

done to introduce carriers, holes or electrons, into these layers by chemical substitutions on the cations sites [6-7]. Some authors claimed the presence of superconductivity around 20 K, however this result was not clearly confirmed by other works. We report here on the synthesis of the compounds $(\text{Ba,Sr})_{2-x}\text{K}_x\text{Cu}_3\text{O}_4\text{Cl}_2$ and $(\text{Ba,Sr})_2\text{Cu}_{3-y}\text{O}_4\text{Cl}_2$ in air and under oxygen flux, where the hole doping is respectively achieved by chemical substitution and copper site deficiency. Their structures are resolved by powder x-ray diffraction using the Rietveld method. The variations of the unit-cell parameters and the inter-atomic distances versus x and y are discussed according to the formal charge distributions in the structure [8]. Moreover, the averaged ionic sizes are also invoked to interpret the stability range of such phases.

[1] R. Kipka, H. Mueller-Buschbaum, *Zeitschrift fuer Anorganische und Allgemeine Chemie* 419, **1976**, 58. [2] B. Grande, H. Mueller-Buschbaum, *Zeitschrift fuer Naturforschung, Teil B. Anorganische Chemie*, 31, **1976**, 405. [3] S. Noro, K. Matunoshita, M. Suzuki, S. Yamada, *Physica B* 366, **2005**, 74. [4] S. Noro, Y. Tuyuki, R. Nakano, Y. Medai, *Physica B* 322, **2002**, 57. [5] K. Ruck, D. Eckert, G. Krabbes, M. Wolf, K.-H. Muller, *J. Solid State Chem.* 141, **1998**, 37. [6] Jinhua Ye, Zhigang Zou, and Akiyuki Matsushita *Physica C* 341-348, **2000**, 489. [7] M. S. da Luz, C. A. M. dos Santos, A. J. S. Machado, B. Ferreira, *Brazilian Journal of Physics.* 32, **2002**, 744. [8] Abderrahim Benabbas, *Acta Cryst.* B62, **2006**, 9–15.

Keywords: copper oxide superconductors; crystal structures; powder diffraction analysis

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Structure and Microstructure of the Solid Solution $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3$ and the Origin of Unusual Evolutions of the Unit-cell Constants of the Nasicon Structures. Nedjemeddine Bounar^a, Abderrahim Benabbas^a. ^a*L.I.M.E Laboratory. University Of Jijel. B.P. 98 Ouled-Aissa 18000 Jijel. Algeria.*

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Nasicon [1] compound have been extensively investigated owing to their interesting physical properties with potential applications as fast ion conductors and low thermal expansions ceramics [2-4]. The Nasicon structure is built up of corner-sharing BO_6 octahedra and PO_4 tetrahedra leading to a frame-work of $\text{B}_2\text{P}_3\text{O}_{12}$ formulas with interconnected channels where cations can be inserted in two types of sites usually noted M_1 at (0,0,0) and M_2 at (2/3,0,1/4) The great flexibility of this structure allows large chemical substitutions and makes it possible that the sites M_1 and M_2 may be empty as in $\text{Nb}_2(\text{PO}_{4/3})_3$, partially occupied or completely full as in $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$. The ionic transport in these compounds is due to the migration of the cations through the cavities in the interconnected channels where an order-disorder phenomenon is possible in the partially filled cases. On the other hand, the thermal behaviour is related to the variation of lattice parameters vs. temperature generally variable in opposite senses. Thus, the detailed structural characterisation particularly of the atomic positions and the bond lengths is essential to understand the underlying mechanisms and to optimise such properties.

Our study deals with the structural and micro-structural characterisations of the solid solution $\text{LiTi}_{2-x}\text{Sn}_x(\text{PO}_4)_3$ using the powder X-ray diffraction and the Rietveld refinements. A comparative study is made with the Na-analog phases [5-6] and a global approach is proposed to explain the structural features of the Nasicon phases, that is, the origin of unusual evolutions of the unit-cell constants.

