

the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

**Keywords:** phase transitions in solids, thermodynamics, X-ray synchrotron powder diffraction

#### P.08.06.6

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#### Diffusion Path Formation for Cu<sup>+</sup> Ions in Superionic Cu<sub>6</sub>PS<sub>5</sub>I Single Crystal

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The knowledge of structural transformations to phases characterized by high ionic conductivity remains still very important in understanding the mechanisms and structural conditions supporting high mobility of ions in solids.

Trying to understand the mechanism for superionic conductivity of Cu<sup>+</sup> ions in Cu<sub>6</sub>PS<sub>5</sub>I argyrodite compound the detailed structure analysis based on single-crystal X-ray diffraction was performed. The main interest was focused on a new cubic superstructure F-43c, stable from 140K to 275K. In the range of this phase ordering of copper ions occurs. The final structure model is given including the detailed temperature evolution of site occupation factors of copper ions. Possible diffusion paths for the copper Cu<sup>+</sup> ions are represented by means of the atomic displacement factors and split model. Ordering process of Cu<sup>+</sup> ions with temperature lowering is found to be similar with ordering of copper in β-Cu<sub>7</sub>PSe<sub>6</sub> [1].

Comparison of the structural data with non-Arrhenius behavior of conductivity [2] indicates significant change in conduction mechanism with temperature increasing: from hopping to liquid like behavior.

[1] Gaudin E., et al., *Acta Cryst.*, 2000, B56, 402-408. [2] Beeken R.B., et al., *Journal of Physic and Chemistry of Solids*, 2003, 64, 1261-1264.

**Keywords:** ionic conductors, phase transition and structure, copper ions

#### P.08.06.7

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#### Tensor Distinction of Domain States in Ferroic Phase Transitions

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Distinction of domain states in ferroic phase transitions by their tensor properties is of importance in domain engineering. This is simple if the ferroic group is a halving subgroup of the parent group. In such cases there are two domains which differ only by the sign of primary transition parameter. However, even in these cases we may run into complications if the transition parameter is not a cartesian tensor components but a linear combination of such components as in cases of parent groups of tetragonal and higher symmetries. For ferroic transitions associated with two- and three-dimensional *R-ireps* we meet even more complicated relations which are a consequence of the fact that symmetry allowed tensor forms are invariants of the symmetry groups while their cartesian components are generally not invariant. The use of the ordinary transformation formulae is awkward and error inviting in these cases.

Transition parameters are generally expressed as components of tensorial covariants [1]. To find changes of cartesian components at the ferroic transition we proposed a method consisting of "labelling of covariants" followed by "conversion equations" This method facilitates the description of individual domain states in terms of cartesian tensor components and hence also their distinction.

[1] Kopský V., *Phase Transitions*, 2001, 73, No.1-2, 1-422.

**Keywords:** domain states, labelling of covariants, conversion equations

#### P.08.06.8

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#### Maximal Symmetry Transition Paths for Reconstructive Phase Transitions

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The transition path of a phase transition with no group-subgroup relation between their phases (as reconstructive phase transitions) can be defined as the set of atomic displacements, and strains that should occur at a local level during the transformation. The maximal symmetry transition paths are characterized by intermediate structural configurations with symmetries given by maximal common subgroups of the space groups of the two end phases. Additional symmetry constraints follow from the compatibility conditions of the occupied atomic positions at both ends of the path. By definition, the symmetry of any possible transition path must be among those maximal symmetry paths, or their subgroups. Recently, we have developed a systematic procedure for the determination of the full set of possible maximal transition paths between two structure types with no group-subgroup relations between their symmetries. A computer program has been implemented at the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>) [1].

Here we present the results of our search of maximal symmetry transition-paths for some typical cases of reconstructive phase transitions (*e.g.* wurtzite to rocksalt, wurtzite to zinblende or zinblende to rocksalt structure types, *etc.*) [2].

[1] Kroumova E., Perez-Mato J.M., Aroyo M.I., Kirov A., Capillas C., Ivantchev S., Wondratschek H., *Phase Transitions*, 2003, 76, 155-170. [2] Perez-Mato J.M., Aroyo M.I., Capillas C., Blaha P., Schwarz, *Phys. Rev. Lett.*, 2003, 90, 4, 049603.

**Keywords:** reconstructive transitions, maximal transition paths, Bilbao crystallographic server

#### P.08.06.9

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#### Melting and Freezing of Bi Nanoclusters Embedded in Glass

