

05.1-17 NEW OBSERVATIONS ON THE LOW-TEMPERATURE PHASE TRANSITIONS IN  $\text{KLiSO}_4$ . By H.-D. Jennissen, P. Willms, J. Glinnemann, H. Klapper & Th. Hahn, Institut fuer Kristallographie der RWTH, D-5100 Aachen, Federal Republic of Germany.

In the last few years contradictory results about symmetry and kinetics of the low-temperature phases in  $\text{KLiSO}_4$  (space group at room temperature  $P6_3$ ) have been published (e. g. Tomaszewski & Lukaszewicz, Phase Transitions 4, 37 (1983); Bhakay-Tamhane & Sequeira, Ferroelectrics 62, 241 (1986)). The space group of the intermediate phase (below 205 K) is described to be  $P6_3mc$  or  $P31c$ , that of the low-temperature phase (below 190 K)  $Cmc2_1$  or  $Cc$ . Also mixtures of phases at different temperatures are discussed.

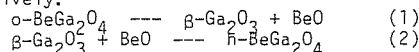
Optical investigations of untwinned (0001) growth sectors exhibit on cooling a sharp drop in optical activity from  $2.75^\circ/\text{mm}$  in the room-temperature form to zero or at least  $\leq 0.1^\circ/\text{mm}$  in the intermediate phase ( $\lambda = 578 \text{ nm}$ ). Low-temperature precession photographs of originally untwinned crystals exhibit for this phase Laue class  $6/mmm$ . Both effects indicate an enhancement of symmetry in the intermediate phase, which, however, is contradicted by the following optical observations: After several cooling and heating cycles across the 205 K and 190 K transitions (both are reversible and of first order) twinned and untwinned crystals retain completely their original grown-in twin-domain structure and original twin-free state, respectively. This is supported by X-ray topographs at room temperature. The exact reproduction of the original domain structure (as well as structural considerations) suggests that the twin elements of the room-temperature phase ( $2_1[001]$ ,  $m[001]$  and  $m[001]$ , Klapper, Hahn & Chung, Acta Cryst. B43, 147 (1987)) do not become symmetry elements in either of the two low-temperature phases;  $m[001]$ , however, may become a pseudo symmetry element (pseudo c glide).

For the low-temperature phase (below 190 K) three optically distinguishable twin-domain variants (rotation twins around the c axis) occur. The domain walls are generally slightly curved and approximately parallel to  $(1120)$ . The reflection condition for the c glide ( $hh\bar{2}h1$ ,  $l=2n$ ) is violated by three reflections:  $11\bar{2}1$ ,  $22\bar{4}1$  and  $33\bar{6}1$  (indices referred to pseudo-hexagonal axes). Experiments are in progress to resolve the presently existing ambiguities and to elucidate the true space groups of the intermediate and the low-temperature phase.

The domain walls in the low-temperature phase are  $W'$ -walls in the sense of Sapriel (Phys. Rev. B12, 5128 (1975)). They are determined by the deformation tensor arising from the lattice discontinuity of the 190 K phase transition, revealing again the first-order nature of this transition.

05.1-18 HIGH PRESSURE PHASE TRANSITION OF  $\text{BeGa}_2\text{O}_4$  TO OLIVINE TYPE STRUCTURE. By Hideyo TABATA, Michihide MACHIDA and Eiichi ISHII, Gov. Ind. Res. Inst. Nagoya, Hirate-cho, Kita-ku, Nagoya 462, JAPAN

