

PS11.05.35 FERROELASTIC PHASE TRANSITION IN CaTiO₃ 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 CaTiO₃. 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, CaTiO₃, 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 CaTiO₃ transforms directly from *Pbnm* to *Pm3m* on increasing temperature at around 1385 K. The behavior is similar to that observed in neighborite, NaMgF₃, 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 CuSO₄*5H₂O 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 (ND₄)₂[Cu(D₂O)₆](SO₄)₂. 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 (ND₄)₂[Cu(D₂O)₆](SO₄)₂ 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(H₂O)₆²⁺ 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 (ND₄)₂[Cu(D₂O)₆](SO₄)₂ using the IPNS SCD [2]. In the current study, the pressure-temperature phase diagram was examined in