T1 - Structure Solution and Refinement

T1 - P1

MOLECULAR REPLACEMENT WITH POWDER DIFFRACTION DATA

Jon Wright[1], Irene Margiolaki[1], Gavin Fox[1], Anders Markvardsen[2] and Andy Fitch[1]

[1]European Synchrotron Radiation Facilty, Grenoble, F-38043, France
[2]ISIS Facility, Rutherford Appleton Laboratories, Chilton, Oxon, UK

As more and more protein structures are determined from single crystal x-ray diffraction data, the molecular replacement method [1] becomes a more attractive method for structure solution, due to the availability of suitable search models. For a significant number (35% [2]) of small protein structures there is only a single amino acid chain to be located in the unit cell, meaning that only the position and orientation of a single molecule within the unit cell need to be found. Thus, solving such a structure only means finding the position and orientation of the origin of the unit cell with respect to the protein molecule. We will demonstrate that powder data are sufficient to solve these simple molecular replacement problems, with a series of real examples.

The difficulties encountered in the more general case of molecular replacement methods depend on both the quality of the search model and the quality of the experimental data. For single crystal data, this essentially reduces to a question of model quality as the data can be considered as error free. For powder data the peak overlap problem can be so severe that significant gains should be possible if peak overlaps are accounted for. The influence of data quality for powder diffraction in terms of both counting statistics and instrumental resolution are investigated. Methods for accounting for the peak overlaps are developed and the effects of model quality with powder data compared to single crystal data are examined.

If the routine application of molecular replacement methods were possible with powder data then this method can offer new opportunities when there are difficulties in obtaining single crystals. While these results are unsurprising considering the complexity of small molecule structures that can be solved from powder data, the applicability to much larger molecules seems worth demonstrating.

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T1 - P2

CRYSTAL-STRUCTURE DETERMINATION OF   -$C_{15}C_{17}C_{17}$ FROM HIGH-RESOLUTION POWDER DIFFRACTION

Jan B. van Mechelen, Dirk J. A. De Ridder, René Peschar, Henk Schenk

University of Amsterdam, Laboratory for Crystallography, IMC, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The crystal structure of the   polymorph of the pure triacylglycerol $C_{15}C_{17}C_{17}$ (2,3-diheptadecanoyl- 1-pentadecanoylglycerol), has been determined using high resolution synchrotron powder diffraction. The simulated annealing approach, as implemented in the program FOX [1], was used to obtain the initial model. The model was refined with the Rietveld refinement program GSAS [2]. Bond- angle- and plane group restraints have been applied.

The crystal structure model shows that the   polymorph of $C_{15}C_{17}C_{17}$ crystallizes in the tuning-fork conformation. The zig-zag planes of the acyl chains are parallel packed.

The methyl end groups of two adjacent layers form a plane but the hydrocarbon chain ends are not in line.

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T1 - P3

A PROPOSAL FOR THE STRUCTURE OF AMMONIUM HYDROGEN (ACID) URATE FROM UROLITHS - X-RAY POWDER DIFFRACTION, INDEX CALCULATION AND FORCE-FIELD CONSTRAINED RIETVELD REFINEMENT

Peter Friedel[1], Jörg Bergmann[2], Reinhard Kleeberg[3], Günter Schubert[4]

[1]*Institute of Polymer Research Dresden, Hohe Str. 6, D-01069, Dresden, FR Germany;*
[2]*Ludwig-Renn-Allee 14, D-01217 Dresden, FR Germany;*
[3]*Freiberg University of Mining and Technology, Institute of Mineralogy, Brennhausgasse14, D-09599 Freiberg i.Sa., FR Germany;*
[4]*Charit'e Berlin, Friedrichshain Hospital, Laboratory of Uroliths, Landsberger Allee 49,D-10249 Berlin, FR Germany.*

From a naturally formed ammonium hydrogen urate, also called uroliths, X-ray powder diffraction measurements, index calculations and force-field-constrained Rietveld refinement including an anisotropic characterization of peak width broadening were performed by the BGMN(reg.) program. The ammonium hydrogen (acid) urate crystallizes in a triclinic unit cell with a = 0.3650(3), b = 1.0215(4), c = 1.0597(5) nm, alpha = 113.9(1), beta = 91.1(1) and gamma = 92.3(1) . The symmetry was determined as P1 (Space group No. 2). The reliability parameter Rwp could be obtained to 7.43% by introducing an anisotropic parameter set as a symmetric tensor of rank 4 for peak width broadening. Inside of the unit cell an additional ammonia molecule was placed with a probability of 0.40. The anisotropic peak width broadening and the ammonia molecule with reduced probability hints to a strong dependence of natural urolith formation from the formation conditions. These are the temperature and the concentration of uric acid and ammonia inside of the urolithic tract. Investigations of artificially crystallized uroliths has been shown peak splittings. Therefore, we assume that incommensurable structure were performed during natural crystallization. Until now, we were not able to investigate them by laboratory x-ray powder diffraction. But we are sure, that these structure problems may be solved by synchrotron X-ray investigations.

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T1 - P4

CRYSTAL STRUCTURE DETERMINATION OF SOME ORGANIC HETEROCYCLES CONTAINING NITROGEN ATOM BY X-RAY POWDER DIFFRACTION METHOD

D. V. Albov[1*], V. B. Rybakov[1], E. V. Babaev[1], D. V. Davydov[1], E. J. Sonneveld[2], V. V. Chernyshev[1], L. A. Aslanov[1]

[1]*Chemistry Department, Moscow State University, Moscow, Russia*
[2]*Laboratory of Crystallography, University of Amsterdam, The Netherlands*
[*]*e-mail: albov@biocryst.phys.msu.su*

The following crystal structures have been determined by powder X-ray diffraction technique:

2-(4-nitrophenyl)-1-methylimidazo[1,2-*a*]pyridin-1-ium chloride   (**1**),
2-(4-nitrophenyl)[1,3]thiazolo[3,2-*a*]pyridin-4-ium perchlorate   (**2**),
3-(trifluoroacetyl)[1,3]oxazolo[3,2-*a*]pyridin-4-ium-2-olate   (**3**)

2-(4-nitrophenyl)-5-methyl[1,3]oxazolo[3,2-*a*]pyridin-4-ium perchlorate   (**4**),
2-chloro-1-[2-(4-nitrophenyl)-2-oxoethyl]pyridinium bromide   (**5**),
[Cu(TMEDA)(OH)]$_2$Cl   (**6**).

