05. PHYSICAL PROPERTIES AND STRUCTURE


In the last few years contradictory results about symmetry and kinetics of the low-temperature phases in KLSiO₃ (space group at room temperature P6₃mc) have been published (e.g., Tomasszewski & Lukassevich). Phase transitions in 37 (1983); Shpakovsky-Tamhane & Jequeira, Ferroelectrics 55, 241 (1986). The space group of the intermediate phase (below 205 K) is described to be P6₃mc or P31c, that of the low-temperature phase (below 190 K) Cw2, 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 2.37°/μm in the room-temperature form to zero or at least 0.01°/μm in the intermediate phase (κ = 578 nm). Low-temperature precession photographs of originally untwinned crystals exhibit for this phase Laue class 6/3. 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 growth-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 (2H[001], m[001] and n[001], Klapper, Hahn & Chung, Acta Crystallogr. 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 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 o glide (h0f0l, l=2n) is violated by three reflections: 1110, 2210 and 3310 (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 V-walls in the sense of Sepkic (Phys. Rev. B33, 5128 (1985)). They are determined by the deformation tensor arising from the drastic asymmetricity of the 120 K phase transition, revealing again the first-order nature of this transition.

05.1-18 HIGH PRESSURE PHASE TRANSITION OF BeGa₂O₄ TO OLIVINE TYPE STRUCTURE. By Hisayuki TABATA, Nichiichi ICHIDA and Eichi ISHII, Gov. Ind. Res. Inst. Nagoya, Hirate-cho, Kita-ku, Nagoya 462, JAPAN

High-pressure phase transition of beryllium gallium oxide (BeGa₂O₄) has been studied. Among most of the A₂B₅ type compounds (K. Kugimiya et al., Inorg. Chem., 1985, 24, 1762-70), BeGa₂O₄ has a quite unique crystal structure (N. Schwerk 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 α-Si₃N₄ structure. The application of high pressure (up to 7.5 GPa) and temperature (up to 1600°C) resulted in phase transition from the hexagonal Be₃O₆ (a=0.77525 nm, c=0.29017 nm, z=2) to the orthorhombic olivine type structure (a=0.5698 nm, b=0.9759 nm, c=0.4551 nm, z=4). The densities for low pressure (h-) and high pressure (o-) type BeGa₂O₄ were 4.548 and 5.576 mg/μm³, respectively. The stable region of o-BeGa₂O₄ was determined to be in the range from 4 to 7.5 GPa and from 800 to 1550°C. At temperatures higher than 900°C and pressure lower than 3.5 GPa, h-BeGa₂O₄ decomposed to BeO and α-Ga₂O₃. When the pressure 18 GPa exceeded 7 GPa, small amount of o-Be₃O₄ (high pressure type) was found. By a heat treatment in an ambient pressure, o-Be₃O₄ was reversibly converted into h-Be₃O₄. DTA study of o-Be₃O₄ showed two exo-thermic peaks at 1110°C and 1220°C which were ascribed to the following reactions, respectively:

\[ \text{o-Be₃O₄} \rightarrow \text{g-Be₃O₄} + \text{BeO} \] \[ \text{g-Be₃O₄} + \text{BeO} \rightarrow \text{h-Be₃O₄} \]

Accordingly, the conversion mechanisms of o-Be₃O₄ to h-Be₃O₄ and converse 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 (CH₃)₂NHCDCl₃ OR HOW TO MINIMIZE ORDER-DISORDER EFFECTS. By G. Chapuis, Institut de Cristallographie, Université de Lausanne, Bâtiment des Sciences Physiques, CH - 1015 Lausanne, Switzerland.

(CH₃)₂NHCDCl₃ 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 374K is characterized by an increase of the cell volume by a factor of 3 and high pressure (o-) type phase transition from the hexagonal phase to a three-dimensional network. The stable region of o-Be₃O₄ was determined to be in the range from 4 to 7.5 GPa and from 800 to 1550°C. At temperatures higher than 900°C and pressure lower than 3.5 GPa, h-Be₃O₄ decomposed to BeO and α-Ga₂O₃. When the pressure 18 GPa exceeded 7 GPa, small amount of o-Be₃O₄ (high pressure type) was found. By a heat treatment in an ambient pressure, o-Be₃O₄ was reversibly converted into h-Be₃O₄. DTA study of o-Be₃O₄ showed two exo-thermic peaks at 1110°C and 1220°C which were ascribed to the following reactions, respectively:

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Accordingly, the conversion mechanisms of o-Be₃O₄ to h-Be₃O₄ and converse 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.