

**P08.06.51***Acta Cryst.* (2008). **A64**, C434**X-ray diffraction study on quartz surface on  $\alpha - \beta$  phase transition**Tsuyoshi Kumagai<sup>1</sup>, Masanori Tanaka<sup>1</sup>, Hiroo Tajiri<sup>2</sup>, Osami Sakata<sup>2</sup>, Hikaru Terauchi<sup>1</sup>, Isao Takahashi<sup>1</sup><sup>1</sup>Kwansei Gakuin University, Faculty of Science and Technology, 2-1 Gakuen, Sanda, Hyogo, 669-1337, Japan, <sup>2</sup>Japan Synchrotron Radiation Research Institute (JASRI/Spring-8), Sayo, 679-5198, Japan, E-mail : cqw85810@gmail.com

Quartz exhibits a structural phase transition known as alpha - beta phase transition at 846K, accompanied by an incommensurate (IC) phase between alpha and beta phases. Although there are many structural studies about the alpha - beta phase transition of bulk quartz, fewer reports on surface structure have been found. In the present study, temperature variation in surface structure and morphology of quartz was observed with X-ray diffraction ranging from room temperature to 1000K. A polished (001) surface of synthetic quartz with an area of 20 mm x 20mm was placed in an ultrahigh vacuum chamber installed on BL13XU of SPring-8. Surface-sensitive X-ray diffractions we exploited for characterizing the surface are the crystal truncation rod (CTR) scattering emanated from 003 Bragg point and X-ray reflectivity (XR). Rocking curves ( $q_x$  scan) and longitudinal curves ( $q_z$  scan) between  $2\theta = 0$  to 5-8 deg. of XR were collected at each temperature. In beta phase (>846K), a noticeable increase in width of specular XR ( $q_x$  scan), obeying ( $T - 846K$ ), is reproducibly observed. Longitudinal scans measured in beta phase also revealed an anomalous broadening in total reflection regime.

Keywords: quartz, X-ray diffraction, phase transitions

**P08.06.52***Acta Cryst.* (2008). **A64**, C434**The effect of hydrostatic pressure on the structural and piezoelectric properties of PbTiO<sub>3</sub>**

Johannes Frantti, Yukari Fujioka, Risto M Nieminen

Helsinki University of Technology, Laboratory of Physics, Otakaari 4, P. O. Box 4100, Espoo, Uusimaa, FIN-02015 HUT, Finland, E-mail : jfr@fyslab.hut.fi

The origin of the very large piezoelectric response observed in the vicinity of the morphotropic phase boundary (MPB) in lead zirconate titanate [Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub>, PZT] and related systems [such as xPb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(1-x)PbTiO<sub>3</sub>, PMN-PT] has been under intensive studies. MPB region separates tetragonal and rhombohedral phases, which do not have group-subgroup relationship and thus no continuous transition between the phases is possible. To understand the mechanisms responsible for the piezoelectric properties in the perovskite systems, both experimental and computational high-pressure studies were dedicated for PbTiO<sub>3</sub> (PT). Our density functional theory (DFT) computations show that the ground state of PT under hydrostatic pressures transforms discontinuously from  $P4mm$  to  $R3c$  at 9GPa and further to  $R-3c$  at 27 GPa [1]. Bridging symmetries allowing a continuous phase transformation sequence were found to be energetically unfavourable. It therefore seems that two-phase co-existence (one phase being metastable over a finite pressure range) in the vicinity of the phase transition region is unavoidable, in an analogous way to the phase transitions seen in PZT as a function of composition. This in turn suggests that the two-phase co-existence has a crucial role for the piezoelectric properties near the first phase transition in PT, analogously to the case of PZT

in the vicinity of the MPB [2]. The DFT code ABINIT [3] was used to compute the total energies, phonon frequencies and piezoelectric properties at different pressures.

[1] J. Frantti, Y. Fujioka, and R. M. Nieminen. *J. Phys. Chem. B Lett.* 4287, 111, (2007).[2] J. Y. Li, R. C. Rogan, E. Üstündag and K. Bhattacharya. *Nature Materials.* 4, 776 (2005).[3] X. Gonze et al. *Comput. Mater. Sci.* 478, 25 (2002).