Powder diffraction data were collected at room temperature in transmission mode in a Guinier camera. The structures were solved using grid search method and refined with MRIA program package [1, 2].
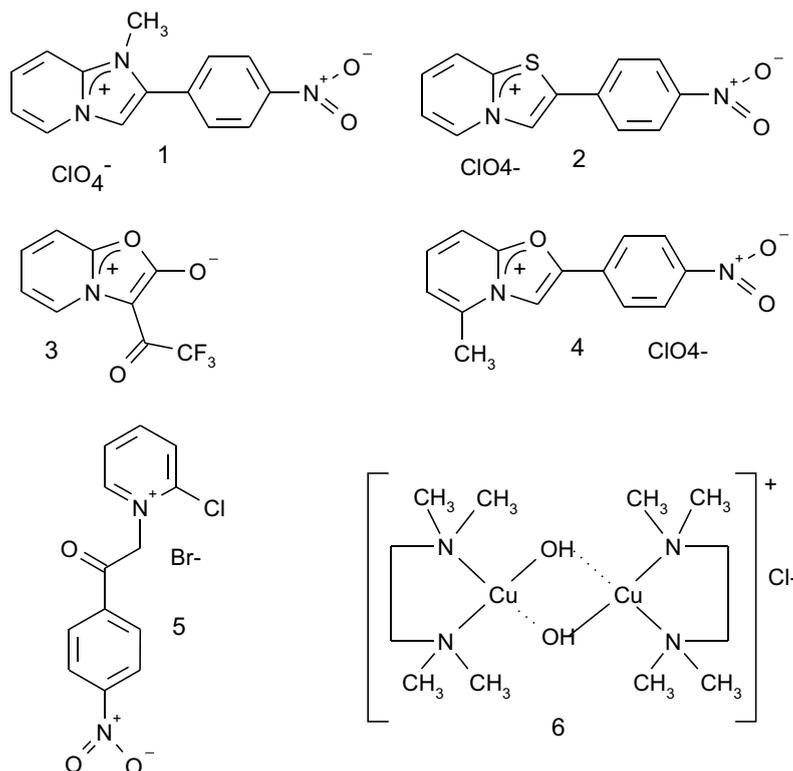
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T1 - P5

STRUCTURE DETERMINATION OF CYCLOHEXANE-DIOLS

Marius Ramírez Cardona[1], Iván Barajas Rosales[2], Carlos Gómez Aldapa[2]

[1]*Centro de Investigaciones en Ciencias de la Tierra, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo, México*
[2]*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo, México*

We have determined the structures of different cyclohexanes presenting two OH groups in different positions: trans-cyclohexane-1,4-diol; trans-cyclohexane-1,2-diol; cis-cyclohexane-1,2-diol. Several molecular configurations have been considered for each compound.

These structures have been determined by powder X-ray diffraction, combining energy minimizations and rigid-body Rietveld refinement. In order to obtain the structure before the refining process we have used a global optimization method based in simulated annealing algorithm. The cost function of this method is a combined expression between potential energy (depending on the parameters defining a lattice energy) and the R value, in this case the R_B, that compares experimental and calculates intensities I(hkl) values from the experimental diffraction pattern. The parameter (Pareto parameter) weights the influence of energy or structure in the final solution.

The different hydrogen bonds (geometrical and energetic characteristics) are studied as comparative manner.

T1 - P6

STUDY OF THE MOLECULAR DISORDER IN 1,3-DIPHENYLTHIOUREA

Marius Ramírez Cardona[1], Iván Barajas Rosales[2], Carlos Gómez Aldapa[2]

[1]*Centro de Investigaciones en Ciencias de la Tierra, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo. México*
[2]*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo. México.*

The polymorphism in 1,3-diphenylthiourea depends directly from the rotational degree of freedom of the two phenyl groups. Two phases occurred within this compound. The stable phase is an orthorhombic form and the other (monoclinic) shows disorder in the molecular conformation. The orthorhombic phase crystallizes in Pnma group with a = 7.951(2) Å, b = 25.576(9) Å and c = 5.689 (2) Å, Z = 4. The monoclinic phase crystallizes in $P2_1/n$ with a = 7.860(1) Å, b = 9.295(1), c = 16.410(1) and = 92.44(1) , Z = 4. In orthorhombic form, the hydrogen bonds link the molecules along the a axis as zigzag chains. This form presents a *cis-cis* configuration of the substituents (phenyl rings) that allows the one-dimensional chains of N-H⋯S hydrogen bond. On the other hand, the *cis-trans* configuration of the phenyl groups in monoclinic form

leads to the formation of two-dimensional layers of thiourea derivatives. The N-H⋯S hydrogen bond formed by the cis-oriented NH group is always stronger than that formed by the *trans*-NH group in the *trans-cis* molecule of thiourea derivatives.

The two structures have been determined by powder synchrotron X-ray diffraction, combining energy minimizations and rigid-body Rietveld refinement. The structure was solved using a global optimization method based in simulated annealing algorithm. The cost function of this method is a combined expression between potential energy (depending on the parameters defining lattice energy) and an R value. A rigid-body Rietveld refinement was performed with the structure derived from the simulated annealing process.

T1 - P7

STRUCTURE DETERMINATION OF 1-PENTANOL ($C_5H_{12}O$) AT 183.15 K

Marius Ramírez Cardona[1], Miquel Ángel Cuevas-Diarte[2], Carlos Gómez Aldapa[3], Iván Barajas Rosales[3]

[1]*Centro de Investigaciones en Ciencias de la Tierra, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo. México*
[2]*Departament de Cristal.lografía. Universitat de Barcelona. Martí i Franqučs s/n. 08028. Barcelona. España*
[3]*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo, km. 4.5. 42184. Pachuca, Hidalgo. México*

We have determined the structure of the 1-pentanol ($C_5H_{12}O$) at 183.15 K combining lattice energy minimization calculations and Rietveld refinement using powder X-ray diffraction with conventional radiation (Debye-Scherrer geometry). A rigid body approach was considered in the Rietveld analysis.

The structural model used in the Rietveld method was extracted from the simulated annealing process, where we considered a combined global optimisation ("Pareto optimisation") based in the next cost function:

$$C \quad E_{pot} \quad (1 \quad)R_B$$

where E_{pot} is the potential energy and R_B denotes the so-called R value. is the Pareto parameter which weights the contributions of the two parts of the cost function.

The preferred orientation is analysed as size effects in the broadening of the peaks of pattern by means of a linear combination of spherical harmonics. That helps us to reach a greater goodness-of-fit in the structure determination.

T1 - P8

STRUCTURE DETERMINATION OF THREE SYMMETRICALLY SUBSTITUTED ORGANIC MOLECULES: A POWDER AND SINGLE-CRYSTAL DIFFRACTION STUDY.

S. Y. Chong[1], B. M. Kariuki[1], M. Tremayne[1], C. C. Seaton[2]

[1]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[2]*School of Pharmacy, University of Bradford, Bradford BD7 1DP, UK*

An established approach in crystal engineering is to investigate a series of materials with one or more characteristics in common, such as a functional group or symmetry element. A combination of techniques may then be required for the structure determination of these materials, as each characterisation method has different limitations. Single crystal X-ray diffraction is a powerful technique, but requires the growth of crystals of sufficient quality and size. Powder diffraction data is an important alternative source of structural information where the material is available only as a microcrystalline powder.

