

**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  $\text{P}2_1/c$  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  $\text{P}2_1/c$  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  $\text{P}2_1/n$ , 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  $c^*$ . The cell for *F12/d1* has  $a' = a$ ,  $b' = b$ ,  $c' = 34.547(2)\text{Å}$ ,  $\beta' = 89.68(1)^\circ$ . 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  $\pm 0.123(3)\text{Å}$ . 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