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A high-pressure synchrotron x-ray powder diffraction study of K_2SnBr_6

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Abstract. Using synchrotron energy-dispersive x-ray powder diffraction (EDXRPD) we have shown that K_2SnBr_6 transforms at pressures of 14 kbar and above from the parent monoclinic cell to a cubic structure of symmetry $Fm3m$, which is stable to 120 kbar. A different phase appears to exist above 120 kbar.

1. Introduction

Structural relationships between K_2SnCl_6 and K_2SnBr_6 are confused. In the hope of clarifying the situation we have studied the behaviour of K_2SnBr_6 under high pressure using synchrotron EDXRPD.

The crystal structure of potassium hexabromostannate, K_2SnBr_6 , was reported first by Markstein and Nowotny (1938) and later confirmed by Higashi *et al* (1979). It has a monoclinic cell ($P2_1/c$, $z = 4$) with $a = 10.621$, $b = 7.427$, $c = 7.442$ Å, and $\beta = 90.18^\circ$. Swanson (1978), using optical microscopy, found that this pseudo-tetragonal ambient phase undergoes a displacive phase transformation at 399 K to a cubic phase with the K_2PtCl_6 (anti-fluorite) structure ($Fm3m$, $z = 4$).

The title compound has also been studied using vibrational spectroscopy, most recently by Butler and Huang (1990) who reviewed earlier work. Theirs is the first high-pressure investigation. Using Raman spectroscopy they found evidence for a structural transition at 19 kbar but were unable to identify the new phase. We have now done so.

2. Experimental procedure

Samples were pressurized within a diamond anvil cell (DAC) using stainless steel gaskets with a central hole of 0.4 mm diameter. The pressure-transmitting medium was 4:1 methanol: ethanol; the shifts of the ruby fluorescence lines were used to estimate pressure (Piermarini and Block 1975, Adams *et al* 1976).

X-ray experiments were carried out on the SERC Daresbury Laboratory synchrotron, Station 9.7, using a white beam reduced to 0.1 mm diameter with molybdenum slits. Diffracted radiation was collimated through 0.5 m molybdenum slits at an angle of

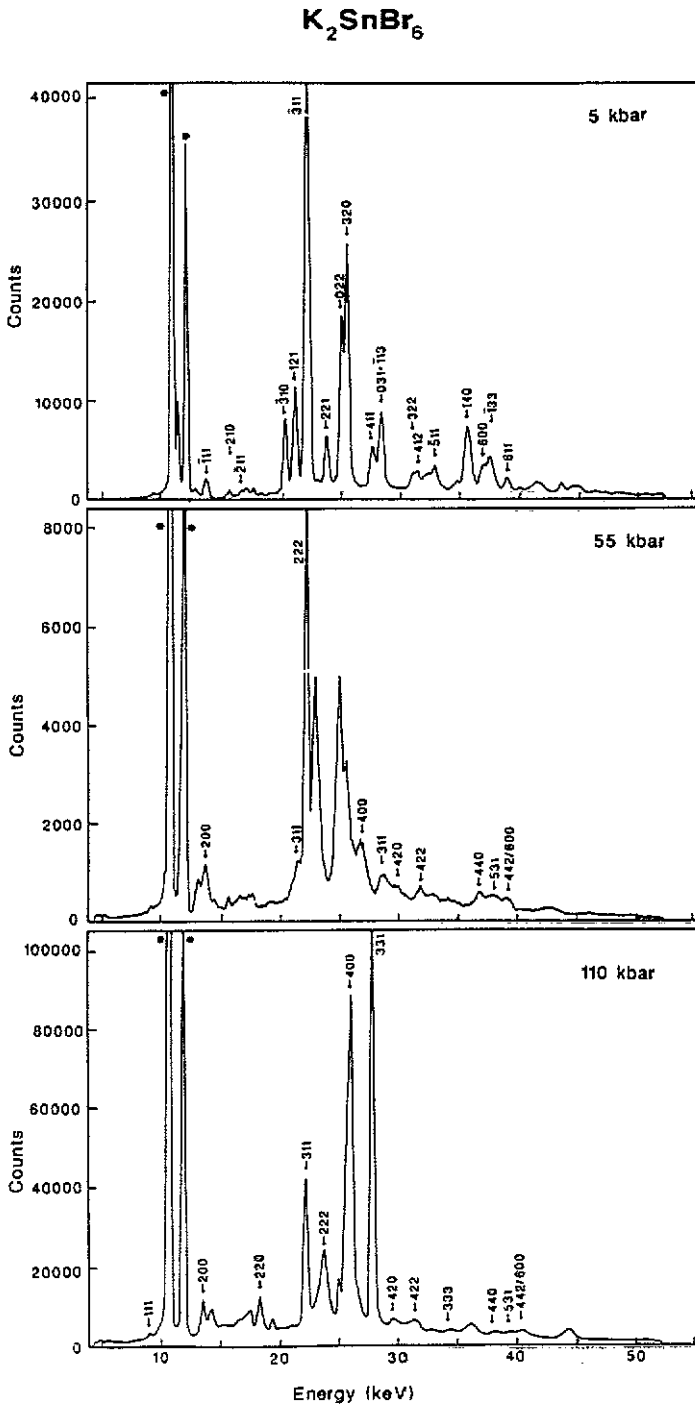


Figure 1. The EDXRPD spectra of K_2SnBr_6 in the parent monoclinic phase at 5 kbar, and in the high-pressure cubic phase at 55 and 110 kbar.