The development of direct space structure solution methods is a major factor in the increasing number of crystal structures determined from PXRD [1]. These techniques involve the generation of trial structures independently of the experimental powder data. The structures are characterised by a set of variables representing position (x, y, z), orientation (and molecular conformation ($_1 \dots _n$). The 'fitness' of each structure is assessed by comparison of its calculated profile to the experimental powder pattern. A global optimisation algorithm, such as Monte Carlo or differential evolution, is applied to locate the global minimum corresponding to the set of variables describing the correct crystal structure.

The Differential Evolution (DE) algorithm is simple to implement, yet offers robust searching of minima [2]. It requires only three control parameters and has achieved efficient structure solution even in cases where the sample is affected by preferred orientation [3]. This poster describes the successful application of the DE algorithm in the structure solution from PXRD of three symmetrically substituted organic molecules (Figure 1), each with conformational flexibility in the alkyl side chains. Single crystal diffraction was employed to aid the proposal of hydrogen-bonding networks and to examine cases where isotropic displacement factors of the powder solution suggest possible disorder.

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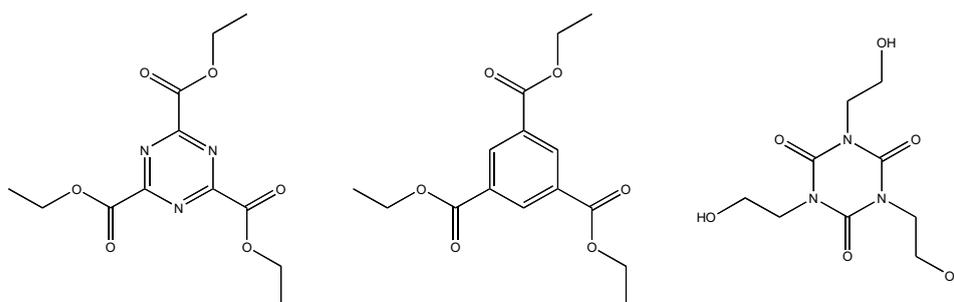
Figure 1.

T1 - P9

CATION DISTRIBUTION IN Li$_2$M(II)Sn$_3$O$_8$, M(II)=Mg, Co, Fe

T. Trendafilova[1], D. Kovacheva[1], K. Petrov[1] and A. Hewat[2]

[1]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev street, bl.11, 1113 Sofia, Bulgaria*

[2]*Institute Laue-Langevin, Grenoble, BP 156, F-38042 Grenoble Cedex 9, France*

New complex oxides with general formula Li$_2$M(II)Sn$_3$O$_8$ (M = Mg, Co, Fe) have been synthesized. The crystal structures were obtained from the refinements of both X-ray and neutron powder diffraction data. The compounds crystallize in the orthorhombic system, space group Cmc2$_1$, Z = 12. The structure consists of a hexagonal close packed array of oxygen layers stacked along <c> direction in a sequence (ABCB) in which cations occupy 1/8 of the tetrahedral and 1/2 of the octahedral interstices. Two different cation layers are formed: one, containing tree cations with octahedral coordination Kagomé layer – (Oh$_3$), and other with two cations in tetrahedral and one in octahedral coordination – (T$_2$O). The polyhedral representation of the structure can be seen on Fig.1. The cation distribution of these phases can be regarded as the intermediate between that of the disordered Li$_{1.6}$Zn$_{1.6}$Sn$_{2.8}$O$_8$ and LiFeSnO$_4$ (S.G.

P6$_3$mc)[1-3] and the completely ordered Li$_2$MnSn$_3$O$_8$ (S.G. Cmc2$_1$)[4].

The more important factor that determines the distribution of cations is the electrostatic factor. From this point of view, the mutual repulsive electrostatic force between high-valence cations occupying two adjacent edge-chairing octahedra is relatively high and leads to the lattice instability.

The second factor is geometrical, or ion size factor. From this aspect the mixed occupation of one interstice by ions with different ionic radii would introduce high local distortions. As greater the size difference as high is the energy of the local strains and mixed occupancy is unfavorable.

The factor usually called "site preference" is a complex one and accounts for the different character of chemical bonding and the crystal field effect connected with the electron configuration (especially for the 3d-metal ions). The ionic character of the bonding corresponds to a higher coordination number thus ions with higher oxidation state should occupy more easily an octahedral site. For ions with predominant covalent or partially covalent type bonding the tetrahedral coordination is more favorable.

The balance between the above-mentioned factors may depend on phase composition and synthesis conditions. We suppose that in the case of a compact structure, the geometrical factor should play a dominant role in the cation distribution.

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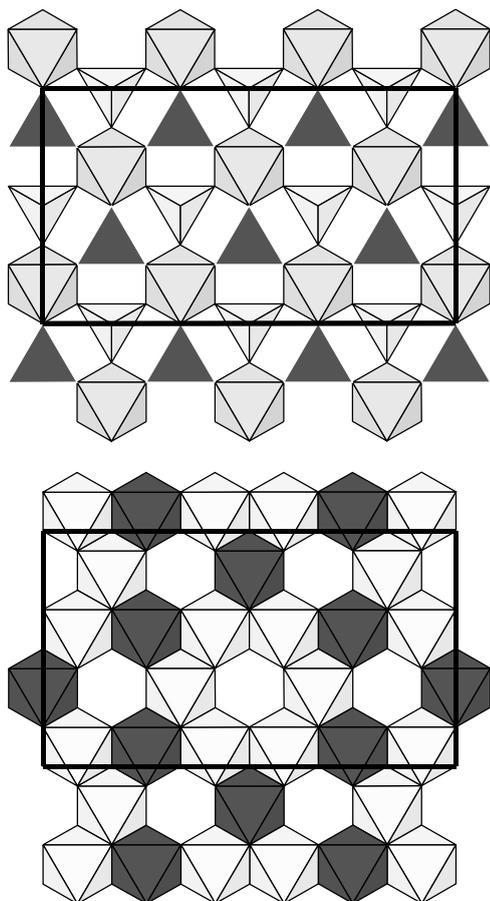
Fig.1. Schematic presentation of the (T$_2$O) and (Oh$_3$) layers in the crystal structure of Li$_2$M(II)Sn$_3$O$_8$ (M = Mg, Co, Fe). Black polyhedra have mixed occupancy by lithium and divalent metal ions. The unit cell is outlined.

