces u čvrstom stanju pri kome krajnji proizvod zadržava veoma finu, tipično nanokristaličnu ili amorfnu strukturu. Zbog toga, ovakvi prahovi se mogu koristiti kao prekursori za naknadne reakcije u čvrstom stanju i eventualno za dobijanje debelih i tankih filmova.

Polikristalni feroelektrici sa perovskitskom strukturom jedni su od najvažnijih materijala za elektroniku koji se često primenjuju za proizvodnju kondenzatora sa velikom dielektričnom konstantom, piezoelektričnih pretvarača, senzora kao i računarske RAM i DRAM memorije.

Ovaj rad prikazuje neke od rezultata naših tekućih istraživanja sinteze i karakterizacije feroelektričnih materijala sa perovskitskom i slojnom perovskitskom strukturom. Praškasta smeša Bi_2O_3 i TiO_2 u stehiometrijskom odnosu i sprašeni $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, predhodno sintetizovan reakcionim sinterovanjem, paralelno su tretirani u planetarnom mlinu pod istovetnim parametrima mlevenja. Strukturne promene koje se dešavaju tokom mlevenja praćene su rendgenskom strukturnom analizom. U smeši prahova odvija se mehanohemijska reakcija između konsituenata Bi_2O_3 i TiO_2 dovodeći do obrazovanja $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ jedinjenja. S druge strane, mehanohemijski tretman polaznog $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ dovodi do postepene deformacije kristalne rešetke i narušavanja perovskitske strukture. Medjutim u oba slučaja posle određenog vremena mlevenja dostiže se postojano stanje koga karakteriše veoma neuredjena struktura slična amorfnoj. Na osnovu toga, može se zaključiti da se za date uslove mlevenja sistemi razvijaju u pravcu neravnotežnog stacionarnog stanja bez obzira na različita početna termodinamička stanja.

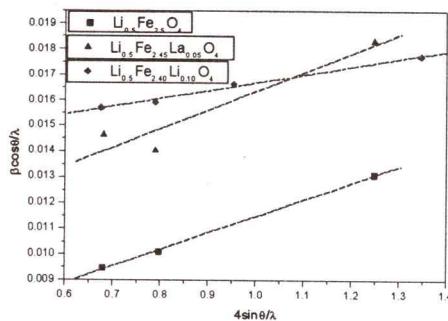
THE DETERMINATION OF THE CRYSTALLITE SIZE IN THE SOLID SOLUTIONS OF $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{La}_x\text{O}_4$ TYPE

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The samples of solid solutions of $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{La}_x\text{O}_4$ type were synthesized by the thermal decomposition of the mixture of corresponding acetyl acetates of $[\text{Fe}(\text{AA})_3]$, $[\text{Li}(\text{AA})_3]$ and $[\text{La}(\text{AA})_3]$, at 500 °C in the nitrogen atmosphere [1] in order to produce nanoparticle materials. They were studied by X-ray diffraction powder method. Recording was performed by the diffractometer PHILIPS PW 1830 (CuKa) in the 2θ range of 10-120 °, with step of 0,02 ° and exposition of 10 s.

Diffractograms were recorded for samples of pure Li-ferite and Li-ferite with addition of La_x ($x = 0.05$ and 0.10). The determination of the crystallite size was based on the value of the line half-width (FWHM) using Williamson-Hall linearization [2] (Figure). Indices of chosen lines were assigned on the basis of most probable space group P4₃32 as (210), (220), (410) and (420). Obtained average crystallite sizes indicate size decrease with the increase of La part in the solid solution of Li-ferite.



An additional measurement was also performed using powder diffractometer at pure Li-ferite, six months after the presented ones. This measurement allowed to express quantitatively the rate of crystallite size increase with time, i.e. it was pointed out to the temporal instability of the initial nanoparticle compound obtained by the above described synthesis procedure.