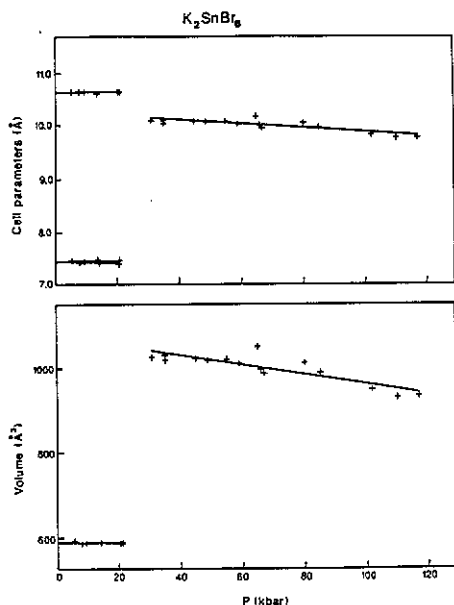


Figure 2. Variation of the lattice constants of K_2SnBr_6 with pressure.

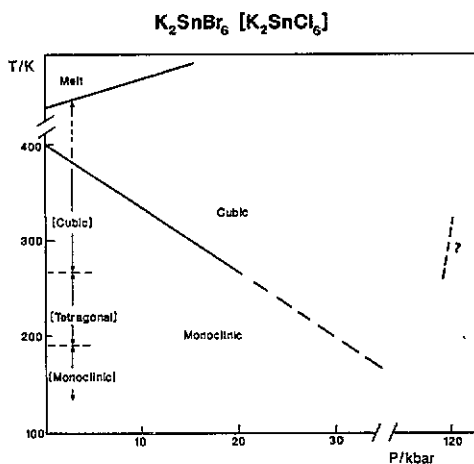


Figure 3. Phase relationships in K_2SnCl_6 and K_2SnBr_6 .

10.082° and fed onto a liquid-nitrogen-cooled solid state detector. Collection times varied from 900 to 3600 s.

3. Results

Data are summarized in figures 1 and 2. For each diffraction peak the d -spacing may be calculated from the Bragg law in the form $d = hc/2E \sin \theta$. Peak positions E were determined by fitting Gaussian peak shapes using the GENIE data analysis package. The DRAGON powder diffraction prediction programme was used to give theoretical d -spacings for the ambient phase, an excellent fit being obtained.

With increase of pressure the diffraction pattern remained essentially unchanged until about 14 kbar was reached when new peaks began to appear. There followed a region of intergrowth until 30 kbar was reached, at which pressure the pattern corresponds to a pure cubic cell of dimension 10.08 Å, figure 2. The cubic phase data could be indexed on the basis of $Fm\bar{3}m$ symmetry up to 120 kbar, beyond which there appears to be another phase change, but these data could not be indexed due to their poor quality.

4. Discussion

The phase transition that we have observed with increase of pressure is undoubtedly the same as that found by Butler and Huang (1990), but the x-ray method allowed identification of the new phase, and is also more sensitive to the onset of the transition.

Combining our new results with those of Swanson (1978) and Butler and Huang (1990) yields the phase diagram of figure 3. The volume compressibility is $1.23 \times 10^{-3} \text{ kbar}^{-1}$, and there is a 12.76% volume decrease at the phase change, allowing for the cell doubling.

The analogous chloride, K_2SnCl_6 , is cubic ($Fm3m$) under ambient conditions, becoming tetragonal ($P4/mnc$) at 265 K and monoclinic ($P2_1/n$) at 190 K (Boysen and Hewar 1978). Moreover, there are no changes in its vibrational spectra to at least 30 kbar (Adams *et al* 1981), which is to be expected if the slope of the cubic/tetragonal phase boundary is similar to that of K_2SnBr_6 . It appears that whereas K_2SnCl_6 has both tetragonal and monoclinic phases at successively lower temperatures, the bromide settles for a single pseudo-tetragonal monoclinic phase, possibly because of the different ionic radius ratio. Data at combined low temperatures and high pressures are needed to confirm the phase diagram of K_2SnCl_6 and the relationships to that of the bromide.

Acknowledgments

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