T1- P10

CRYSTAL STRUCTURE OF THE MONOCLINIC Ba$_2$MgSi$_2$O$_7$ PERSISTENT LUMINESCENCE MATERIAL

T. Aitasalo[1,2], J. Hölsä[1], T. Laamanen[1], M. Lastusaari[1], L. Lehto[1], J. Niittykoski[1,2], F. Pellé[3]

[1]*University of Turku, Department of Chemistry, FI-20014 Turku, Finland,*
[2]*Graduate School of Materials Research, Turku, Finland,*
[3]*Laboratoire de Chimie Appliquée de l'Etat Solide, CNRS, UMR 7574, ENSCP, 11, r. P. et M. Curie, F-75231 Paris Cedex 05, France.*

Silicates with rigid and stable crystal structures are well known for their use as luminescent materials. For example, SrMg(SiO$_4$)$_2$:Eu^{2+} and Zn$_2$SiO$_4$:Mn^{2+} are employed in displays, whereas alkaline earth disilicates such as (Sr,Ba)$_2$MgSi$_2$O$_7$:Pb^{2+} are used in lamps [1].

Ba$_2$MgSi$_2$O$_7$ was found to be a potential persistent luminescence material (Fig. 1) usable e.g. in exit signage. It has been reported to crystallize in two different structures. The first one is melilite type tetragonal with the space group (No. 113), Z = 2 [2], while for the second one only an experimental diffraction pattern has been reported [3]. The aim of this work was to solve this structure from X-ray powder diffraction data.

The Ba$_2$MgSi$_2$O$_7$ sample was prepared by a solid state reaction of stoichiometric amounts of barium carbonate, magnesium nitrate and silicon dioxide heated at 1250 $^{\circ}$C for 5 hours in a reducing N$_2$ + 12 % H$_2$ atmosphere. The X-ray powder diffraction pattern was collected at room temperature by a Huber 670 Guinier camera using copper K$_1$ radiation (λ = 1.5406 Å).

The Ba$_2$MgSi$_2$O$_7$ sample, possessing the unresolved crystal structure [3], was observed to crystallize in the monoclinic system with C2/c (No. 15), Z = 4, as the space group (Fig. 2). The unit cell parameter values were: a = 8.419, b = 10.723, c = 8.449 Å, β = 110.8°. The oxygen positions could not be found by using the laboratory X-ray powder diffraction data. However, this structure with one Ba^{2+} site (CN = 8, C$_1$ symmetry) was found to be similar to that of Ba$_2$CoSi$_2$O$_7$ [4], whose atomic coordinates could be used as the starting values in the structure refinement yielding good agreement factors: R$_B$ = 8.9 and R$_{wp}$ = 1.9 %. Finally, the two structural types of Ba$_2$MgSi$_2$O$_7$ sample were compared by bond valence calculations [5].

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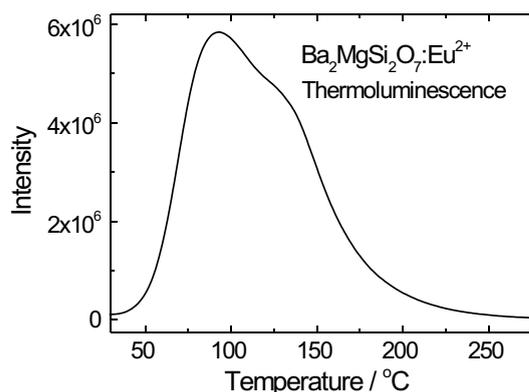
Figure 1. Thermoluminescence glow curve.
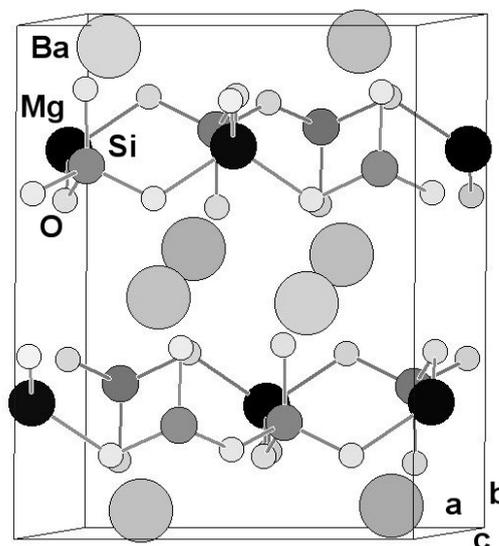
Figure 2. Unit cell of monoclinic Ba$_2$MgSi$_2$O$_7$.

T1 - P11

RIETVELD ANALYSIS OF POLYTYPIC (Zn,X)Se SOLID SOLUTION

W. Paszkowicz[1], R. Minikayev[1], F. Firszt[2], S. Łęgowski[2], H. Męczyńska[2], and A. Marasek[2]

[1]*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland*
[2]*Institute of Physics, N. Copernicus University, ul. Grudziądzka 5, 87-100 Toruń, Poland*

ZnSe based solid solutions are components of heterostructures which are of interest in optoelectronic technologies as components of blue-green lasers and UV-visible photodetectors. The occurrence of crystal defects leads to structure degradation of Mg-containing layers. Studies of polytypism in this kind of crystals may lead to a better understanding of phase relationships and defect nature.

Higher polytypes occur for those tetrahedrally bonded semiconducting compounds, for which the formation energies of wurtzite (2H) and sphalerite (3C) polymorphs do not differ much. For semiconducting solid solutions, the polytypes appear close to the transition point between the wurtzite and sphalerite phases, and their formation may be influenced by the thermal history of the crystal (in annealed crystals, the contribution of higher polytypes is markedly reduced). At the vicinity of the transition, an enhanced tendency to form stacking faults is observed. An X-ray and electron microscopic study [1] has allowed for systematis-ing the conditions at which the higher polytypes (4H and 8H) form in bulk $Zn_{1-x}Mg_xSe$ crystals. Additional substitution of Zn atoms by Be atoms was expected to cause an increase of the bandgap value as well as to improve the resistance against defect propagation.

In this work, Rietveld refinement was performed for Bridgman-grown (ZnSe based) crystals exhibiting higher polytypic structures 4H and 8H and for polytypic mixtures involving these phases. Phase analysis[1] has indicated the polytypes occurring in some of those crystals. In $Zn_{0.83}Mg_{0.17}Se$ and $Zn_{0.84}Mg_{0.12}Be_{0.04}Se$ crystals 8H phase with a contribution of 3C phase have been identified, while for $Zn_{0.82}Mg_{0.18}Se$ a 'pure' 4H polytypic structure has been found. For (Zn,Mg,Be)Se, the polytypism is observed for a specific Mg and Be content.

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T1 - P12

SYNTHESIS AND *AB INITIO* STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA OF $K_2ZrSi_3O_9.2H_2O$

A. Ferreira[1], Z. Lin[2], M. R. Soares[3], J. Rocha[2]

[1]*ESTGA, University of Aveiro, Apartado 473, 3754-909 Águeda, Portugal*
[2]*Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[3]*Laboratório Central de Análises, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

The crystal structure of a new potassium zirconosilicate $K_2ZrSi_3O_9.2H_2O$ has been determined *ab initio* from powder X-ray diffraction data. The unit cell is orthorhombic, space group $C222_1$ (no. 20), Z=4 with cell dimensions a = 8.1051(3), b = 10.6842(5), c = 12.0300(5) Å, V = 1041.76(7) Å^3. The structure is made up of ZrO_6 octahedra (MO_6) and SiO_4 tetrahedra (TO_4) by sharing corners. The SiO_4 tetrahedra form a helix chain, periodically repeating every six tetrahedral (step of 12.03 Å), along [001] interconnected by ZrO_6 octahedra, forming a three-dimensional MT framework structure with channels delimited by seven and eight member rings. The potassium ions and water molecules are locate in this channels. The water molecules are reversibly lost on heating that is typical of zeolites and molecular sieves.