[1] A. S. Nikolić, N. Cvetković, S. Đurić, J. Puzović, M. B. Pavlović, Mat.Sci.Forum, 199, (1998), 282

[2] S. B. Qadri, P. Yang, E. F. Skelton, B. R. Ratna, Appl. Phys. Lett., 70 (1997), 1020

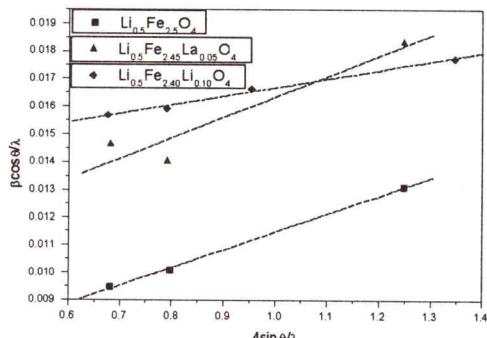
ODREĐIVANJE VELIČINE KRISTALITA U ČVRSTIM RASTVORIMA TIPO $\text{Li}_{0,5}\text{Fe}_{2,5-x}\text{La}_x\text{O}_4$

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Uzorci čvrstih rastvora tipa $\text{Li}_{0,5}\text{Fe}_{2,5-x}\text{La}_x\text{O}_4$ sintetisani su termalnom dekompozicijom odgovarajućih acetil acetata $[\text{Fe}(\text{AA})_3]$, $[\text{Li}(\text{AA})_3]$ i $[\text{La}(\text{AA})_3]$, na 500°C u atmosferi azota [1] a u cilju dobijanja nanočestičnih materijala. Uzorci su ispitivani difrakcijom rendgenskih zraka na praškastom uzorku na difraktometrom PHILIPS PW 1830 (CuKa) u ugaonom opsegu 2θ 10 – 120° , sa korakom $0,02^\circ$ i eksponencijom od 10 s.

Difraktogrami su snimljeni za uzorce čistog Li-ferita i Li-ferita sa dodatkom La_x ($x = 0,05$ i $0,10$). Veličina kristalita određivana je na osnovu merenja poluširine (FWHM) linija korišćenjem linearizacije Williamson-Halla [2] (slika). Odabrane linije su indeksirane na osnovu najverovatnije prostorne grupe $P4_332$ kao (210) , (220) , (410) i (420) . Dobijene usrednjene veličine kristalita pokazuju smanjenje veličine sa povećanjem udela La u čvrstom rastvoru Li-ferita.



Izvršeno je takođe jedno dodatno merenje difraktometrom za prah na čistom Li-feritu, u razmaku od pola godine nakon pomenutih. Ovim merenjem je bilo moguće kvantitativno izraziti stepen ukrupnjavanja kristalita usled stajanja, odnosno ukazano je na vremensku nestabilnost polaznog nanočestičnog jedinjenja dobijenog opisanim postupkom sinteze.

- [1] A. S. Nikolić, N. Cvetković, S. Đurić, J. Puzović, M. B. Pavlović, Mat.Sci.Forum, 199, (1998), 282
[2] S. B. Qadri, P. Yang, E. F. Skelton, B. R. Ratna, Appl. Phys. Lett., 70 (1997), 1020

CONNECTION BETWEEN THE GROWTH RATE DISTRIBUTION AND THE SIZE DEPENDENT CRYSTAL GROWTH

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The results of investigations of the connection between the growth rate dispersions and the size dependent crystal growth of potassium dihydrogen phosphate, Rochelle salt and sodium chlorate are presented. A possible way out of the existing confusion in the size dependent crystal growth investigations is suggested. It is shown that the size independent growth exists if the crystals belonging to one growth rate distribution maximum are considered separately [1]. In other hand, the linear correlation between the arithmetic mean of growth rates in one group and the arithmetic mean of corresponding initial crystal sizes exists. Connection between the parameters describing distributions of growth rates and the growth parameters in classical BCF crystal growth theory is established. The investigations suggest possible reason for the observed distribution maxima widths, and the high data scattering on the growth rate versus the crystal size dependence for all crystals grown under the same external conditions.

