

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 α 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 β 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 α -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 α -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 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, β 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) Å, β' 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 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 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 V_8O_{16} -framework and A-cation located at the tunnel sites of V_8O_{16} -framework. The V_8O_{16} -framework is constructed from the double chains formed by sharing the edges of 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 KNbO_3**

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As it is known, the physical properties of KNbO_3 are similar to the properties of BaTiO_3 . Though the nano-size effects in BaTiO_3 are researched rather well, such studies of KNbO_3 have never been held

before.

In this report the results of structural studies of phase transitions in KNbO₃ powder specimens are presented. For preparation of KNbO₃ samples with different sizes of ideal crystal structure (crystallites or blocks) different synthesis conditions is used. The study of KNbO₃ phase transitions using X-ray diffractometer DRON-3M (CuK_α radiation) and special temperature cell at 20 ≤ T ≤ 960°C is made.

It is found that the decrease of coherent scattering areas below critical size (50 nm) lead to reduce of phase transition temperatures. It is established that there are strong changes of atomic positions and thermal parameters at these temperatures.

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Keywords: perovskites, phase transitions, nanocrystals

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Substitution of Manganese by Iron or Gallium in Electron-doped Manganites

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We investigate the temperature-dependant evolution of the magnetic moments in electron-doped manganites (Y_{0.1}Ca_{0.9}MnO₃, Y_{0.15}Ca_{0.85}MnO₃) Y_{0.1}Ca_{0.9}MnO₃ shows mainly G-type antiferromagnetic ordering with a Néel temperature of 110K and a minority ferromagnetic phase with an identical ordering temperature. For higher Yttrium concentrations as in Y_{0.125}Ca_{0.875}MnO₃ and Y_{0.15}Ca_{0.85}MnO₃ an additional phase develops with monoclinic nuclear space group P2₁/m and C-type magnetic ordering, leading to a phase separated state below a magnetic phase transition temperature of approximately 160K.

The substitution of Manganese by other trivalent ions influences the temperature-dependant behaviour of this phases. For Y_{0.1}Ca_{0.9}MnO₃, Ga reduces the phase transition temperatures, while Fe reduces the Ferromagnetic intensities. Fe retains this behavior for higher concentrations of Yttrium while Ga changes additionally the phase fractions of the G- and C-type phases.

[1] Martin C., *Phys. Rev. B*, 2000, **62**, 10, 6442-6449. [2] Amann U., et al., *Z. Krist. Suppl.*, 2000, **18**, 79. [3] Hagdorn K., et al., *Eur. Phys. J. B*, 1999, **11**, 243. [4] Aliaga H., et al., *J. Phys.: Condens. Matter*, 2003, **15**, 249.

Keywords: magnetic perovskite materials, magnetic phase transitions, magnetic structures

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Dynamic Phase Transition of the Charge-density Wave Lattice

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The dynamic behaviour of the periodic media with lattice imperfections is ubiquitous and long-standing problem in many condensed material systems, because of the correlation to the unusual physical phenomena, for instance, the charge-density waves/spin-density waves to the nonlinear conductivity, the charge/spin stripes to the CMR and the high-T_C superconductivity, and the vortex lattice to superconductivity. In static systems, the imperfections in a medium result in a disordered ground state which prevents the system from forming a long-range order at low temperatures, therefore giving rise to unusual physical properties. In dynamic systems under a driving force, the disordered medium produces a more fascinating phase diagram. Analogous to the vortex lattice, the inhomogeneous distribution of charge densities also forms a periodic lattice below the transition temperature, namely charge-density waves (CDWs). Combining x-ray scattering and multiple diffraction, we demonstrate that the CDW lattice can be driven by a driving force to move and

undergo a dynamic phase transition, i.e. from the disordered pinning state → ordered moving solid state → disordered moving liquid, and the nonlinear conductivity occurs through a phase jump of 2π.

Keywords: charge-density wave, phase transition, X-ray scattering

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Phase Transitions in Tetrachlorobenzene Studied by Neutron Powder Diffraction

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Polymorphism and phase transitions are a major issue in the understanding of the organic solid state. The 'Control and Prediction of the Solid State' (CPOSS) project[1] aims to increase our understanding of the polymorphic state using detailed screening to discover 'all' polymorphic forms and solid state phases combined with cutting edge experimental studies and computational studies.

Two polymorphs of tetrachlorobenzene have been reported[2-4]; the room-temperature β form (P2₁/n), and a low-temperature α form (P-1), with the phase change occurring at approximately 170K.

The nature of the phase transition, as well as the structure of the two polymorphic forms, has been investigated using the complimentary crystallographic techniques of single-crystal X-ray diffraction and neutron powder diffraction. In particular, the effect of temperature on the lattice parameters is considered, providing insights into the nature and mechanism of the phase transition.

[1] <http://www.chem.ucl.ac.uk/basictechorg/index.htm> . [2] Herstein F.H., *Acta Cryst.*, 1965, **18**, 997-1000.[3] Halac E.B., Burgos E.M., Bonadeo H., D'Alessio E.A., *Acta Cryst A*, 1977, **A33**, 86-89. [4] Anderson D.G., Blake A.J., Blom R., Craddock S., Rankin D.W.H., *Acta Chemica Scandinavica*, 1991, **45**, 158-164.

Keywords: neutron powder diffraction, polymorphism, phase transitions

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Polyhedral Compressibilities Drive Structural Phase Transitions in Perovskites

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Recent advances in laboratory based single-crystal techniques for measuring the intensities of diffraction from crystals held at high pressures in the diamond-anvil cell have been used to determine the role of polyhedral compression in the response of the ABO₃ perovskite structure type to high pressures. All perovskites studied exhibit compression of the BO₆ octahedra. We have been able to show that when the BO₆ octahedra are less compressible than the AO₁₂ sites the octahedra become more tilted with increasing pressure [1]. In such perovskites there are no structural phase transitions to high-symmetry structures.

When the BO₆ octahedra are more compressible than the AO₁₂ sites the structure becomes less tilted and evolves towards a higher-symmetry configuration [2]. Thus LaGaO₃ undergoes a Pbnm to R-3c transition with first-order character at approximately 2.5 GPa at room temperature. The structural evolution of LaAlO₃ has been followed in the R-3c phase before its transition to Pm3m at about 14GPa [3].

We have also developed a new model, based on the bond valence concept, that successfully predicts the relative compressibilities of the cation sites in most oxide perovskites [4] and hence their response, including phase transitions, to pressure.

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Keywords: perovskites, phase transitions, pressure