

**PS11.05.35 FERROELASTIC PHASE TRANSITION IN CaTiO<sub>3</sub> PEROVSKITE.** Simon AT Redfern, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom.

High-temperature (293 - 1523 K) X-ray powder diffraction has been used to investigate the nature of the transition from orthorhombic *Pbnm* to highersymmetry polymorphs in CaTiO<sub>3</sub>. While the behavior of perovskite is often quoted as a textbook example of a displacive phase transition, the nature of the high-symmetry phase in the type-mineral, CaTiO<sub>3</sub>, has been the subject of recent debate [1,2,3]. There have been suggestions that the structure transforms to an intermediate tetragonal phase prior to the transition to cubic symmetry. In this investigation, the first X-ray powder diffraction study through the ferroelastic transition, it is demonstrated that CaTiO<sub>3</sub> transforms directly from *Pbnm* to *Pm3m* on increasing temperature at around 1385 K. The behavior is similar to that observed in neighborite, NaMgF<sub>3</sub>, at high-temperature[4]. The temperature-dependence of the spontaneous strain in the ferroic phase has been determined, and shows that while the transition is weakly first-order, the strain conforms to near-second-order behavior over a wide temperature interval. These results provide no evidence for the existence of an intermediate tetragonal phase, or of cell-doubling within the orthorhombic stability field, nor of a higher temperature transition near 1520 K as was suggested by previous calorimetric[1] and inferred from lower-temperature X-ray studies[2].

References:

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**PS11.05.36 LOW-TEMPERATURE PHASE OF t-BUTYL CHLORIDE (tBC): CRYSTAL STRUCTURE AND NOMENCLATURE.** Reuben Rudman, Adelphi University, Chemistry Dept., Garden City, NY 11530, USA rudman@sable.adelphi.edu

tBC, with a pseudo-spherical molecular envelope, forms an orientationally disordered, plastic crystalline phase as it is cooled below its freezing point. Although plastic crystals often have only one solid-solid phase transition (between the disordered and ordered phases), tBC has long been known to form a partially-ordered crystalline phase prior to forming the ordered phase [R. Rudman and B.Post, *Mol. Cryst.* 5, 95-110 (1968)]. These three tBC phases have been labeled Phases I, II, and III in dozens of articles in the scientific literature. However, S. Ohtani and T. Hasabe (OH) [*Chem. Lett.* 1986, 1283-1286] reported a newly discovered phase, stable over a 1.8K range (217.7K - 219.5K), between the historic Phases I and II. This phase, which was identified on the basis of differential thermal analysis and not characterized further, was labeled by them Phase II, with the historic Phases II and III relabeled as Phase III and Phase IV, respectively. This relabeling will lead to a great deal of confusion in the literature and subsequent databases.

Single-crystal X-ray diffraction data have been obtained for the disordered and partially ordered phases of tBC (Rudman & Post, *loc. cit.*). However, because single crystals of tBC shatter as they transform to the low-temperature ordered phase (our Phase III), the crystal structure of this ordered phase has not been experimentally investigated previously. In 1993, J. Chen and L. S. Bartell [*J.Chem.Phys.* 97, 10645-8] published a theoretical Molecular Dynamics study of this phase which they identify, following OH, as Phase IV. They determined the unit cell, space group, and crystal structure of this phase using computational methods and stated

that they verified their proposed structure by indexing neutron powder diffraction data (not published).

This paper will report on the results of a low-temperature synchrotron X-ray powder diffraction investigation of the various phases of tBC. The crystal structure of the ordered phase, an investigation of the newly reported phase (stable only over a 1.8K temperature range), and recommendations for the proper nomenclature of these various phases will be presented.

**PS11.05.37 ELASTIC PROPERTIES OF SELECTED MINERALS AND DECAGONAL QUASICRYSTALS AT HIGH TEMPERATURES APPLICATIONS OF THE RPR-METHOD.** Jurgen Schreuer & Walter Steurer, Laboratory of Crystallography, ETH Zentrum, CH-8092 Zurich, Switzerland.

The elastic constants and their temperature derivatives of orthorhombic cordierite, monoclinic sanidine, triclinic CuSO<sub>4</sub>\*5H<sub>2</sub>O and a decagonal quasicrystal of the Al-Co-Ni-system will be presented. The examples demonstrate the potential of resonant ultrasound spectroscopy.