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Bi-glass nanocomposites were obtained by quenching homogeneous Bi-doped soda-borate melts followed by an annealing at  $T = T_a$ . This process induces the formation of spherical Bi nanoclusters embedded in a glass matrix [1]. Since  $T_a \neq T_{mb}$ ,  $T_{mb}$  being the melting temperature of bulk Bi, we have in fact obtained liquid Bi droplets that, after cooling, became spherical nanocrystals. The nanocrystal-to-liquid transition was investigated using simultaneously the SAXS and WAXS techniques [2]. The melting temperature  $T_m$  decreases for decreasing radius and is a linear function of  $1/R$ ,  $T_m = T_{mb} - a/R$ ,  $a$  being a positive constant related to surface energy parameters. For Bi nanocrystals with  $R = 1.5$  nm, the magnitude of the melting temperature reduction is about 200 K. An additional study of the liquid-to-crystal transition was performed. The freezing temperature of bulk Bi,  $T_{cb}$ , is much lower than  $T_{mb}$ , ( $T_{mb} - T_{cb} = 150$  K). We have established that the freezing temperature also decreases linearly for increasing values of  $(1/R)$ , but at a rate lower than the melting temperature, in such a way that the magnitude of the overcooling is progressively reduced for nanodroplets with decreasing radius. The overcooling vanishes for droplets with radius close to 2 nm. The linear nature of  $T_c$  vs.  $1/R$  is explained by using a simple thermodynamic model of heterogeneous crystal nucleation at the liquid-glass interfaces.

[1] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2003, 67, 085405. [2] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2002, 65, 134204.

**Keywords:** nanocrystals, melting, SAXS WAXS

**P.08.06.10***Acta Cryst.* (2005). A61, C321**Jahn Teller Transition Phase in  $\text{Cu}_{0.5}\text{TiO}(\text{PO}_4)$  Oxyphosphate**

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In our research interest on titanium oxyphosphates, several compounds  $\text{M}^{\text{II}}_{0.5}\text{TiO}(\text{PO}_4)$  have been prepared with  $\text{M}^{\text{II}} = \text{Mg}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ . They all belong to the monoclinic  $\text{P2}_1/\text{c}$  structural type determined "ab initio" for  $\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$  from X-ray powder diffraction [1]. Thermostructural study of  $\text{Cu}_{0.5}\text{TiO}(\text{PO}_4)$  shows a phase transition  $\alpha \rightarrow \beta$  ( $\sim 800^\circ\text{C}$  during heating,  $\sim 400^\circ\text{C}$  during cooling).

Single crystals of the  $\alpha$  phase have been obtained. Its cell presents a Jahn Teller deformation with Cu-O elongation in the (a,c) plane:  $a=7.5612(4)$ ;  $b=7.0919(4)$ ;  $c=7.4874(4)\text{Å}$ ;  $\beta=122.25(6)^\circ$ ;  $V=339.55(6)\text{Å}^3$ . The single crystal structure confirms and states more precisely the previous powder model ( $R_1=0.023$ ;  $wR_2=0.063$ ).

The  $\beta$  phase has been obtained stabilised at room temperature in a powder mixture  $\alpha(38\%)+\beta(62\%)$  without impurities. X-ray diffraction pattern of this powder can be indexed in a like  $\alpha$ -type  $\text{P2}_1/\text{c}$  monoclinic cell:  $a=7.1081(10)$ ;  $b=7.7384(12)$ ;  $c=7.3013(10)\text{Å}$ ;  $\beta=119.28(1)^\circ$ ;  $V=350.3(1)\text{Å}^3$ . As the  $\alpha$ -structure is not a good starting model for Rietveld refinement (divergence), an "ab-initio" structure determination has been done. The refined structure corresponds to a "rocking" of the Jahn Teller elongation from the (a,c) plane to the b direction.

[1] Graveriau P., Chaminade J.P., Manoun B., Krimi S., El Jazouli A., *Powder Diff.*, 1999, 14, n.1, 10.

**Keywords:** oxyphosphates, phase transition, Jahn Teller effect

**P.08.06.11***Acta Cryst.* (2005). A61, C321**A Temperature-Induced Phase Transition in Barbituric Acid Dihydrate**

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In recent years the subject of phase transitions has become more and more popular for scientific investigation. Indeed virtually the whole of the January 2005 issue of *Acta Crystallographica Section A: Foundations of Crystallography* was devoted to the topic. By a combination of careful experimentation and some serendipitous good fortune we have determined a phase transition at low temperature in barbituric acid dihydrate.

The structure of barbituric acid dihydrate appears twice in the literature: an X-ray study [1] and a neutron study [2]. Both sets of experiments were carried out at room temperature and both report the crystal system and space group as orthorhombic Pnma. We have found that this only holds true at temperatures above  $\sim 220\text{K}$ . Below  $\sim 200\text{K}$  the structure is non-merohedrally twinned monoclinic  $\text{P2}_1/\text{n}$ , and at intermediate temperatures it appears to be a *mélange* of sorts of both crystal systems.

[1] Jeffrey G.A., Ghose S., Warwicker J.O., *Acta Cryst.*, 1961, 14, 881. [2] Al-Karaghoulis A.R., Abdul-Wahab B., Ajaj E., Al-Asaff S., *Acta Cryst.*, 1977, B33, 1655.

