21-Crystallography at Non-Ambient Temperatures and/or Pressures: Phase Transitions

In this short lecture, we will perform a review of the experimental and theoretical works related to these phase transformations.

MS-21.03.08

ATHERMAL TRANSFORMATION KINETICS AND THERMAL HYSTERESIS AT WEAKLY FIRST ORDER PHASE TRANSITIONS. By W.W. Schmahl, Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Germany. Although thermal hysteresis is a common feature of first order phase transitions, there is only rudimentary knowledge about its origin and characteristics. The non-squashable αβ-crystallite phase transition near 520 K is associated with a thermal hysteresis of ± 15 K and αβ-phase coexistence in the hysteresis loop. Measurement by x-ray diffraction (0.03 K/min) or DSC (5K/min) gives practically the same result (see figure). The transformation proceeds instantly as a function of temperature; thermal activation is not a relevant factor. These 'athermal' features are similar to martensitic transformations in metals and alloys and to field-reversal hysteresis in ferroics. The bulk Landau-free energy isotherms suggest that local strain-fields control nucleation and initiate both phase coexistence and thermal hysteresis.

MS-21.03.10

A 2θ-RESOLVED HADOX STUDY OF BaTiO3 LINZ CRYSTALS. By H. Ohtsuka, M. Hatakaya, Y. Soejima and A. Okazaki*, Department of Physics, Kyushu University, Fukuoka 812, Japan.

X-ray diffraction intensities in a reciprocal-lattice plane can be measured with high resolution in two dimensions by improved high-angle double-crystal X-ray diffactometry (HADOX). In addition to the original experimental arrangement in HADOX, two-axis rotation has been introduced: one for limiting the area of the specimen crystal to be examined, and the other for defining the resolution of 2θ. Thus we can correlate the original to scanning of the specimen with the 2θ scanning of the detector, and determine two-dimensional intensity distribution. This technique, named the 2θ-resolved HADOX, enables us to determine separately and precisely changes in lattice constants and changes in crystal orientation. This is required in the structural study of first-order transitions. The method has been applied to the cubic-to-tetragonal phase transition in BaTiO3 Linz crystals grown by the method of 2θ-resolved solution growth; the results are compared with those of previous experiments on butterfly crystals of BaTiO3. It is found that the two types of crystals behave in qualitatively different manners around the transition: the transition temperature, the temperature range of two-phase coexistence etc. are different. In...
both types of crystals, on the one hand, the lattice constant of the cubic phase shows a different temperature dependence when the tetragonal phase coexists, and the orientation of crystal grains shows anomalous behaviour. The results are discussed in terms of the effect of stresses, and in connection with dielectric properties.


At ambient temperature NiTiO has the ordered ilmenite structure (space group R3) which may be described as a nearly hexagonal close packing of oxygen, the cations occupying 1/3 of the octahedral voids in an ordered sequence along the threefold axis. At 1,150°C a second order phase transition leads to a disordered corundum structure (R3c) with a random occupation of the same cation sites. Besides the order parameter η describing the cation exchange, there are further critical (displacive) degrees of freedom $\mathbf{q}_\parallel$ which belong to the same irreducible representation $\Gamma^{\ast}$ ($\Delta_2$). The temperature dependence of the order parameter was investigated by Rietveld analysis of neutron powder diffraction data measured between 300 K and 1550°C. η shows a critical behaviour starting at $\eta_c = 200$ K. Only one of the other displacive parameters ($\mathbf{q}_\parallel$) matches this behaviour, while the other two follow their own different temperature dependence starting far below $\eta_c$.

The excess strain $\Delta \mathbf{c}/\mathbf{c}$ couples quadratically to η, while $\Delta \mathbf{a}/\mathbf{a}$ follows $\mathbf{q}_\parallel$. The temperature factors strongly increase as $T \to \eta_c$.

The reasons for these unexpected deviations from common phase transition theories (e.g. Landau) could be found from refinements with anharmonic temperature factors. In the average structure the probability densities of the cations show deformations which may be attributed to the fact that different cation species occupy different positions in their individual unit cells. Furthermore, close to (below) $\eta_c$, some additional density is found in normally empty octahedral.

Therefore, these (probably dynamic) delocalizations of the atoms have to be included in more accurate phase transition theories.

This work was supported by funds of the BMFT (03SC3LMU).

PS-21.03.12 LASER-INDUCED PHASE TRANSITIONS IN LAYERED SEMICONDUCTOR PbI₃. By S.K. Chaudhary, University College, M.D. University, Bhopal - 124001 (INDIA).