Keywords: lead titanate, hydrostatic pressure, piezoelectricity

**P08.06.53***Acta Cryst.* (2008). **A64**, C434**Computational and experimental studies of the phase transitions of WO<sub>3</sub>**Yukari Fujioka<sup>1</sup>, Johannes Frantti<sup>1</sup>, Vilho Lantto<sup>2</sup>, Sami Saukko<sup>2</sup>, Risto M Nieminen<sup>1</sup><sup>1</sup>Helsinki University of Technology, Laboratory of Physics, P. O. Box 1100, Otakaari 1, Espoo, Uusimaa, FIN-02015 HUT, Finland, <sup>2</sup>Microelectronics and Materials Physics Laboratory, University of Oulu, P.O. Box 4500, FIN-90014 Oulu, Finland, E-mail : yukari.fujioka@hut.fi

Tungsten trioxide (WO<sub>3</sub>) exhibits several phase transitions below its melting point at 1700 K, summarized as:  $Pc Z=4 \rightarrow D P-1 Z=8 \rightarrow D P2_1/n Z=8 \rightarrow C Pbcn Z=8 \rightarrow D P4/ncc Z=4 \rightarrow C P4/nmm Z=2$  where Z is the number of formula units per primitive cell. First order and continuous phase transitions are indicated by D and C, respectively. The phase transitions, from left to right, occur at around 230, 300, 623, 1070, and 1170 K, respectively [1]. Most of the transitions involve oxygen octahedral tilts, which are central for the phase transition mechanisms, since they allow the ratio between oxygen octahedral and cuboctahedral volumes to vary. The changes in bond lengths and angles correlate with the changes in electronic energy band structure: large changes in optical band gap and electrical resistivity occur at the  $P-1$  to ferroelectric  $Pc$  phase transition [2], consistently with our density functional theory (DFT) computations. The ferroelectric distortion, spontaneous polarization and piezoelectric constants were estimated by DFT computations. The crystal size affects the phase transition temperatures and symmetries. We prepared small particle size WO<sub>3</sub> powders to systematically study the size effects on the crystal symmetry and physical properties.

[1] P. Woodward et al. *J. Solid State Chem.* 9, 131 (1997); E. Salje et al. *J. Phys. Condens. Matter.* 6563, 9 (1997); R. Diehl et al. *Acta Cryst. B.* 1105. 34 (1978); P. Woodward et al. *J. Phys. Chem. Solids.* 1305, 56 (1995); S. Tanisaki. *J. Phys. Soc. Japan.* 573, 15 (1960); B. O. Loopstra et al. *Acta Cryst.* 158, 21 (1965); T. Vogt et al. *J. Solid State Chem.* 209, 144 (1999); K. R. Locherer et al. *J. Phys. Condens. Matter.* 4143, 11 (1999); E. Salje. *Acta Cryst. B.* 574, 33 (1977).[2] E. Salje et al. *Acta Cryst. A.* 356, 31 (1975).

Keywords: tungsten trioxide, particle size, density functional theory

**P08.06.54***Acta Cryst.* (2008). **A64**, C434-435**Low-melting organic salts: A study of symmetry modification through phase transitions**Victor G Young<sup>1</sup>, Wesley A Henderson<sup>2</sup><sup>1</sup>University of Minnesota, Chemistry, 207 Pleasant St. SE, Minneapolis, Minnesota, 55455, USA, <sup>2</sup>Department of Chemical and Biomolecular

Engineering, North Carolina State University, Box 7905, 911 Partners Way, Raleigh, NC 27695, E-mail: vyoung@umn.edu

Low-melting organic salts often exhibit complex temperature-dependent properties. Below melting temperatures these are best described as crystalline materials with liquid-like properties where some or all of the cations and/or anions are disordered. At yet lower temperatures, as monitored by DSC, these undergo stepwise phase transitions to ordered phases. Many of these have intermediate phases with both ordered and/or disordered species. These cascades of phase transitions often produce the lowest temperature phases with pseudo-symmetric, high- $Z'$  structures that are often twinned by non-merohedry. For example, the material  $[\text{N}(\text{CH}_3)_4][\text{IM14}]$ , where IM14 is  $\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ , exhibits two first-order phase transitions by DSC at 168 K and 193 K before melting at 390 K. Phase I is found in space group  $P2_1/m$  where the IM14 anion is disordered over the crystallographic mirror and the  $[\text{N}(\text{CH}_3)_4]$  is bisected by it. In Phase II the unit cell doubles as the crystallographic mirror transforms to a glide plane as the space group  $P2_1/n$  emerges. The IM14 anion is disordered in both Phases I and II, but not in III. The space group for Phase III is  $P2_1/n$ , as is Phase II, however the order/disorder phase transition causes a major reconstruction of the contents and the  $a$ - and  $c$ -axes. The inter-phase symmetry modifications of this and several other low-melting organic salts with multiple phase transitions will be the focus of this paper.