Experimental Section
Synthesis. This phase was synthesised by calcination of Umbite [1] in air at 910 C for 30 hours.

Materials Characterisation. Powder XRD data were collected on an X'Pert MPD Philips difractometer (CuK X-radiation) with a curved graphite monochromator, a fix divergence slit of 0.25 , and a flat plate sample holder, in a Bragg-Brentano para-focusing optics configuration. Intensity data were collected by the step counting method (step 0.02 and time 20 s) in the range 2 12–140 .

Results and Discussion
The powder X-ray diffraction pattern was indexed with the PowderX package [2] using the first 20 well resolved lines. The orthorhombic a = 8.110, b = 10.695, c = 12.038 Å was indicated by the TREOR90 indexing program [3] with high figures of merit M_{20} = 40 and F_{20} = 68. The space group was obtained with the programme Chekcell [4] that suggested $C222_1$ (no. 20).

The *ab initio* crystal structure determination from powder XRD data was carried out with Fullprof [5] and EXPO [6]. Firstly, the structure factor amplitudes were extracted by the Le Bail method [7] from the powder pattern in Fullprof and, subsequently, the structures were solved by

direct methods with Expo. Although all atoms were located at once, re-labelling of atoms was required, coupled with changes in bond distances and bond angles. This modus operandi was alternated with least-squares refinements. The coordinates of atoms obtained from direct methods were used in the Rietveld refinement of the structure by the FullProf programme. The final profile analysis refinement was carried out in the range 12.00 – 140 2 .. The final profile fit is shown in Fig. 1. The structure of $K_2ZrSi_3O_9.2H_2O$ are presented in Figure 2.

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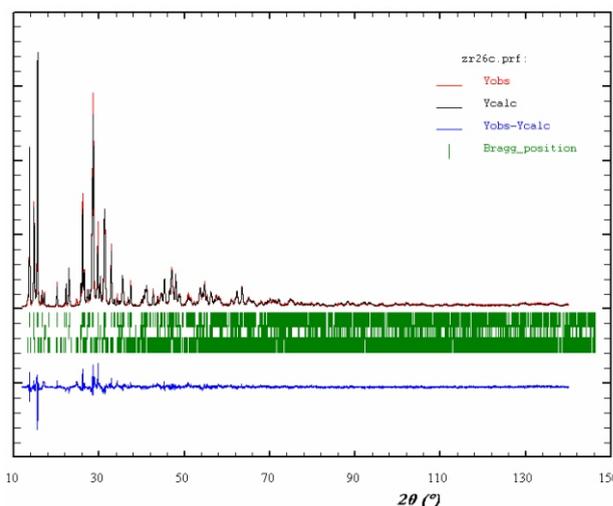
Fig. 1: Observed, calculated, and difference X-ray diffraction patterns of $K_2ZrSi_3O_9.2H_2O$
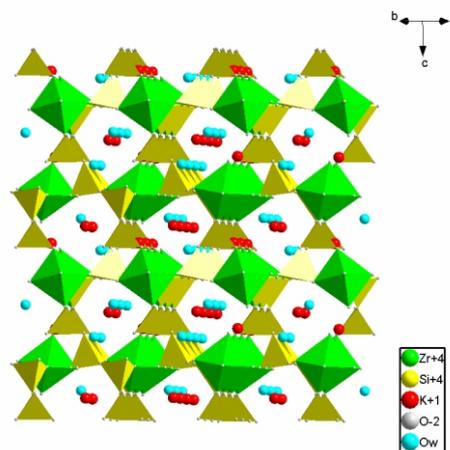
Fig. 2: Projection of the structure of $K_2ZrSi_3O_9.2H_2O$

T1 - P13

CRYSTAL STRUCTURE AND MICROSTRUCTURE OF NANOSIZE Li-La FERRITES

M. Vučinić-Vasić[1], A. S. Nikolić[2], J. Blanusa[3], A. Kremenović[4], S. Rakić[5], A. Kapor[5] and B. Antić[2]

[1]*Faculty of Technical Sciences, University of Novi Sad, Trg D. Obradovica 6, 21000 Novi Sad, Serbia and Montenegro*

[2]*Faculty of Chemistry, Department for Inorganic Chemistry, University of Belgrade, P. O. Box 158, 11001 Belgrade, Serbia and Montenegro*

[3]*Institute of Nuclear Sciences "Vinca", Laboratory of Solid State Physics, P. O. Box 522, 11001 Belgrade, Serbia and Montenegro*

[4]*Faculty of Mining and Geology, Laboratory for Crystallography, University of Belgrade, P. O. Box 162, 11001 Belgrade, Serbia and Montenegro*

[5]*Institute of Physics, University of Novi Sad, Trg D. Obradovica 4, 21000 Novi Sad, Serbia and Montenegro*

Ferrites with spinel structure have a general formula AB_2X_4 with cations occupying two sites, tetrahedral 8a (A site) and octahedral 16d (B site) in the space group (S.G.) Fd-3m. Some spinels possess ordered structure with possible cation ordering at tetrahedral or/and octahedral sites, where this ordering causes formation of two new sublattices in one (or both) A/B sublattice [1]. Nanosize ferrites are important magnetic materials both for application in technology and in basic researches, as convenient systems for studies of nanomagnetism. It is well known that properties of nanomaterials strongly depend on the preparation conditions. One of the most interesting methods for preparation of ultrafine powders is from complex compounds as precursors. Most metals make complexes with -diketonato ligands: acetylacetone (AA), benzoylacetone (BA), dibenzoyl-methane (DBM), trifluoracetone (TFA), etc. [2]. Prepared complex compounds have relatively low temperatures of thermal de-
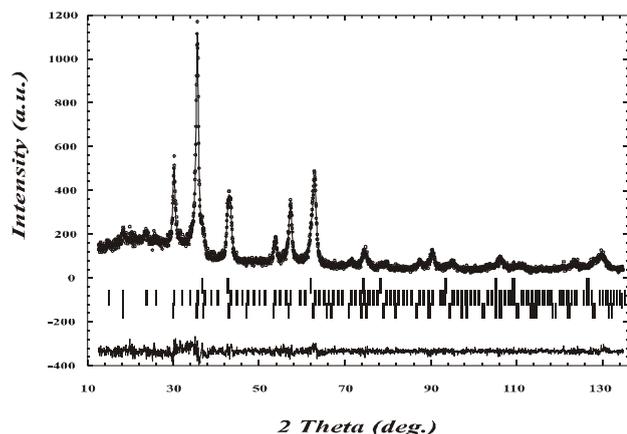
Figure 1. X-ray diffraction patterns of Li-La ferrite sample. Dots denote experimental values, line represents calculated values. The difference between experimental and calculated values is given in the bottom. The vertical bars indicate reflection positions for all three phases separately.
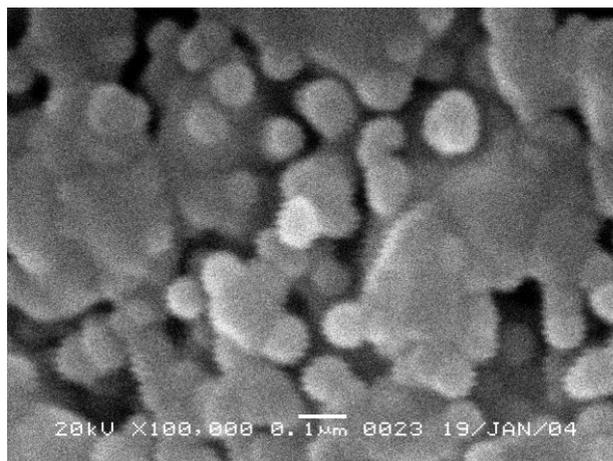
Figure 2. SEM micrograph of particles for Li-La ferrite sample