[1] M. M. Mitrović, A. A. Žekić, Z.Z. Ilić, Chem. Phys. Letters 361 (3–4) (2002) 312–316.

VEZA IZMEDJU RASPODELA BRZINA RASTA KRISTALA I ZAVISNOSTI BRZINA RASTA KRISTALA OD NJIHOVE VELIČINE

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Proučavana je veza izmedju disperzija brzina rasta kristala i zavisnosti brzine rasta kristala kalijum dihidrogen fosfata, Rošelske soli i natrijum hlorata od njihove veličine. Ukažano je na moguće objašnjenje postojeće konfuzije u proučavanju uticaja veličine kristala na njegovu brzinu rasta. Pokazano je da brzina rasta kristala ne zavisi od početne veličine kada se posmatraju kristali koji pripadaju jednom od maksimuma distribucija brzina rasta [1]. S druge strane, srednja vrednost brzina rasta u okviru maksimuma linearno zavisi od srednje vrednosti početnih veličina kristala. Uspostavljena je veza izmedju parametara koji opisuju distribucije brzina rasta kristala i parametara koji opisuju brzinu rasta kristala po klasičnoj BCF teoriji. Istraživanja ukazuju na moguće uzroke širenja maksimuma distribucija brzina rasta i veoma slabe zavisnosti brzine rasta kristala od njihove početne veličine kada se posmatraju svi kristali rasli pod istim uslovima.

- [1] M. M. Mitrović, A. A. Žekić, Z.Z. Ilić, Chem. Phys. Letters 361 (3–4) (2002) 312–316.

COMPARATION OF MICROSTRUCTURAL PARAMETERS OF ZnO OBTAINED BY VARIOUS PROGRAMS

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Microstructure parameters of ZnO specimens are obtained from XRPD data using FULLPROF[1], XFIT[2] and BREADTH[3] programs. Calculation in program FULLPROF is based on Rietveld method. Deconvolution of diffraction peak in two maxima is done. First describes standard specimen (instrumental profile) and second represent microstructure influence. Program XFIT is based on fundamental parameters convolution approach to generate line profiles and BREADTH stands for modified Warren-Averbach method. Results obtained with different programs for same specimens showed some differences in values. On the other hand, comparation of results obtained on all specimens by one program with corresponding results obtained with other programs shows large correlation.

- [1] J. Rodriguez-Carvajal, "FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis", Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France (1990) 127.
- [2] R. W. Cheary & A. A. Coelho, Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England. (<http://www CCP14.ac.uk/tutorial/xfit-95/xfit.htm>), (1996).
- [3] D. Balzar, J. Res. Natl. Inst. Stand. Technol. 98 (1993) 321-353.

POREĐENJE MIKROSTRUKTURNIH PARAMETARA ZnO DOBIVENIH RAZLIČITIM PROGRAMIMA

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Mikrostrukturalni parametri uzoraka ZnO određeni su pomoću programa FULLPROF[1], XFIT[2] i BREADTH[3] iz podataka dobivenih rendgenskom difrakcijom na polikristalnim uzorcima. U programu FULLPROF izračunavanje bazira na Rietveldovoj (Rietveld) metodi. Dekonvolucijom difrakcionog maksimuma na dva maksimuma od kojih jedan opisuje standardni uzorak (tj. instrumentalni profil), a drugi predstavlja uticaj mikrostrukturnih karakteristika. Program XFIT se zasniva na metodi aproksimacije instrumentalnog uticaja pomoću poznatih parametara instrumenta, BREADTH predstavlja modifikovanu metodu Vorena i Averbaha (Warren-Averbach). Poredenjem rezultata dobivenih različitim programima za iste uzorce zapoža se izvesna razlika u vrednostima mikrostrukturnih parametara. Sa druge strane, ako se porede rezultati dobiveni jednim programom na svim uzorcima sa odgovarajućim rezultatima dobijenim drugim programima, uočava se visoka korelacija.