The phenomenon of polytypism has attracted the attention of both physicists and mineralogists for many years. Recently, it has also attracted the attention of solid-state physicists by virtue of the fact that various polytypic modifications of the same substance have been found to possess different semiconducting, dielectric and photovoltaic properties.

The phase transitions in PbI₃ crystals have been studied by various workers. When heated, the 2H structure transforms to 12R. High-purity single-crystals of PbI₃ were grown by the zone-refinement method. Their structure was shown to be of the 12R type by X-ray diffraction techniques. A pulsed ruby laser was then used to irradiate the crystal at room temperature. It is observed that its structure changes to 2H, the most stable polytype, after the laser irradiation. The results have been explained by thermodynamical and structural considerations.

PS-21.03.13 STRUCTURAL PROPERTIES OF GUEST MOLECULES IN UREA INCLUSION COMPOUNDS AT LOW TEMPERATURE. By Ian J. Shannon* and Kenneth D.M. Harris, Department of Chemistry, University of St. Andrews, St. Andrews, Scotland, U.K.

Urea inclusion compounds are examples of crystalline "host-guest" systems, comprising an extensively hydrogen-bonded "host" substructure which contains essentially infinite, unidirectional tunnels. The host substructure is stable only when each tunnel contains a dense packing of "guest" molecules; such suitable guest molecules include straight-chain alkanes and certain derivatives such as α,ω-dialkylalkanes (K.D.M. Harris, S.P. Small and M.D. Hollingsworth, J. Chem. Soc., Faraday Trans., 1991, 87, 3423-3429) and diacyl peroxides (K.D.M. Harris and M.D. Hollingsworth, Proc. Roy. Soc. Lond. A, 1990, 431, 245-269). At ambient temperature, the urea inclusion compounds of each of these families of guest species have been shown to exhibit different characteristic modes of inter-tunnel packing of guest molecules. For example, for the diacyl peroxide/urea inclusion compounds predominantly three-dimensional ordering of the guest is observed, with $\Delta_2 = 4.6$ Å irrespective of the length of the guest molecule ($\Delta_2$ is the offset along the tunnel axis, between positions of guests in adjacent tunnels).

In the present study, urea inclusion compounds containing n-alkanes, α,ω-dialkylalkanes, diacyl peroxide and carboxylic acid anhydride guest molecules have been analysed, using single crystal X-ray diffraction, at temperatures between 90 K and 296 K. Transitions have been found to occur in the guest substructure for several of the guests considered.

The structural changes associated with these transitions will be discussed in detail.

PS-21.03.14 REVERSIBLE SOLID-STATE PHASE TRANSITION OF A "THERMOSALIENT CRYSTAL". By S. Zamir* and J. Bernstein, Department of Chemistry, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, Israel; and Daniel J. Greenwood, Boehringer Ingelheim Pharmaceuticals Inc., Ridgefield, CT 06877, U.S.A.

"Thermosalient behaviour" was first noted by Gigg et al. (1987), J. Chem. Soc. Perkin Trans. 1, 2411, and described also as "hopping crystals" or "jumping crystals". These terms characterize vigorous mechanical movements of a crystal on heating or cooling through a phase transition. The phenomenon was previously studied in two systems: napinoisitol derivatives (Gigg et al., 1987) and phenylpropyrene (Ding et al., 1991). Acta Crystal. B47, 739. We present here a third compound, oxtiolom bromide, with similar behaviour.

The reversible phase transition to be discussed involves highly anisotropic parameter changes corresponding to about 4% volume expansion upon heating. The lower and upper temperature crystal forms, both orthorhombic, have been characterized by their different IR spectra, DSC and powder diffraction patterns.

Upon heating, the transition is endothermic, and occurs around 58.5-57.5°C, with enthalpy of transition of about 2 kJ/mole. Upon cooling, the transition occurs around 34-35°C, due to hysteresis. Various aspects of the transition and crystal chemistry will be presented.

Crystal Data: Oxitolom Bromide, C₁₂H₂₂NO₂Br.

Orthorhombic, SG P2₁2₁2₁, $\varepsilon$4 for both forms.

Low Temp. Form High Temp. Form
\begin{align*}
\mathbf{a} \text{(Å)} & \begin{array}{c}
7.388 (2) \\
10.118 (3)
\end{array} \\
\mathbf{b} \text{(Å)} & \begin{array}{c}
11.254 \\
22.890
\end{array} \\
\mathbf{c} \text{(Å)} & \begin{array}{c}
24.765 (4) \\
1846.7
\end{array} \\
\mathbf{v} \text{(Å)} & \begin{array}{c}
1926.6
\end{array}
\end{align*}