composition, giving ultrafine powder as a product [2]. Nanosize Li-La ferrite sample was synthesised by thermal decomposition of appropriate mixture of complex compounds with acetylacetone – (2,4 pentadione) ligands ([M(AA)$_x$]; M = Li, La and Fe) in molar ratio 1(Li):0.1(La):4.9(Fe) at 500 C. crystal structures of obtained phases were determined by the Rietveld method. Magnetic properties of ferrites are sensitive on the microstructure. Consequently, one of the aims was microstructure determination.

X-ray diffraction data for ferrite sample was collected at a Philips PW 1830 (CuK radiations) difractometer. The scanning range was 10-110 in 2 , with the step of 0.02 and scanning time of 10s per step. The element analysis (microanalysis) was performed by inductively coupled plasma optical emission spectroscopy (Spectroflame ICP, 2.5KW, 27MHz). Scanning electron microscope (SEM) measurement on the sample was performed on JEOL JSM6460LV. The sample has been sputtered under vacuum with gold metal.

The crystal structure of as-prepared sample was checked by X-ray diffraction. Previously investigation of Li ferrites prepared by the same method has shown that this method leads to multiphase content [3]. ICP element analysis data show La contents larger than in expected phase Li$_{0.5}$La$_{0.05}$Fe$_{2. 45}$O$_4$. To choose an appropriate structure model, we have considered the literature data on the formation of multiphase samples of the Li-ferrites together with the ICP results. Crystal structure refinement for the Li-La ferrite sample, based on three-phase model (Li$_{0.5}$La$_x$Fe$_{2.5-x}$O$_4$+ La$_x$Fe$_3$O$_4$+ LiFeO$_2$) has given the best results. The refinement was performed with the Fullprof computer program [4]. The chemical composition of the present phases was determined by the refinement of the oc-

cupation numbers. The obtained results show good agreement with the ICP element analysis data: 63±3 % of Fe (66±1 % from ICP), 2.2±0.2 % Li (1.73±0.05 % from ICP) and 4.9±0.3 % of La (4.86±0.08 % from ICP). The partial results of the Rietveld refinement listed in Table 1. Diffraction patterns for three phases sample is shown in the Figure 1.

In the crystal structure of Li$_{0.5}$La$_{0.08}$Fe$_{2. 42}$O$_4$ Li$^+$ and Fe^{3+} ions dominantly occupy 4b sites and 12d sites, respectively, while La^{3+} ions preferably occupy octahedral 12d site. However, beside lithium in 4b sites a significant quantity of iron is present, and vice versa for 12d sites. Phase La$_{0.14}$Fe$_3$O$_4$ was produced by lanthanum insertion into Fe$_3$O$_4$. The mechanism of lithium insertion in ferrite with spinel structure was suggested in reference [5].

Microstructure parameters (crystallite size of ~ 11 nm and strain of ~ 1.2 x 10^3) were determined by the Rietveld refinement of the TCH-pV parameters. To simplify model for the profile Rietveld refinement it was assumed that size-strain X-ray line broadening is the same for all three phases. The particle size determined from SEM micrograph (Figure 2) is ~ 50-60 nm. Thus, the particles are composed of few crystallites.

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T1 - P14

SYNTHESIS AND CHARACTERIZATION OF METAL 4-(4'-PHOSPHONOPHENOXY)PHENYL PHOSPHONATES HYBRIDS

A. Cabeza,[1] M.M. Gómez-Alcántara,[1] M. Martínez-Lara,[1] M.A.G. Aranda,[1], R. N. Bhuvanesh,[2] and A. Clearfield[2]

[1]*Departamento de Química Inorgánica, Universidad de Málaga, Campus Teatinos, 29071 Málaga, Spain*
[2]*Department of Chemistry, Texas A & M University, College Station, Texas, 77842-3012, USA*
e-mail: aurelio@uma.es

Hybrid organo-inorganic solids provide numerous compounds whose frameworks are built from the ionocovalent connection of inorganic moieties via organic molecules functionalized by complexing groups such as phosphonates. One of the possible strategies followed to prepare these solids has been the use of alkyl and/or aryl diphosphonates. These phosphonic acids act as cross-linking agents bridging covalently the metal inorganic layers. Therefore, their use could allow manipulation of the length of the carbon chains to increment and modulate the size of the pores. In general, microporous materials are of great importance as molecular sieves, catalysis, ion-exchangers, and sensors materials [1].

Here, we present the synthesis and structural characteristics of a new bisphosphonic acid, 4-(4'-phosphonophenoxy)phenyl phosphonic acid, $[H_2O_3P-C_6H_4]_2$-O, as well as a new family of hybrid materials with transition metals (Mn, Fe, Co, Ni, Cu and Zn) using this bisphosphonic acid as a complexing agent. The structure of the phosphonic acid was determined by single crystal X-ray diffraction. Nine new compounds were isolated depending on the synthesis conditions. Some materials showed low crystallinity, but the Cu and Zn derivatives had high crystallinities.