- [1] J. Rodriguez-Carvajal, "FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis", Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, (1990) 127.
- [2] R. W. Cheary & A. A. Coelho, Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England. (<http://www ccp14.ac.uk/tutorial/xfit-95/xfit.htm>), (1996).
- [3] D. Balzar, J. Res. Natl. Inst. Stand. Technol. 98 (1993) 321–353.

STRUCTURAL PROPERTIES OF DOUBLE PEROVSKITE $\text{La}_2\text{FeCrO}_6$

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We have successfully synthesized for the first time by ceramic method, double perovskite, $\text{La}_2\text{FeCrO}_6$, with random distribution of transition metal ions within Fe-Cr sublattice [1]. The polycrystalline sample was investigated by the X-ray powder diffraction method with Philips PW 1050 diffractometer. The obtained data were refined using Rietveld method considering two possible space groups: $\text{P}2_1/\text{n}$ which corresponds to the rock salt structure with tilted oxygen octahedra (ie. with ordered distribution of transition metal ions within Fe-Cr sublattice), and Pbnm which corresponds to random distribution of aforementioned ions [2]. Analysis of R-factors showed that $\text{P}2_1/\text{n}$ structure provides better correspondence to experimental data. However, based on refinement results (occupation numbers) it is concluded that the ordering of Fe and Cr ions at corresponding crystallographic sites is relatively small.

- [1] K. Ueda, H. Tabata, T. Kawai, Science 280 (1998), p. 1064.
- [2] M. T. Anderson, K. B. Greenwood, G. A. Taylor, K. R. Poepelmeier, Progress in solid state chemistry 22 (1993), p. 197.

STRUKTURNЕ OSOBINE DVOJNOГ PEROVSKITA $\text{La}_2\text{FeCrO}_6$

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Po prvi put je uspešno sintetizovan keramičkom metodom dvojni perovskit $\text{La}_2\text{FeCrO}_6$ sa slučajnom raspodelom jona prelaznih metala u okviru Fe–Cr podrešetke [1]. Metodom rendgenske difrakcije na difraktometru za prah PHILIPS PW1050 izmereni su podaci na dobijenom polikristalnom uzorku. Utačnjavanje strukture Ritveldovom metodom uredjeno je u dve moguće prostorne grupe P21/n koja odgovara strukturi kamene soli sa pomerenim kiseoničnim oktaedrima tj. sa uredjenom raspodelom jona prelaznih metala u okviru Fe–Cr podrešetke i Pbnm koja odgovara slučajnoj raspodeli pomenutih jona [2]. Na osnovu analize faktora greške (R-faktora) utvrđeno je da P21/n struktura bolje odgovara rezultatima merenja. Medjutim na osnovu dobijenih rezultata (faktora zauzeća) zaključeno je da je stepen uredjenja Fe i Cr jona po odgovarajućim kristalografskim položajima relativno mali.

- [1] K. Ueda, H. Tabata, T. Kawai, Science 280 (1998), p. 1064.
- [2] M. T. Anderson, K. B. Greenwood, G. A. Taylor, K. R. Poeppelmeier, Progress in solid state chemistry 22 (1993), p. 197.

A CRYSTALLIZATION COOLERS

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A model of air cooler installed in a laboratory crucible furnace, which allows regulation and simultaneous crystallization of several substances at different temperature gradients and crystallization rates intervals, for obtaining crystals of a family compounds with unknown crystallization parameters is presented (Fig. 1).

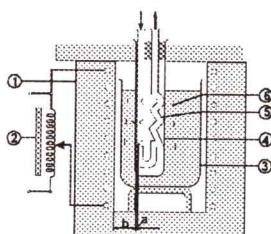


Figure 1. Crystallization cooler in a crucible furnace. (1) Caboratory crucible furnace, (2) Continuously changeable transformer, (3) Crucible (4) Test tube (5) Moving air cooler ("cold ear-rings"), and (6) Tammann test tubes.