[1]- L. Hagman and P. Kierkegaard, *Acta Chem. Scand.* 22, **1968**, 1822. [2]- J. B. Goodenough, H. Y.-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.* 11, **1976**, 203. [3]- T. Maruyama, S. Sasaki, and Y. Saito, *Solid State Ionics* 23, **1987**, 107. [4]- A. Aatiq, C. Delmas, A. El Jazouli, *Journal of Solid State Chemistry* 158, **2001**, 169. [5]- M.P. Carrasco, M. C. Guillem, and J. Alamo, *Mat. Res. Bull.* 27, **1992**, 603. [6]- M.P. Carrasco, M. C. Guillem, and J. Alamo, *Mat. Res. Bull.*, 28, **1993**, 547.

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FA5-MS01-P08

Structural Resolution of One Lanthanide Phosphonate Family, Combining Monocrystal and Powder Diffraction Data. Eva Fernández-Zapico^a, Jose Montejo^a, Laura Rocés^a, Santiago García-Granda^a, Sergei A. Khainakov^b, José R. García^b, Feng-Yi Liu^c, João Rocha^c. ^a*Departments of Physical and Analytical Chemistry.* ^b*Organic and Inorganic Chemistry, University of Oviedo, Spain.* ^c*Chemistry, CICECO, University of Aveiro, Portugal.*

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Metal phosphonate chemistry is of great interest in material science due to their potential applications in many fields such as ion-exchange, catalysis, and sensor devices. Often, metal phosphonates exhibit polymeric structures consisting of chains, layers, or three-dimensional networks, but monomeric structures are also known. In particular, the tunable organic units in diphosphonate $[\text{R}(\text{PO}_3)_2]$ allow the construction of metal phosphonate materials with new architectures. We have recently reported the crystal structure of $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]\text{La}[\text{hedpH}][\text{hedpH}_2]$. The crystal structure of this compound, which crystallize in space group P-1, is built up from one-dimensional covalent lanthanum phosphonate cross-linked chains and $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^+$ cations [1,2]. Following with the work previously developed [3] we presented here single crystal data of new members of this family, and new structures solved by combination of the known single crystal data and the powder data of the new structures. The powder data were measured in ESRF Synchrotron (Spline). It has been carried out a Rietveld refinement using FullProf with the heavy atoms being the geometry of the remaining H-atoms completed using Mercury. The final structural results show the isostructurality of all compounds, the differences on the intra and intermolecular network will be presented and discussed.

[1] Rocés, L., García-Granda, S., García, J.R., Liu, F., Carlos, L.D. *Acta Cryst.*, **2006**, A62, s268. [2] Liu, F.-Y., Rocés, L., Sa Ferreira, R. A., García-Granda, S., García, J. R., Carlos, L. D., Rocha, J., J.

Mater. Chem., **2007**, 17, 3696. [3] E. Fernández-Zapico, L. Roces, S. García-Granda, J.R. García, F. Liu, J. Rocha, *Acta Cryst.*, **2007**, A63, s183.

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Keywords: lanthanides; phosphonates; singlecrystal; powder diffraction; structural characterization; rietveld

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Polytypism, Polymorphism and Compositional Faults in Layered Ternary and Quaternary Compounds. Mahmud Kyazumov^a, Lale Rustamova^a, Mahbub Kazimov^a. ^a*Institute of Physics of the National Academy of Sciences of Azerbaijan, Baku, Azerbaijan.*

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It has been determined that on depend on various growth conditions in crystals and type of their synthesis the multicomponent layered crystals have a big variety of polytypic and polymorphic modifications. Not only separate crystal's bits taken from various places of the same ampoule may distinguish by their structures but many other polytypic phases can also exist in the same crystal. It is naturally that the presence of one phase on the basis of another one is connecting with packing defects of sulphur atoms and formation of cation's base of a new phase. Deficit of sulphur atoms as a rule is leading to change the cation's valency in crystals as a result of which the ionic radii of cations are also changed and element's base of a new phase is forming. An increase of octahedral (O) position's shares due to decrease of tetrahedral (T) ones in $\text{O}^{\text{I}}\text{O}^{\text{II}}\text{O}^{\text{III}}$, $\text{O}^{\text{I}}\text{O}^{\text{II}}$, $\text{O}^{\text{I}}\text{O}^{\text{II}}$, $\text{O}^{\text{I}}\text{O}^{\text{II}}\text{O}^{\text{III}}$ types of structural units stimulates creation of such a phases. In shares of the octahedral position in common tetrahedral and octahedral share's positions are as followed: 20%, 25%, 33%, 50%, 50%, 50%, 60%. In case when cations have a permanent valences a creation of a new phase becomes impossible and for packing defects of sulphur atoms only compositional faults are coming up.

