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Thermal behavior of potassium bromostannate

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Auszug

K_2SnBr_6 ist bei Zimmertemperatur tetragonal, pseudokubisch; es wird kubisch bei 125,6 °C. Die Umwandlung ist reversibel und displaciv (nach BUERGER). Die Ausdehnungskoeffizienten sind $\lambda_a = 4{,}96 \cdot 10^{-5}$, $\lambda_c = 5{,}65 \cdot 10^{-5}$ für die tetragonale Modifikation zwischen 0 °C und 100 °C und $\lambda_a = 5{,}22 \cdot 10^{-5}$ für die kubische zwischen 130 °C und 250 °C.

Die Umwandlung erfolgt ohne Volumenänderung (Umwandlung zweiter Art).

Abstract

K_2SnBr_6 is tetragonal, pseudocubic at room temperature and becomes cubic at 126.5 °C. The transition is reversible and "displacive" (BUERGER). The expansion coefficients are: $\lambda_a = 4.96 \cdot 10^{-5}$, $\lambda_c = 5.65 \cdot 10^{-5}$ for the tetragonal phase between 0 °C and 100 °C; and $\lambda_a = 5.22 \cdot 10^{-5}$ for the cubic phase between 130 °C and 250 °C.

In the transition point no change of volume occurs, indicating a second order transition.

The symmetry of K_2SnBr_6 has been studied by KETELAAR, RIETDIJK and VAN STAVEREN[1] and by MARKSTEIN and NOWOTNY[2]. According to KETELAAR *et al.* the compound is cubic and has the K_2PtCl_6 structure, with $a = 10.48$ Å. According to MARKSTEIN and NOWOTY, it is tetragonal, pseudocubic, space group $P42_12$ with a slightly distorted K_2PtCl_6 structure, and with $a = 10.51$ and $c = 10.61$ Å. The unit diagonal to the pseudocubic cell has the dimensions $a = 7.43$ and $c = 10.61$ Å.

We have found[3] that the cell, tetragonal or pseudo-cubic at room temperature, becomes cubic at 126.5 °C, with $a = 10.61$ Å at 130°. The transition is reversible and a "displacive transition" in the sense defined by

[1] J. A. A. KETELAAR, A. A. RIETDIJK und C. H. VAN STAVEREN, Die Kristallstruktur von Ammonium-, Kalium-, Rubidium- und Cäsiumstannibromid. Rec. Trav. Chim. **56** (1937) 907—908.

[2] G. MARKSTEIN und H. NOWOTNY, Die Kristallstruktur von Bromostannaten A_2SnBr_6 (A = Cs, Rb, NH_4, K). Z. Kristallogr. **100** (1939) 265—271.

[3] E. E. GALLONI y M. R. DE BENYACAR, Estudio cristalográfico del bromoestannato de potasio. Anal. Acad. Nac. Cien. Córdoba (R. A.) **42** (1961) 241—243.

BUERGER[4]. No other point of transformation was found below 0 °C down to − 80 °C. On heating, the temperature of decomposition was reached above 250 °, without any new change of phase being observed. The transition temperature was determined on a polarizing microscope fitted with a Kofler hot stage. Crystals grown from solution are polyhedra looking like single crystals, but thin sections observed on a polarizing microscope (Fig. 1) show domain structures similar to those in barium titanate[5]. On heating, the domains disappear at 126.5 °C, as the symmetry changes to cubic; they reappear if the sample cools below the transition temperature, the domain boundaries occupying their original positions.