Due to their close relationship with many physical properties the elastic constants play a key role for the structural interpretation of physical properties. They can be either used to scrutinize and improve existing models for the atomic interaction potentials or, following the quasi inverse way, to obtain information on the bonding system of an unknown crystal. Especially in the case of decagonal quasicrystals where the axial structure allows an anisotropic elasticity tensor in contrast to the situation found in icosahedral quasicrystals [1] the experimental study of their elastic behaviour contributes to the understanding of their atomic configuration.

Furthermore elastic constants represent not only a highly sensitive probe for the detection of phase transitions but their anomalies offer valuable hints on the driving mechanisms of certain phase transitions.

Our experimental setup is based on the RPR-method introduced by Ohno [2], where the elastic constants are derived from an experimentally measured ultrasonic resonance spectrum of a free vibrating crystal prepared as a rectangular parallelepiped. This relatively new powerful technique is particularly suited for the study of elastic properties at elevated temperatures, because no medium is required for transducer-sample coupling. Further advantages are the small sample size and the short data acquisition time.

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**PS11.05.38 NEUTRON POWDER DIFFRACTION STUDY OF THE HIGH PRESSURE JAHN-TELLER SWITCH IN (ND<sub>4</sub>)<sub>2</sub>[Cu(D<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>.** A. J. Schultz, IPNS, Argonne National Laboratory, Argonne, IL 60439, USA; H. Stratemeier, M. A. Hitchman, Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia; C. J. Simmons, Mathematics and Science Division, Brigham Young University - Hawaii, Laie, Hawaii 96762, USA.

The Jahn-Teller distortion switch in the deuterated ammonium copper(II) Tutton salt (ND<sub>4</sub>)<sub>2</sub>[Cu(D<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub> was observed to occur at room temperature at about 200 bar when increasing pressure, and at about 100 bar when decreasing pressure. This salt is especially interesting because the long axis of the distorted hydrogenated Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> complex switches to a different pair of water molecules upon deuteration [1], and then switches back to the structure of the hydrogenous compound upon raising the pressure, as first shown from the single crystal study of (ND<sub>4</sub>)<sub>2</sub>[Cu(D<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub> using the IPNS SCD [2]. In the current study, the pressure-temperature phase diagram was examined in

greater detail by powder neutron diffraction and the switching is shown to occur at very mild pressure at room temperature with a hysteresis of about 100 bar. The role of hydrogen bonding, lattice strain, and the pressure dependence of the EPR spectrum [3] will be discussed in light of these results.

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**PS11.05.39 MOLECULAR REARRANGEMENTS IN TETRAMETHYLAMMONIUM TETRAFLUOROBORATE (TMT).** Thomas M. Schultz, Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark, and Finn K. Larsen, Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

The thermal behaviour of tetraalkylammonium tetrafluoroborates includes series of phase transitions.<sup>1</sup> The present study is part of an attempt to characterize the molecular rearrangements over an extended temperature range in terms of constrained rigid body motion. TMT at room temperature crystallizes in a tetragonal space group,  $P4/nmm$ . The  $(CH_3)_4N^+$  ions sit ordered at special positions ( $3/4$ ,  $1/4$ ,  $1/2$ ) of point symmetry  $42m$ , while the  $BF_4^-$  ions are placed at general positions near a  $4mm$  axis. This imposes an eight-fold disorder on the  $BF_4^-$  ion. Furthermore, two equilibrium positions exist for each group. They are nearly related by a rotation of approximately 40 degrees around an axis near one of the BF bonds. A rigid body TLX refinement gives  $R(F) = 3.7\%$  with 78% occupation for the major set. Lowering the temperature to 160 K, just above the phase transition at 154 K, depopulates the minor set completely,  $R(F) = 3.1\%$ .

The phase transition is accompanied by a doubling of unit cell volume and a change to monoclinic space group symmetry. Twinning is involved and most diffraction peaks split up at the phase transition. A twin model allowed to establish a fully ordered structure for data collected at 140 K.

