

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

both types of crystals, on the other 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.

**MS-21.03.11 ORDER PARAMETER COUPLING AT THE O/D PHASE TRANSITION IN NiTiO<sub>3</sub>.** By H. Boysen\* and F. Frey, Institut f. Kristallographie, Universität München, Germany and M. Lerch, FB Materialwissenschaften, TH-Darmstadt, Germany.

At ambient temperature NiTiO<sub>3</sub> has the ordered ilmenite structure (space group  $R\bar{3}$ ) which may be described as a nearly hexagonal close packing of oxygens, the cations occupying 2/3 of the octahedral voids in an ordered sequence along the threefold axis. At  $T_c \approx 1560$  K a second order phase transition leads to a disordered corundum structure ( $R\bar{3}c$ ) with a random occupation of the same cation sites. Besides the order parameter  $\eta$  describing the cation exchange, there are further critical (displacive) degrees of freedom  $\Phi_{1,3}$  which belong to the same irreducible representation  $\Gamma_{2}^{+}$  ( $A_{2g}$ ). The temperature dependence of the order parameters was investigated by Rietveld analysis of neutron powder diffraction data measured between 300 K and 1650 K.  $\eta$  shows a critical behaviour starting at  $T_1 \approx T_c - 200$  K. Only one of the other displacive parameters ( $\Phi_2$ ) matches this behaviour, while the other two follow their own different temperature dependence starting far below  $T_1$ . The excess strain  $\Delta c/c$  couples quadratically to  $\eta$ , while  $\Delta a/a$  follows  $\Phi_3$ . The temperature factors strongly increase as  $T \rightarrow T_c$ . 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)  $T_c$  some additional density is found in normally empty octahedra. 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 PbI<sub>2</sub>.** By S.K. Chaudhary, University College, M.D. University Rohtak - 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 PbI<sub>2</sub> crystals have been studied by various researchers. When heated, the 2H structure transforms to 12R. High-purity single-crystals of PbI<sub>2</sub> 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 urea "host" substructure which contains essentially infinite, uni-directional tunnels. This 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  $\alpha, \omega$ -dihalogenoalkanes (K.D.M. Harris, S.P. Smart 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  $\Delta_g = 4.6$  Å irrespective of the length of the guest molecule ( $\Delta_g$  is the offset, along the tunnel axis, between positions of guests in adjacent tunnels).

In the present study, urea inclusion compounds containing n-alkane,  $\alpha, \omega$ -dihalogenoalkane, 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: *myo*-inositol derivatives (Gigg *et al.*, 1987) and perhydropyrene (Ding *et al.* (1991). *Acta Cryst.* B47, 739). We present here a third compound, oxitropium 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 56.5-57.5°C, with enthalpy of transition of about 2 kJ/mole. Upon cooling, the transition occurs around 34-36°C, due to hysteresis. Various aspects of the transition and crystal chemistry will be presented.

Crystal Data: Oxitropium Bromide, C<sub>19</sub>H<sub>26</sub>NO<sub>4</sub>Br. Orthorhombic, SG P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, Z=4 for both forms.

	Low Temp. Form	High Temp. Form
<i>a</i> (Å)	7.388(2)	7.479
<i>b</i> (Å)	10.118(3)	11.254
<i>c</i> (Å)	24.705(4)	22.890
<i>V</i> (Å <sup>3</sup> )	1846.7	1926.6