The crystallization procedure is described as well as the possible variations. The formula is derived and numerically analyzed for the crystallization rates as a function of the parameters of the coolers and substances. The possibilities are considered for simultaneous regulation of several different temperature gradients. It was pointed out to the possibility for the cooler's shape variation, and simultaneous tests of a family of Tamman's test tubes [1]. The cooler can be modified into a rectilinear shape and installed into a tube furnace in a horizontal position ("crystallization bench") [2]. Several coolers (a family group of "crystallization horseshoes") can be installed in the chamber furnace for simultaneous test of the matrix different test tubes, temperature gradients, crystallization rate intervals and substances.

[1] K.-Th.Wilke, J. Bohm, Kristallzuchtung, Deutscher Verlag der Wissenschaften, Berlin, (1988), p. 591.

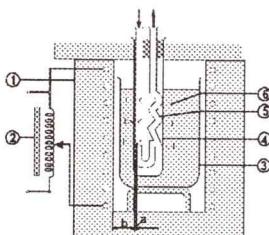
[2] B. Čabrić, T. Pavlović, J. Appl. Cryst., 33 (2000), pp. 387-388.

KRISTALIZACIONI HLADNJACI

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Za regulaciju i simultanu kristalizaciju nekoliko supstanci pri različitim temperaturskim gradijentima i intervalima brzina kristalizacije, radi dobijanja kristala familije jedinjenja sa nepoznatim parametrima kristalizacije, prikazan je model vazdušnog hladnjaka instaliran u laboratorijskoj tigl peći (sl. 1).



Slika 1. Kristalizacioni hladnjak u tigl peći. (1) laboratorijska tigl peć, (2) kontinualno promenljivi transformator, (3) tigl, (4) epruveta (5) pokretni hladnjak ("hladne minduše") i (6) Tamanove epruvete.

Opisan je postupak kristalizacije kao i njegove moguće varijacije. Izvedena je i numerički analizirana formula za brzinu kristalizacije u zavisnosti od parametara hladnjaka i supstanci. Razmatrane su mogućnosti za simultanu regulaciju nekoliko različitih temperaturnih gradijenata. Ukazano je na mogućnost varijacija oblika hladnjaka i simultane probe familije Tamanovih epruveta [1]. Hladnjak se može modifikovati u pravolinijski oblik i instalirati u cilindričnoj peći u horizontalnom položaju ("kristalizaciona klupa") [2]. Nekoliko hladnjaka (familija "kristalizacionih potkovica") može se instalirati u komornoj peći za simultanu probu matrice različitih Tamanovih epruveta, temperaturnih gradijenata, intervala brzina kristalizacija i supstanci.

[1] K.-Th.Wilke, J. Bohm, Kristallzuchtung, Deutscher Verlag der Wissenschaften, Berlin, (1988), p. 591.

[2] B. Čabrić, T. Pavlović, J. Appl. Cryst., 33 (2000), pp. 387-388.

TAMMAN-STOBER'S METHOD FOR OBTAINING CRYSTALS IN A CHAMBER FURNACES

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In the course of investigation on the method of regulation crystallization in a laboratory chamber furnace, with the purpose of obtaining crystals compound with unknown crystallization parameters, we have found that Tamman-Stober's method [1] can be applied. The original apparatus that we constructed, based on Tamman-Stober's method, is schematically presented in Figure 1. It enables simultaneous testing of several different Tamman's test tubes and intervals of crystallization rates for obtaining crystals.