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**PS11.05.40 STRUCTURES AND PHASE TRANSITIONS OF HALOGENOMETALLATES(II) OF GERMANIUM AND TIN WITH MONOVALENT COUNTERCATION.** B.R. Serr, G. Wittenburg, D.G. Ebling, H.W. Rotter and G. Thiele, Institut f. Anorg. & Analyt. Chemie und Materialforschungszentrum der Albert-Ludwigs-Universität, D-79104 Freiburg i. Br., Germany

Systematics of structures and phase transitions of the title compounds were studied by X-ray diffraction, Raman spectroscopy, DTA/DSC and impedance spectroscopy. A set of 45 structures at ordinary temperature and 27 high temperature or high pressure phases was used to study the effects of size and shape of the counterion (Rb, Cs,  $MeNH_3$ ,  $Me_2NH_2$ ,  $Me_3NH$  and  $Me_4N$ ), the used halogen (Cl, Br or I) and above all to characterize and quantify the influence of the stereochemically active lone pair of divalent germanium and tin [1,2]. Besides other compositions, the main part of the title compounds crystallize in perovskite type structures  $AMX_3$ . Normally, M(II) is coordinated by a halogen octahedron. While regular coordination is found among the tin compounds, the environment of Ge(II) is always [3+3] distorted, due to the effect of the lone pair. Raman spectroscopy shows, that Ge(II) and Sn(II) are disordered in the hexagonal packed structures of  $AMX_3$  with  $A = Me_4N$ , while they are fixed for  $A = Me_2NH_2$ . Many of the studied compounds are polymorphous and transform

to the cubic modification at elevated temperatures. The studied phase transitions show reconstructive or dilatative / displacive mechanisms, the HT-phases are strongly disordered due to cation libration and disordering of M(II) in its  $X_6$ -octahedron. The transitions are accompanied by drastic changes of the dielectric properties. The characterisation of the thermal behaviour proofs impedance spectroscopy as a splendid tool for the examination of phase transitions.

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**PS11.05.41 PRESSURE-INDUCED MODULATED PHASES OF  $[N(CH_3)_4]_2CuCl_4$ .** S. Shimomura, N. Hamaya<sup>1)</sup>, Y. Fujii<sup>2)</sup>, T. Fukui, H. Terauchi, Department of Physics, Kwansai-Gakuin University, Nishinomiya, Hyogo 662, Japan, <sup>1)</sup>Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan, <sup>2)</sup>Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, Shirakata, Tokai, Ibaraki 319-11, Japan

The  $A_2BX_4$  type dielectrics are known to have various commensurate (C) and incommensurate (IC) phases. Tetramethylammonium tetrachlorocuprate  $[N(CH_3)_4]_2CuCl_4$ , which belongs to the  $A_2BX_4$  type, undergoes the successive phase transitions with decreasing temperature from the prototypical normal (N) phase to the IC phase at 26°C and to the C phase characterized by  $q = c^*/3$  at 19°C. We carried out x-ray diffraction measurements under hydrostatic pressure using a beryllium-cylinder pressure cell and a diamond-anvil cell in order to determine the pressure and temperature dependence of the modulation wave vector and to explore additional pressure-induced phases.

The IC phase characterized by  $q < c^*/3$  decreases its stable range with increasing pressure and finally vanishes at a point (23.4MPa, 30.0°C), which is denoted by  $L^*$ . Another IC region characterized by  $q > c^*/3$  is found to appear at  $L^*$  and widen with increasing pressure. The second-order N-IC phase line and the first-order IC-C phase line meet at  $L^*$ , where the phase transition between the N and C phases is considered to take place directly. The modulation wave vector in both IC regions tends to  $c^*/3$  monotonically as the  $L^*$  point is approached. These facts suggest that the  $L^*$  point is a multicritical one in incommensurate systems. Applying higher pressure at room temperature, we found the existence of three more phases up to about 4 GPa.

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**PS11.05.42 LOW-FREQUENCY DIELECTRIC DISPERSION AND PYROEFFECT AT PHASE TRANSITION FOR MONOCLINIC TELLURIUM ACID AMMONIUM PHOSPHATE CRYSTAL.** I.A. Smirnova, N.N. Bolshakova\*, N.D. Gavrilova Moscow State University, Moscow, Russia, \*Tver State University, Tver, Russia

In this paper temperature dependencies of pyroelectrical effect and low-frequency dielectrical dispersion of monoclinic Tellurium Acid Ammonium Phosphate crystal (TAAP)  $Te(OH)_2 \cdot 2NH_4H_2PO_4 \cdot (NH_4)2HPO_4$  ( $T_c = 318K$ ) in frequency range 20Hz-10kHz and temperature region 220-320K were investigated. Temperature dependence of pyrocoefficient is unusual for ferroelectric crystals - the peak has a 40K shift to ferroelectric phase and has a diffuse shape. We connect it with the turn of crystal cell total dipole moment, in which, probably, hydrogen bonds play important role. Dielectric dispersion data were used to