THERMAL PROPERTIES OF POTASSIUM DICHROMATE

G. M. CLARK, M. TONKS and M. TWEED

Department of Chemical Sciences, The Polytechnic, Queensgate, Huddersfield HD1 3DH, U. K

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Thermosonimetry, DTA, high temperature XRD and hot stage microscopy have been used to study the thermal behaviour of \( \text{K}_2\text{Cr}_2\text{O}_7 \). A rapid triclinic to monoclinic phase transformation occurs at 543 K slowly reversible at 508 K. Severe crystallite fracturing is associated with the reverse transition and manifests anomalous X-ray intensities which have been previously interpreted as metastable phase formation. On reheating, the transformation occurs at 528 K. Possible interpretations of the temperature hystereses are given.

The stable ambient temperature polymorph of anhydrous potassium dichromate, \( \text{K}_2\text{Cr}_2\text{O}_7 \), is triclinic \([1-3]\) and undergoes a monotropic crystalline transformation at 542 K \([4]\). The high temperature polymorph is thought to be monoclinic \([5]\) but no full single crystal determination has been reported. According to Klement and Schwab \([5]\), this high temperature (monoclinic) polymorph when cooled below 509 K reverts to the ambient temperature triclinic polymorph but according to Vesnin and Khrinpin \([4]\) and Jaffray and Labary \([6]\) the transformation is not reversible and a metastable low temperature (also monoclinic) polymorph is obtained below 513 K and which, on reheating, transforms at 528 K to the high temperature (monoclinic) polymorph. Vesnin and Khrinpin \([4]\) also report that enantiotropic phase transformations occur at 618 K and 653 K. In an attempt to resolve these conflicting data, we have report on the results of a study of the thermal behaviour of crystalline \( \text{K}_2\text{Cr}_2\text{O}_7 \) using a combination of DTA, high temperature X-ray diffraction (XRD), hot stage microscopy and thermosonimetry.

Experimental

The potassium dichromate used was BDH "AnaIaR" \( \text{K}_2\text{Cr}_2\text{O}_7 \) recrystallised from aqueous solution and dried at 400 K.

DTA measurements were performed with a Stanton Redcroft 673 - 4 apparatus capable of operation to 1500°. The sample and reference (\( \text{Al}_2\text{O}_3 \)) were contained in Pt crucibles and were heated, unless otherwise stated, in static air at 10 K min\(^{-1}\). Quoted temperatures are extrapolated onset temperatures and are estimated to be ±1 K.
XRD traces were obtained using a Philips PW 1009/80 X-ray generator in conjunction with a PW 1050/25 powder diffraction set. A motor driven spinner attachment was fitted to minimise crystallite-preferred orientation effects. High temperature data were obtained by means of small heating elements located above and to the sides of the sample and controlled by a Stanton Redcroft linear temperature variable rate programmer. The sample temperature was measured by a Pt/Pt, 13% Rh thermocouple located at the sample surface and just outside the X-ray beam. The radiation was Ni filtered Cu Kα and the scan rate was normally 1 degree (2θ) per minute. d(pm) spacings calculated from 2θ angles are estimated to be ± 1%.

The hot stage microscope was a Reichert 350°C hot stage unit operated at ×10 magnification.

The thermosonimetry apparatus was based on Lønvik's [7] original design. In