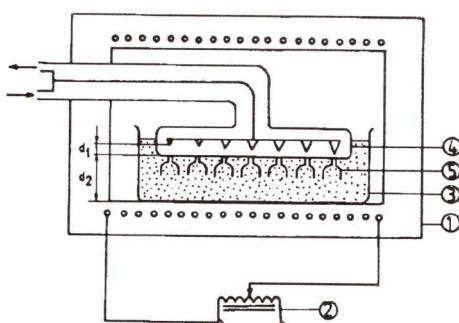


Figure 1. Crystallization apparatus. (1) Laboratory chamber furnace, (2) Continuously changeable transformer, (3) Crucible, (4) Air cooler ("sucker for crystals") and (5) Tamman's test tubes (family group).

The crystallization rate interval in each Tamman's test tube is regulated by the cross-section of the air flow (d_1) i.e. position of test tube. The temperature gradient in test tubes is regulated by the distance d_2 . Different gradients in test tubes can be simultaneously regulated using an inclined cooler. Tamman's test tubes with various shapes and dimensions [1] can be "pinned" onto the cooler i.e. simultaneously tested. This enables simultaneous testing of different test tubes, temperature gradients and crystallization rate intervals for obtaining crystals. By varying the dimensions of the cooler, a family of "suckers for crystals" can be modelled for tests in a wider range of crystallization rate intervals (formula (1) in [2]).

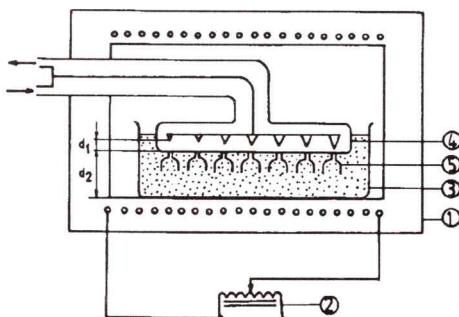
- [1] K.-Th. Wilke, Virashchivanie kristallov, Nedra, Leningrad (1977), p. 260.
- [2] B. Čabrić, T. Pavlović, B. Žižić, J. Appl. Cryst. 29 (1996), p. 745.

TAMAN-STEBEROVA METODA ZA DOBIJANJE KRISTALA U KOMORNOJ PEĆI

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U toku istraživanja metoda za regulaciju kristalizacije u laboratorijskoj komornoj peći, radi dobijanja kristala jedinjenja sa nepoznatim parametrima kristalizacije, našli smo da se može primeniti Taman-Steberova metoda [1]. Originalna aparatura koju smo konstruisali, na osnovu Taman-Stoberove metode, šematski je prikazana na slici 1. Ona omogućava simultanu probu nekoliko različitih Tamanovih epruveta i intervala brzina kristalizacije za dobijanje kristala.



Slika 1. Aparatura za kristalizacije. (1) laboratorijska komorna peć, (2) kontinualno promenljivi transformator, (3) tigl, (4) vazdušni hladnjak ("usisivač za kristale") i (5) Tamanove epruvete (kolona familije).

Interval brzine kristalizacije u svakoj Tamanovoj epruveti reguliše se pomoću preseka vazdušne struje (d_1) tj. položaja epruvete. Temperaturski gradijent u epruvetama se reguliše pomoću rastojanja d_2 . Različiti temperaturski gradijenti u epruvetama mogu se simultano regulisati pomoću nagnutog hladnjaka. Tamanove epruvete različitog oblika i dimenzija [1] mogu se "nabosti" na hladnjak tj. simultano testirati. Ovo omogućava simultano testiranje različitih epruveta, temperaturskih gradijenata i intervala brzina kristalizacije za dobijanje kristala. Variranjem dimenzija hladnjaka može se modelirati familija "usisivača za kristale" za testiranje šireg intervala brzina kristalizacija (formula (1) u [2]).

- [1] K.-Th. Wilke, Virashchivanie kristallov, Nedra, Leningrad (1977), p. 260.
[2] B. Čabrić, T. Pavlović, B. Žižić, J. Appl. Cryst. 29 (1996), p. 745.