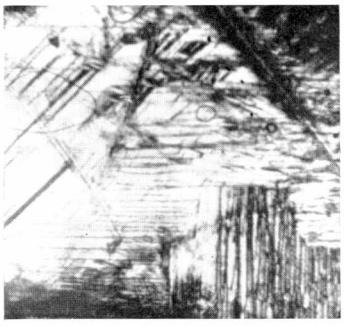

Fig. 1. Thin section of K_2SnBr_6 between crossed nicols, showing domain structures at room temperature

We have measured the expansion coefficient of both the tetragonal and the cubic phase. For the determination of the unit-cell edges at different temperatures we employed a Philips Geiger-counter diffractometer to which an electrically heated sample holder was adapted. Temperatures were controlled and measured with a chrome-alumel thermocouple. To secure a uniform temperature the sample was placed in a cavity drilled in a thick copper block, and covered with an iron foil which also acted as a filter for the Co radiation. The thermocouple indications were read on a recording potentiometer with an accuracy better than 0.02 mV, equivalent to 0.5 °C.

The progress of the expansion was followed determining at each temperature, by counting, the position of the peaks representing the 400 and 004 reflections in the powder pattern of the tetragonal or pseudocubic cell; above the transition temperature these reflections join in a single peak.

To put the cell edges on an absolute scale, the NaCl 200 spacing, $d = 2.8201$ Å at 26 °C, was taken as a standard[6]. Results obtained between

[4] M. BUERGER, Crystallographic aspects of phase transformation. Chapter in: Phase transformation in solids. (Ed. Smoluchowski) (1951) 183—211.

[5] P. H. FORSBERGH, JR., Domain structures and phase transition in barium titanate. Physic. Review **76** (1949) 1187—1201.

[6] H. E. SWANSON and R. K. FUYAT, Investigation by x-ray powder data. Nat. Bur. Standards Report NBS project 0907—41—0921, NBS report No. 1300. Structure reports **15** (1951) 149.

20° and 250 °C are plotted in Fig. 2; the curves show that the transition takes place between 120° and 130°. The expansion is aproximately linear for the tetragonal phase between 20° and 100°, and for the cubic phase between 130° and 250 °C. All the coefficients are positive.

Applying least squares, the following values were obtained:

$$\textit{Tetragonal phase} \quad 0° < t < 100° \quad a = 10.5096\,(1 + 4.96 \times 10^{-5}\,t)$$
$$c = 10.6120\,(1 + 5.65 \times 10^{-5}\,t)$$

$$\textit{Cubic phase} \quad 130° < t < 250° \quad a = 10.5428\,(1 + 5.22 \times 10^{-5}\,t)$$

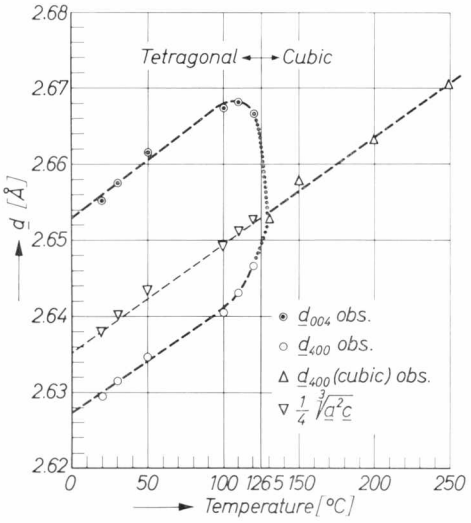

Fig. 2. Variation with temperature of spacings for 400 and 004 reflections, and cube root of cell volume of K_2SnBr_6

As shown in Fig. 2, the values for the average cell edge $\frac{1}{4}\sqrt[3]{a^2c}$ below the transition temperature fall very aproximately on the straight line belonging to the cubic phase, indicating that at the transition point no change of volume occurs (second-order transition).

The behavior of K_2SnBr_6 and its structure at low temperature suggest the presence of some kind of ferroelectric or antiferroelectric phenomenon. A. Levialdi and co-workers, though[7], have not been able to detect any such characteristic. R. Grahmann[8] measured the dielectric constant up to 160° and did not found any anomaly at the transition temperature. Our experiments have failed to show, up to the present, any shift of domains under the effect on an electric field. More conclusive experiments are being planned.

[7] Private communication.

[8] Private communication.