$Cu_2(O_3PC_6H_4OC_6H_4PO_3)$ crystallizes in an orthorhombic unit cell and its structure was solved by *ab initio* powder diffraction methodology and refined by the Rietveld method to $R_F = 0.042$. Its structure, see Figure 1, shows a pillared layer framework with highly distorted CuO_5 groups sharing edges to give isolated dimmers. The structure of $Zn[HO_3PC_6H_4OC_6H_4PO_3H]$, could be refined by the Rietveld method, $R_F = 0.054$, since it is isostructural with the known compound, $Zn[HO_3P(C_6H_4)_2PO_3H]$ [2]. The synthetic conditions as well as the structural details of the prepared hybrid materials will be presented and discussed.
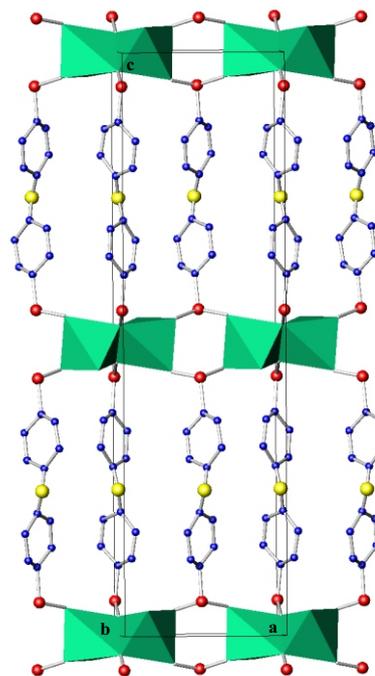
Figure 1: Three dimensional packing of $Cu_2(O_3PC_6H_4OC_6H_4PO_3)$.

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T1 - P15

TOF-NEUTRON STRUCTURE REFINEMENT OF Y- -SiAlON

Lubo Smrčok[1], David Salamon[1], James W.Richardson[2]

[1]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9,*
SK-845 36 Bratislava, Slovak Republic

[2]*Argone National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA*

Silicon nitride form two groups of solid solutions based on -Si_3N_4 and -Si_3N_4 where Si could be replace by Al and N for O. Each group contains engineered material for special applications like construction ceramics that exhibits excellent strength, toughness, hardness and high temperature properties. The term SiAlON was originally coined to describe materials containing mainly Si, Al, O and N, of very wide compositions and different crystal structures [1]. Nowadays the meaning has been more restricted to solid-solution phases with the   or -Si_3N_4 crystal structures, named   and -SiAlONs. Structure of -Si_3N_4 must be stabilized by different ions, e.g. by Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+} or   rare   earths.   The   general   formula   is $M_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$. -SiAlONs are isostructural with -Si_3N_4 where *m* Si-N bonds are replaced by longer *m* Al-N bonds and *n* Si-N bonds by similar *n* Al-O bonds. In recent years there have been several investigations in the field of -SiAlONs regarding phase relationships and the stability area of the -SiAlONs with different rare earth cations [2-4]. These investigations were made in the classical way by determining the phases by X-ray diffraction and in some cases by additional analysis of the microstructure.

Y -Sialon was prepared using the starting powders : 71.95% -Si_3N_4 (Permascand S95P, containing 1.4 wt. % O), 15.48% AlN (HC Starck Grade C, containing 1.6 wt. % O), 9.55% Y_2O_3 (HC Starck 99,99 %), 3.02% La_2O_3 (Merck 99,5%). Theoretically calculated composition is $Y_{0.42}Si_{9.63}Al_{2.37}O_{1.12}N_{14.88}$. This composition takes into account the oxygen content in Si_3N_4 and AlN powders, a small amount extra liquid phase containing 1.0 mol% of Y_2O_3 and 0.4 mol% La_2O_3 was also considered. All starting powders were homogenized in isopropanol with Si_3N_4 balls for 12 h. Powders were dried and pressed into cubic shape under a pressure of 100 MPa, followed by cold isostatic pressing with 250 MPa. Sintering was carried out in a gas-pressure-sintering furnace (GPS, KCE GmbH, Germany) at 1670 °C for 2 hours in 3 MPa nitrogen using fast cooling regime (>100 °C/min) and again at same conditions at 1750 °C for 2 hours using slow cooling regime (7 °C/min).The reason for this temperature regime was to avoid formation of kinetically promoted metastable phases. Final powders were chemically treated in the hot H_3PO to dissolve amorphous phase .

Phase compositions of sintered and chemically cleaned sample were analyzed by X-ray diffraction (Stoe STADI P) using Co*K* radiation. Except for the main Y- -sialon phase the sample contained detectable amount of -Si_3N_4. Time-of-flight neutron powder diffraction data were collected for 3 hours using the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory [5]. For this measurement, the sample was sealed in a 5 cm^3 vanadium container. Time-focussed and summed data in detector banks centered at 2-theta = ±145°, ±125°, ±107°, ±90° and +60° were available for Rietveld analysis. Unrestrained structure refinement was done with the GSAS package [6] using all diffraction data. The initial positions of the atoms were taken from [7]. The list of refined atomic parameters included atomic positions, individual temperature parameters and the occupancy parameter of Y. All attempts to refine Si/Al on O/N occupancies (constrained) led either to occupancy parameters > 1 or to negative temperature parameter(s).
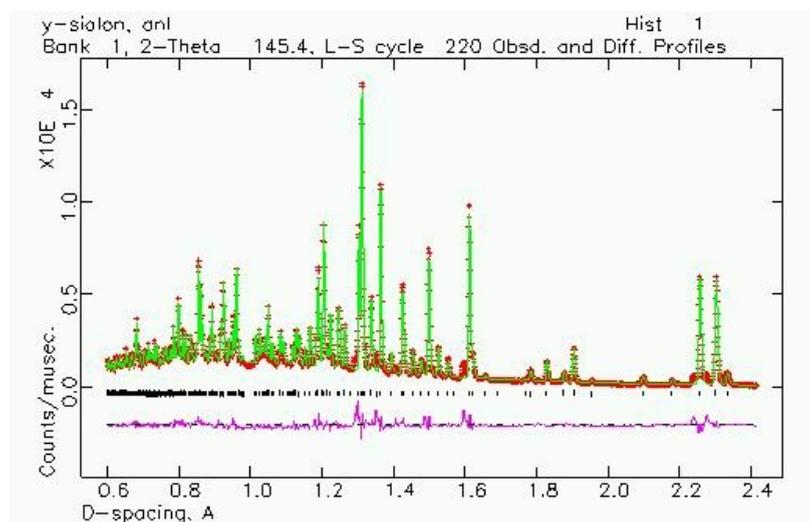
Final interatomic Si-N distances in [SiN$_4$] tetrahedra varied from 1.722 to 1.770 Å. Those values are in good agreement with 1.704-1.767 Å found for -Si$_3$N$_4$ from X-ray single crystal data [8]. The Y-atom is irregularly coordinated by seven N-atoms (1x2.27, 6x2.66 Å).

The unit cell contents calculated using refined Y-occupancy is Y$_{0.58}$Si$_{12}$N$_{16}$.

