

**FA5-MS01-P04**

**Crystal Structures of Six Industrial Benzimidazolone Pigments from X-ray Powder Data.** Svetlana N. Ivashevskaya<sup>a</sup>, Jacco van de Streek<sup>b</sup>, Martin U. Schmidt<sup>c</sup>, Jürgen Brüning<sup>c</sup>, Martin Ermrich<sup>d</sup>. <sup>a</sup>*Institute of Geology Karelian Research Centre RAS, Petrozavodsk, Russia.* <sup>b</sup>*Avant-garde Materials Simulation, Freiburg, Germany.* <sup>c</sup>*Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt, Frankfurt am Main, Germany.* <sup>d</sup>*Röntgenlabor Dr. Ermrich, Am Kandelborn 7, D-64354 Reinheim, Germany.*  
E-mail: [ivashevskaja@yahoo.com](mailto:ivashevskaja@yahoo.com)

Solving the crystal structures of organic pigments is not just an academic exercise: the majority of organic pigments are polymorphic, and the polymorphic form determines the colouristic properties. Pigments are practically insoluble in their application media; their crystal structures are maintained and the properties of the final product depend on the solid state structure.

Benzimidazolone pigments cover the spectrum from greenish yellow to orange and are produced industrially on a large scale. They have an excellent fastness to light and weathering and good hiding power. They are used in the automobile industry, to colour plastics and as high grade printing inks [1].

On account of very low solubility of pigments in all solvents, it was impossible to grow single crystals suitable for X-ray analysis. For a better understanding of the pigments' properties, their crystal structures were determined from laboratory X-ray powder diffraction data.

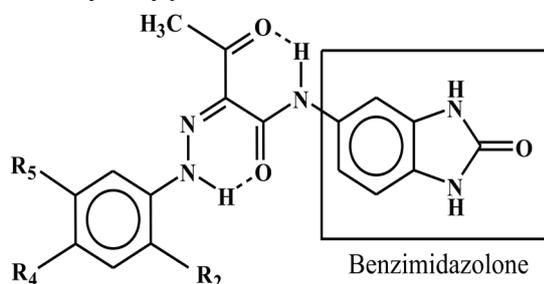


Fig. 1 The general framework of the benzimidazolone pigments.

The crystal structures of six benzimidazolone pigments were determined from laboratory X-ray powder diffraction data by real-space methods using the programs *DASH* [2] and *MRIA* [3]. Powder patterns were indexed by the program *DICVOL91* [4]. Rietveld refinements were carried out with *TOPAS* [5].

All crystal structures are different and exhibit five different hydrogen-bond topologies. Apparently, the good application properties of the benzimidazolone pigments are the result of a combination of efficient molecular packing and strong intermolecular hydrogen bonds.

[1] Herbst W. & Hunger K., 2004, *Industrial Organic Pigments: Production, Properties, Applications*. 3th ed. Weinheim: Wiley-

VCH. [2] David W.I.F., Shankland K., van de Streek J., Pidcock E., Motherwell W.D.S. & Cole J.C., *J. Appl. Cryst.*, 2006, 39, 910. [3] Zlokazov V.B. & Chernyshev V.V., *J. Appl. Cryst.*, 1992, 25, 447. [4] Boulitif A. & Louër D., *J. Appl. Crystallogr.*, 1991, 24, 987. [5] Coelho A.A., *TOPAS-Academic 4.1 Version 4*, 2007.

**Keywords:** crystal structure determination; X-ray powder data; pigments

**FA5-MS01-P05**

**In situ X-ray Diffraction Study of Titanium Sesquioxide.** Afir Arezki. *Université des sciences et de la technologie USTHB, Faculté de chimie - BP 32 El-Alia, Bab Ezzouar - Alger, Algeria.*  
E-mail: [houriachikh@yahoo.fr](mailto:houriachikh@yahoo.fr)

High-temperature X-rays diffractometry is used to study  $Ti_2O_3$  rhombohedral oxide formed by reduction of titanium dioxide, under vacuum and in the presence of graphite or metallic titanium. The sesquioxide is characterized by a homogeneous field of very low oxygen pressure, both boundary phase appearing independently from one another between 800 and 1715°C. The  $c/a = 2.660$  value for  $Ti_{2-x}O_3$  oxidized from of the equivalent hexagonal cell reaches  $c/a = 2.735$  for  $Ti_2O_3$  reduced form, which does not undergo quenching ( $c/a = 2.640$  at room temperature)

**FA5-MS01-P06**

**Synthesis and Crystal Structures of the Hole-doped Oxy-chlorides  $(Ba,Sr)_2Cu_3O_4Cl_2$ .** Abderrahim Benabbas. *L.I.M.E Laboratory. University Of Jijel. B.P. 98 Ouled-Aissa 18000 Jijel. Algeria.*  
E-mail: [Abderrahim.benabbas@gmail.com](mailto:Abderrahim.benabbas@gmail.com)

There is still no general microscopic model for superconductivity, particularly for high-Tc cuprates both in their normal, pseudo-gap and superconductor states. Any proposition of such mechanisms should need the knowledge of accurate details of the crystal structures and their evolution with doping, temperature, pressure... The crystal structures of high-Tc cuprates are composed of the so-called charge-reservoir blocks and  $CuO_2$  planes where the superconductivity is thought to take place. In the undoped compositions, these materials are antiferromagnetic insulators. The long-range magnetic order is destroyed upon doping and is replaced by superconductivity.  $(Ba,Sr)_2Cu_3O_4Cl_2$  oxychloride [1-2] noted 2342 is a prototype of these undoped compounds since it is an antiferromagnet with a layered body-centred tetragonal structure which presents great similarities either to that of  $La_2CuO_4$  or to an anion-ordered perovskite one. However, this phase is slightly different since it has a  $Cu_3O_4$  planes with two independent Cu-sites. The Two-thirds of these sites (A-sites) are surrounded by four equatorial oxygen and two apical chlorine anions and the rest (B-sites) are coordinated by four oxygen. These sites interact by super-exchange along  $Cu_A-O-Cu_A$  or along  $Cu_A-O-Cu_B$  [3-5]. Magnetization measurements show two transitions at  $T \approx 380$  K and  $T \approx 40$  K corresponding to the ordering of moments in the sub-lattices indicated before. In order to obtain superconductivity, several attempts were

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

#### FA5-MS01-P07

**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<sup>a</sup>, Abderrahim Benabbas<sup>a</sup>. <sup>a</sup>*L.I.M.E Laboratory. University Of Jijel. B.P. 98 Ouled-Aissa 18000 Jijel. Algeria.*

E-mail: [nedjmbounar@yahoo.fr](mailto:nedjmbounar@yahoo.fr)

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  $\text{BO}_6$  octahedra and  $\text{PO}_4$  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.

**Keywords:** nasicon; crystal structures; powder diffraction analysis

#### FA5-MS01-P08

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

E-mail: [fernandezeva.uo@uniovi.es](mailto:fernandezeva.uo@uniovi.es)

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.