**Keywords:** organic phase transitions, variable-temperature study, single-crystal structure determination

**P.08.06.12***Acta Cryst.* (2005). A61, C321**An Order-Disorder Phase Transition in  $[\text{Ag}(\text{bipy})\text{NO}_3]_n$** 

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The room temperature *Fddd* form of  $\text{Ag}(\text{bipy})\text{NO}_3$  contains a disordered  $\text{NO}_3$  ion and shows previously unreported planes of diffuse scattering indexed as  $3k \pm l = 4n$  for the 296 K,  $a$  12.8424(2),  $b$  9.9429(1),  $c$  34.4621(4) Å. Synthetic precession photographs showed the symmetry was *Fddd* at 160 K and above but a loss of systematic absences indicated *F12/d1* (i.e. *C2/c*) at 150 K and below. The 100 K structure, *C2/c*,  $a$  12.751(1),  $b$  9.860(1),  $c$  18.379(2) Å,  $\beta$  109.98(1)° has twin components related by a rotation around  $\mathbf{c}^*$ . The cell for *F12/d1* has  $a' = a$ ,  $b' = b$ ,  $c'$  34.547(2) Å,  $\beta'$  89.68(1)°. Refinement gave a 0.754(1):0.246 twin with no disorder and  $R(F) = 0.022$  for 2294 obsd. rflns. Along a chain alternate, Ag atoms,  $(3b \pm c)/4$  apart, are displaced 0.221(1) Å in opposite directions perpendicular to the chain. Chains are cross linked by Ag–Ag contacts of 2.958(1) Å and Ag–O contacts of 2.749(2) and 2.747(2) Å. The chains zig-zag so that Ag atoms avoid closer contact with the  $\text{NO}_3$ . The 200 K structure, *Fddd*,  $a$  12.823(1),  $b$  9.937(1),  $c$  34.450(1) Å was refined as a 1:1 disorder of all atoms initiated by disordering the 100 K structure. Constrained refinement gave  $R(F) = 0.028$  for 1004 obsd. rflns. The Ag displacements reduced to  $\pm 0.123(3)$  Å. The alternative orientation of the nitrate gave three Ag–O contact distances indicating an intermediate step for a change of local ordering. The diffuse scattering indicates that mistakes in  $\text{NO}_3$  positions cause a localized straightening of the adjacent chains that moves substantial amounts of these chains along their lengths. In contrast, the actual position of a nitrate only affects the closest Ag atoms.

**Keywords:** polymorphic structure, phase transition, order-disorder transition

**P.08.06.13***Acta Cryst.* (2005). A61, C321**Metal-Insulator Transition in Hollandite Vanadate,  $\text{K}_2\text{V}_8\text{O}_{16}$** 

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Vanadium oxides have attracted considerable interest in the novel properties such as metal-insulator transition [1], charge order transition [1], pressure-induced superconductivity [2] and so on. Some vanadium oxides with the Hollandite-type structure were also reported. Among them,  $\text{Bi}_2\text{V}_8\text{O}_{16}$  is famous in its metal-insulator transition [3]. The structure of Hollandite vanadate  $\text{A}_2\text{V}_8\text{O}_{16}$  consists of  $\text{V}_8\text{O}_{16}$ -framework and A-cation located at the tunnel sites of  $\text{V}_8\text{O}_{16}$ -framework. The  $\text{V}_8\text{O}_{16}$ -framework is constructed from the double chains formed by sharing the edges of  $\text{VO}_6$  octahedra. We successfully synthesized  $\text{K}_2\text{V}_8\text{O}_{16}$  by a solid state reaction under 4 GPa at 1473 K for 30 minutes. Small crystals were also found in the sintered sample.  $\text{K}_2\text{V}_8\text{O}_{16}$  shows a metal-insulator transition with the jump of resistivity about three orders around 170 K, accompanied by the structure change from tetragonal to orthorhombic and the large reduction of magnetic susceptibility. Electron diffraction study reveals a superlattice of  $\sqrt{2} \times \sqrt{2} \times 2$  in the low-temperature insulator phase. Taking these results into consideration, we propose a charge ordered model for the low-temperature insulator phase in which  $\text{V}^{4+}\text{-V}^{4+}$  spin singlet pairs are formed. We also first synthesized  $\text{Rb}_2\text{V}_8\text{O}_{16}$  and discovered a metal-insulator transition around at 150 K.

[1] Ueda Y., *J. Phys. Soc. Jpn.*, 2000, 69, Suppl. B. 149. [2] Yamauchi T., Ueda Y., Mōri N., *Phys. Rev. Lett.*, 2002, 89, 057002-1. [3] Kato H., Waki T., Kato M., Yoshimura K., Kosuge K., *J. Phys. Soc. Jpn.*, 2001, 70, 325.

**Keywords:** metal oxide, metal-insulator transition, structure transformation

**P.08.06.14***Acta Cryst.* (2005). A61, C321-C322**Re-examination of Phase Transitions in  $\text{KNbO}_3$** 

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As it is known, the physical properties of  $\text{KNbO}_3$  are similar to the properties of  $\text{BaTiO}_3$ . Though the nano-size effects in  $\text{BaTiO}_3$  are researched rather well, such studies of  $\text{KNbO}_3$  have never been held