High pressure phase transition of beryllium gallium oxide ( $\text{BeGa}_2\text{O}_4$ ) has been studied. Among most of the  $\text{AB}_2\text{X}_4$  type compounds (K. Kugimiya et al., Inorg. Chem., 1968, 7, 1762-70),  $\text{BeGa}_2\text{O}_4$  has a quite unique crystal structure (M. Schweizer et al., Z. Naturforsch., 1979, 34B, 1067-69) where Be and Ga atoms are statistically distributed at tetrahedrally coordinated sites within a three dimensional network which is similar to that of  $\beta\text{-Si}_3\text{N}_4$  structure. The application of high pressure (up to 7.5 GPa) and temperature (up to  $1600^\circ\text{C}$ ) resulted in phase transition from the hexagonal  $\text{BeGa}_2\text{O}_4$  ( $a=0.77525\text{nm}$ ,  $c=0.29817\text{nm}$ ,  $z=2$ ) to the orthorhombic olivine type structure ( $a=0.5698\text{nm}$ ,  $b=0.9759\text{nm}$ ,  $c=0.4551\text{nm}$ ,  $z=4$ ). The densities for low pressure (h-) and high pressure (o-) type  $\text{BeGa}_2\text{O}_4$  were 4.548 and 5.576  $\text{g}/\text{cm}^3$ , respectively. The stable region of o- $\text{BeGa}_2\text{O}_4$  was determined to be in the range from 4 to 7.5 GPa and from  $800$  to  $1550^\circ\text{C}$ . At temperatures higher than  $900^\circ\text{C}$  and pressure lower than 3.5 GPa, h- $\text{BeGa}_2\text{O}_4$  decomposed to BeO and  $\beta\text{-Ga}_2\text{O}_3$ . When the pressure level exceeded 7 GPa, small amount of  $\alpha\text{-Ga}_2\text{O}_3$  (high pressure type) was found. By a heat treatment in an ambient pressure, o- $\text{BeGa}_2\text{O}_4$  was irreversibly converted into h- $\text{BeGa}_2\text{O}_4$ . DTA study of o- $\text{BeGa}_2\text{O}_4$  showed two endothermic peaks at 1115 and  $1220^\circ\text{C}$ , which were ascribed to the following reactions, respectively.



Accordingly, the conversion mechanisms of h- $\text{BeGa}_2\text{O}_4$  to o- $\text{BeGa}_2\text{O}_4$  and vice versa were attributed to the two step reactions, namely, decomposition of the starting compound to the constituent oxides and formation of the final compound from them.

05.1-19 THE HEXAGONAL PHASES OF  $(\text{CH}_3)_3\text{NHCDCl}_3$  OR HOW TO MINIMIZE ORDER-DISORDER EFFECTS. By G. Chapuis, Institut de Cristallographie, Université de Lausanne, Bâtiment des Sciences Physiques, CH - 1015 Lausanne, Switzerland.

$(\text{CH}_3)_3\text{NHCDCl}_3$  exhibit three phases up to 415K. The structure consists of parallel columns of face sharing Cl-octahedra which are disposed on a hexagonal net. The trimethylammonium ions are located in the free space between the columns and linked by hydrogen bonds to the Cl-atoms. The low temperature phase stable below 342K has orthorhombic symmetry and each octahedra is symmetrically surrounded by two trimethylammonium ions. A temperature dependent disorder of the organic ions has been detected in the room temperature phase which increases up to the transition temperature at 342K. The two phases detected above this temperature are hexagonal and have been determined by single crystal diffraction. The phase stable between 342 and 374K is characterized by an increase of the cell volume by a factor of 4.5. Above 374K, the cell volume is reduced by a factor of 3. In the hexagonal phases, all the trimethylammonium ions are statistically distributed among two possible orientations with different probabilities. In addition, part of the Cl octahedra are also disordered. Below 374K, one out of nine octahedra is disordered whereas above this temperature, one out of 3 octahedra is disordered. Accordingly, two different types of disorder has also been identified for the organic ions.

The solution of the hexagonal phases shows that the structures tend to maximize the distances between the disordered octahedra. The resulting structures can be interpreted as a three-dimensional array of connected octahedra and trimethylammonium ions which leaves channels of disordered octahedra free of any interaction with the remaining part of the structure. The two hexagonal phases differ essentially by the distance separating the channels of disordered octahedra which decreases by increasing temperature. The models derived from diffraction measurements have been independently confirmed by the measurements of the EFG-tensors. The directions of the field gradient orientations corresponds within a few degrees to the various orientations of the disordered H-bonded trimethylammonium.