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T1 - P16

CRYSTAL STRUCTURE STUDY OF THE SEMICONDUCTING SYSTEM Ag-In-VI (VI = S, Se, Te) BY X-RAY POWDER DIFFRACTION

Gerzon E. Delgado[1], Asiloé J. Mora[1], Tibaire Tinoco[2], Carlos Pineda[2]

[1]*Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias,*
[2]*Centro de Estudios Avanzados en Óptica, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela*

Introduction

The ternary silver chalcogenides of the type Ag-In-VI (VI = S, Se, Te) form very stable stoichiometric compounds with potential application in non-linear optics and solar cells [1,2], due to its electro-physical properties independent of impurities [2]. Stoichiometric compounds with three compositions can be found: AgInVI$_2$, AgIn$_3$VI$_5$ and AgIn$_5$VI$_8$. These materials belong to the normal structure compounds (I III VI$_2$) and the defect structure compounds (I III$_3$ VI$_5$, I III$_5\square_2$VI$_8$), respectively [3]. Compositions of the type AgIn$_3$VI$_5$ has not been reported in the literature. In this work, we present the structural characterization of some members of the system Ag-In-VI, using X-ray powder diffraction.

Experimental

The samples were synthesized by the melt and annealing technique. Stoichiometric quantities of Ag, In and X (S, Se, Te) were evacuated in sealed quartz ampoules and deposited into an one zone furnace, and then submitted to direct fusion. Chemical analysis of the resultant ingots were carried out with a Hitachi S-2500 SEM equipped with a Kevex EDX accessory. Small quantities of each the samples were ground mechanically in an agate mortar and pestle. The resulting fine powders were mounted on a flat zero-background holder. The X-ray powder diffraction data were collected at room temperature, in / reflection mode using a Siemens D5005 diffractometer (Bragg-Brentano) equipped with an X-ray tube (CuKá radiation; 40kV, 30mA) and a diffracted beam graphite

AgInS$_2$
(orthorhombic, Pna2$_1$)   AgIn$_5$S$_8$ (cubic, Fd-3m)
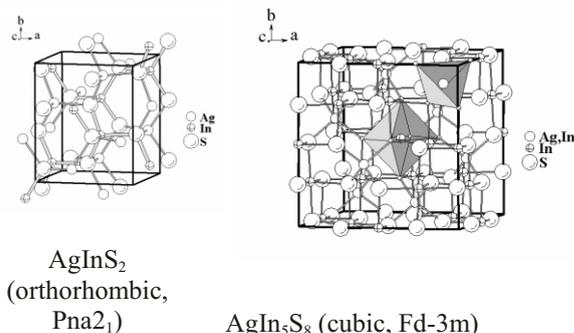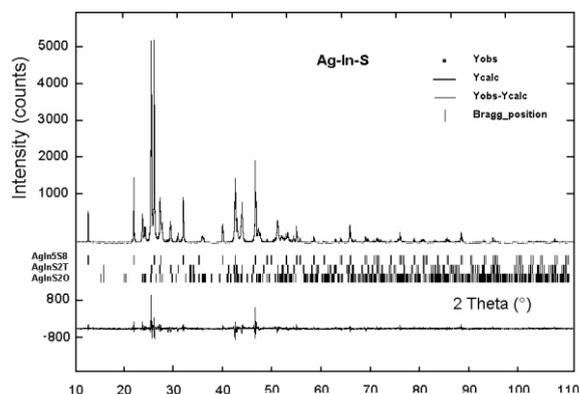
Figure 1. (a) Final Rietveld refinement plot for the three phases of the Ag-In-S system. (b) Unit cell diagram of AgInS$_2$ (orthorhombic) and AgIn$_5$S$_8$ (cubic) phases.
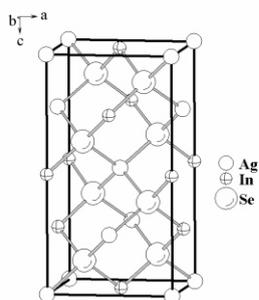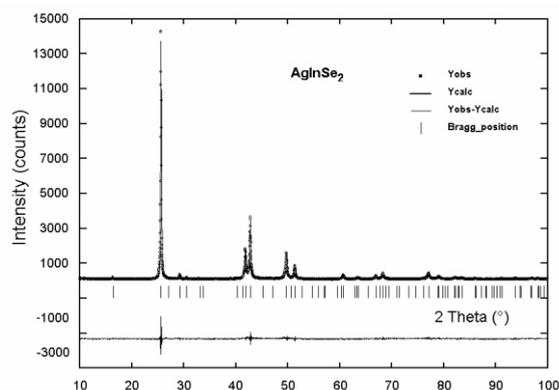
Figure 2. Final Rietveld refinement plot for AgInSe$_2$ and unit cell diagram

Figure 3. Final Rietveld refinement plot for AgIn$_5$Te$_8$ and unit cell diagram showing the tetrahedral coordination around the cations

monochromator. All the Rietveld refinements were carried out using the Fullprof program [4] available in the software package WinPlotr [5].

Results and discussion

In the Ag-In-S system, three phases were simultaneously characterized from a single X-ray powder diffraction pattern using the Rietveld method [6]. The X-ray powder pattern was composed of AgIn$_5$S$_8$ (42.7%), AgInS$_2$ tetragonal phase (32.7%) and AgInS$_2$ orthorhombic phase (24.6%) [7]. The AgIn$_5$S$_8$ crystallizes in the cubic space group $Fd\bar{3}m$, Z = 8, with a = 10.8265(2) Å, in a spinel-type structure. The description of the structure of AgIn$_5$S$_8$ in this space group implies a random distribution of the Ag and In atoms among the tetrahedral sites. The AgInS$_2$ ternary compound crystallizes in two polymorphs: a tetragonal chalcopyrite-type phase ($I\bar{4}2d$), Z = 4, with unit cell parameters a = 5.8760(2) Å, c = 11.2007(7) Å, and an orthorhombic wurtzite-like phase (Pna2$_1$), Z = 4, with a = 6.9972(6) Å , b = 8.2733(6) Å, c = 6.6939(6) Å. These structures can be described as a derivative of the sphalerite structure and the wurtzite structure, respectively. Ag-S and In-S average distances in both structures are 2.58(5) Å and 2.44(5) Å, respectively.

For the Ag-In-Se system, a chalcopyrite-type structure was found with composition AgInSe$_2$. This compound crystallizes with tetragonal symmetry ($I\bar{4}2d$) and unit cell parameters: a = 6.1010(8) Å, c = 11.708(2) Å. The Ag-Se bond distance is 2.621(2) Å and In-Se 2.593(2) Å.

For the Ag-In-Te system, AgIn$_5$Te$_8$ is isostructural with the AgIn$_5$Se$_8$ compound [8]. Crystallize in the tetragonal space group $P\bar{4}2m$ with a = 6.1952(2) Å, c = 12.419(4) Å,

and consists of a three-dimensional arrangement of distorted AgTe$_4$ and InTe$_4$ tetrahedra connected by common faces [9]. The Ag-Te [2.890(6) Å] and In-Te [2.764(7) Å] bond distances agree well with those observed in other adamantane structures such as AgGaTe$_2$, LiInTe$_2$, CuInTe$_2$, MnIn$_2$Te$_4$ and CdIn$_2$Te$_4$.

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