

P08.06.51*Acta Cryst.* (2008). **A64**, C434**X-ray diffraction study on quartz surface on α - β phase transition**Tsuyoshi Kumagai¹, Masanori Tanaka¹, Hiroo Tajiri², Osami Sakata², Hikaru Terauchi¹, Isao Takahashi¹¹Kwansei Gakuin University, Faculty of Science and Technology, 2-1 Gakuen, Sanda, Hyogo, 669-1337, Japan, ²Japan 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 PbTiO₃**

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The origin of the very large piezoelectric response observed in the vicinity of the morphotropic phase boundary (MPB) in lead zirconate titanate [Pb(Zr_xTi_{1-x})O₃, PZT] and related systems [such as xPb(Mg_{1/3}Nb_{2/3})O₃-(1-x)PbTiO₃, 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 PbTiO₃ (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.

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Keywords: lead titanate, hydrostatic pressure, piezoelectricity

P08.06.53*Acta Cryst.* (2008). **A64**, C434**Computational and experimental studies of the phase transitions of WO₃**Yukari Fujioka¹, Johannes Frantti¹, Vilho Lantto², Sami Saukko², Risto M Nieminen¹¹Helsinki University of Technology, Laboratory of Physics, P. O. Box 1100, Otakaari 1, Espoo, Uusimaa, FIN-02015 HUT, Finland, ²Microelectronics and Materials Physics Laboratory, University of Oulu, P.O. Box 4500, FIN-90014 Oulu, Finland, E-mail : yukari.fujioka@hut.fi

Tungsten trioxide (WO₃) 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 WO₃ powders to systematically study the size effects on the crystal symmetry and physical properties.

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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 Young¹, Wesley A Henderson²¹University of Minnesota, Chemistry, 207 Pleasant St. SE, Minneapolis, Minnesota, 55455, USA, ²Department of Chemical and Biomolecular