Keywords: polytypism; polymorphism; layered compounds

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Two-Level Genetic Algorithm for Direct-Space Structure Solution and Refinement. Yaroslav I. Yakimov^a, Eugene S. Semenko^a, Igor S. Yakimov^a. ^a*Siberian Federal University, Krasnoyarsk, Russian Federation.*

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Genetic algorithms (GA) have been used to generate crystal structure models from the knowledge of only the

unit cell and constituent elements by powder diffraction data in the direct space [1]. This work is dedicated to GA spread-out to Rietveld method including full-profile fitting and refinement of crystal structure models. A two-level genetic algorithm has been developed for this purpose. The two-level genetic algorithm is based on a combination of conventional GA similar to [2] with a new Rietveld-like derivative difference minimization (DDM) method [3]. First-level GA chromosomes comprise values of profile and structure parameters used in the Rietveld method. Since initial population is generated randomly, a priori known parameter values are not required. GA fitness function is based on the weighted profile R-factor of DDM (R_{DDM}). Second-level GA chromosomes are bit strings containing one bit per parameter of first-level parameter string, where bit values specify parameters to be refined with the DDM on a current iteration. In whole, a path of local descent on R_{DDM} - hypersurface is defined by second-level GA. Both levels are executed alternately with transferring better found parameter values to another level.

The algorithm was tested on some powder patterns of single and multi-phase samples with known crystal structures. As an example, the crystal structure of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ which initially had been solved from powder diffraction data by the Patterson method [4] was found from X-ray powder diffraction data by applying the proposed GA method. All general atomic coordinates and thermal factors including coordinates of hydrogen atoms were searched and refined successfully in a fully automatic way (26 structural parameters in total). The GA was applied for quantitative phase analysis of three- and four-phase samples CPD1 and CPD2 from Round Robin on QPA [5] as well. All profile parameters, general atomic coordinates and thermal factors (20 profile and 9 structural parameters in total in case of CPD1 sample) were searched with the GA simultaneously and then phase concentrations were calculated as usual for QPA by Rietveld method with mean error about 0.3% mass.

[1] Rizzi, R. (Ed.), *CPD IUCr Newsletter*, **2007**, 35. [2] Turner, G.W., Tedesco, E., Harris, K.D.M., Johnston, R.L., Kariuki, B.M., *Chem. Phys. Lett.*, **2000**, 321, 183. [3] Solovyov, L.A., *J. Appl. Cryst.*, **2004**, 37, 743. [4] Blokhin, A.I., Solovyov, L.A., Blokhina, M.L., Yakimov, I.S., Kirik, S.D., *Rus. J. Coord. Chem.*, **1996**, 22, 185. [5] Scarlett, N.V.Y., Madsen, I.C., Cranswick, L.M.D., Lwin, T., Groleau, E., Stephenson, G., Aylmore, M., Agron-Olshina, N., *J. Appl. Cryst.*, **2002**, 35, 383.

Keywords: genetic algorithm; structure solution; powder diffraction

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Successful Cryocooling of Protein Microcrystalline Samples for Powder Diffraction. Yves Watier^{a*}, Irene Margiolaki^a, Jonathan Wright^a, Andrew Fitch^a, Mathias Norrman^b, Gerd Schluckebier^b. ^a*European Synchrotron Radiation Facility (ESRF), Grenoble, France.* ^b*Novo Nordisk A/S, Copenhagen.*

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