Keywords: low-melting compounds, phase transitions, organic inorganic materials

## P08.06.55

*Acta Cryst.* (2008). A64, C435

### Intrinsic ferroelectric instability in $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ revealed by changing B-site randomness

Kenji Ohwada

Japan Atomic Energy Agency / Japan, Quantum Beam Science Directorate, 1-1-1 Koto, Sayo, Sayo, Hyogo, 679-5148, Japan, E-mail: ohwada@spring8.or.jp

Antiferroelectric (AFE), ferroelectric (FE) or relaxor states can appear in  $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PIN) depending upon the perovskite B-site randomness. We studied the effects of this randomness on the dynamics of PIN by high resolution inelastic x-ray scattering using ordered PIN (AFE) and disordered PIN (relaxor) single crystals. We have found a clear softening of a transverse optic mode at the Gamma-point in both the samples, indicating a robust and intrinsic ferroelectric dynamical correlation regardless of the actual ground state. We believe that the correlation results in a FE instability mode, which gives yield to the FE and relaxor states. We interpret that AFE is stabilized only when In and Nb ions are spatially ordered enough to overwhelm the FE instability. As the B-site randomness becomes larger, AFE is suppressed and the hidden FE state starts appearing. Ultimately, the randomness begins to predominate over the development of FE regions and blocks a long range FE order, which we believe yields polar nanoregions resulting in relaxor behaviors. This work was performed in collaboration with Prof. K. Hirota (Osaka Univ.), Dr. T. Fukuda (JAEA), Dr. S. Tsutsui (JASRI/Spring-8), Dr. A. Q. R. Baron (RIKEN), Dr. J. Mizuki (JAEA), Prof. H. Terauchi (Kwansei Gakuin Univ.), Prof. H. Ohwa (Gifu Univ.) and Prof. N. Yasuda (Gifu Univ.).

Keywords: relaxor, ferroelectrics, inelastic x-ray scattering

## P08.07.56

*Acta Cryst.* (2008). A64, C435

### A new conformation of *meso*-tetraphenylporphyrin free-base structure

Chuttree Phurat<sup>1</sup>, Narongsak Chaichit<sup>2</sup>, Nongnuj Muangsin<sup>1</sup>

<sup>1</sup>Research Centre for Bioorganic Chemistry, Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai, Bangkok, 10330, Thailand, <sup>2</sup>Department of Physics, Faculty of Science and Technology, Thammasart University, Patumthani, 12120, Thailand, E-mail: freshytulip@yahoo.com

The new conformation of *meso*-tetraphenylporphyrin was prepared accidentally. It is named T1. T1 has been characterized by a three-dimensional X-ray structure determination and refined by least-squares methods on a R value of 0.0451 based on  $F$ . The complex crystallizes in the triclinic space group  $P-1$ , with  $a=6.436$ ,  $b=10.477$ , and  $c=12.416$  Å. There are two molecules in the unit cell and no solvent molecules in lattice. The out-of-plane distortions of porphyrins are characterized by displacements along the lowest-frequency out-of-plane normal coordinates of macrocycle and comparison with other porphyrins. It shows some differences, especially the dihedral angle between *meso*-substituents and pyrrole rings.

Keywords: porphyrins, *meso*-tetraphenylporphyrin, porphyrin conformations

## P08.07.57

*Acta Cryst.* (2008). A64, C435

### Probability density analysis for mobile ions in a hollandite superstructure

Yuichi Michiue

National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan, E-mail: MICHIE.Yuichi@nims.go.jp

Ordering schemes for guest ions and the host structure in a hollandite superstructure of  $\text{K}_x(\text{Mg,Sb})_8\text{O}_{16}$  ( $x=1.76$ ) were investigated by a single-crystal X-ray diffraction technique. Superlattice formation is primarily attributed to the Mg/Sb occupational modulation in the host structure. Two types of the cavity are linearly connected forming a one-dimensional tunnel, where K ions are accommodated. Parts of K ions deviate from the cavity center along the tunnel direction. Probability densities of K ions in the two cavities are different from each other, which seems to have arisen from the Mg/Sb modulation. Transport property of K ions was investigated by considering additional constraint conditions in least-squares refinements so that the average structure obtained from the refinement was consistent with possible microscopic pictures. One-particle potential along the conduction path was drawn from probability density functions for specific K ions concerning the hopping process between neighboring cavities. Energy barriers in three types of K hopping processes, 62, 90, 110 meV, were estimated using harmonic atomic displacement parameters (ADPs), which were reduced to 45, 79, and 96 meV in the anharmonic ADP model. The values are generally consistent with results from impedance measurements in microwave frequencies reported so far.

Keywords: hollandite, superstructures, ion transport