THERMAL EXPANSION AND CRYSTALLOGRAPHIC PHASE TRANSFORMATION IN K_2CrO_4

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The unit cell parameters of potassium chromate were determined between 56 and 880°C from high temperature X-ray powder data and the thermal expansion parameters were derived. These were compared with those of potassium sulphate.

As a continuation of earlier studies on the nature of the phase transformations in Na_2CrO_4 [1], work on the thermal expansion and phase transformation in anhydrous K_2CrO_4 is reported. It is known that K_2CrO_4, which has a β-K_2SO_4 type structure at room temperature (space group P_{mcn}), assumes a hexagonal structure of Na_2SO_4 (1) type when heated above 663° [2]. Accurate cell data and X-ray powder data at room temperature and 705° are available in ASTM 15–365 and 15–359. The results obtained now are compared with those on K_2SO_4 to determine the extent of similarity between them.

Experimental

The experimental technique used was the same as that described earlier [1]. X-ray powder patterns at 56, 154, 257, 358, 446, 640, 705, 738, 850 and 888° were recorded. (The temperature measurements have an error of about 1–3 deg.) The d values obtained have been least square fitted to arrive at the lattice parameters of the orthorhombic and hexagonal forms at these temperatures and are plotted with their ESD's (Fig. 1). At high temperatures the ESD's are larger because of the weakening of some of the X-ray reflections and a consequent reduction in the number of observables used in the least square process.

Results and discussion

As seen in Fig. 1, the thermal expansions for a_0 and $b_0/\sqrt{3}$ are linear. The expansion for c_0 consists of 2 linear portions, one below and the other above 350°. After

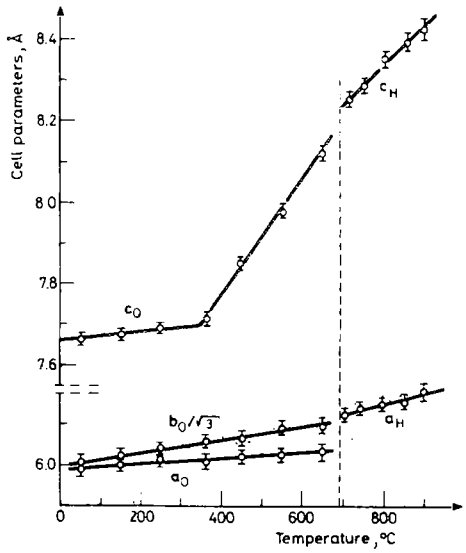

Fig. 1 The thermal expansion of K_2CrO_4

the phase transformation, a_H and c_H expand almost linearly, and there is also a smooth change-over of $b_O/\sqrt{3}$ to a_H and c_O to c_H across the critical temperature. The values obtained for the expansion coefficients using the slopes of least square fitted straight lines are $\%\, B_{b,\,ortho} = 2.44 \cdot 10^{-3}$, $\%\, B_{c,\,ortho}$ (below 350°) = $= 1.68 \cdot 10^{-3}$ and $\%\, B_{c,\,ortho}$ (above 350°) $= 22.13 \cdot 10^{-3}$. These values are not calculated for the high-temperature phase because of the large ESD's in the a_H and C_H values.

By and large, this thermal expansion behaviour of K_2CrO_4 appears similar to that of K_2SO_4, but there is a significant difference in the expansions of a_O and b_O. Whereas in β-K_2SO_4, a_O and b_O expand in the same proportion (the straight lines are nearly parallel) [3], here we found that b_O alone is expanding faster and the $b_O/\sqrt{3}$ values near the transition temperature continuously approach the values of a_H. It is probable that the high order–disorder kind of transition found in K_2SO_4 [4] may be less in this case. However, an accurate redetermination of the thermal expansion of K_2SO_4 and an accurate structure analysis of K_2CrO_4 in both the low- and the high-temperature form is essential for a critical assessment of the above conclusion.

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