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THERMAL PROPERTIES OF POTASSIUM DICHROMATE

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Thermosonimetry, DTA, high temperature XRD and hot stage microscopy have been used to study the thermal behaviour of $K_2Cr_2O_7$. 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, $K_2Cr_2O_7$, 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 Khripin [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 Khripin [4] also report that enantiotropic phase transformations occur at 618 K and 653 K. In an attempt to resolve these conflicting data, we here report on the results of a study of the thermal behaviour of crystalline $K_2Cr_2O_7$ using a combination of DTA, high temperature X-ray diffraction (XRD), hot stage microscopy and thermosonimetry.

Experimental

The potassium dichromate used was BDH "AnalaR" $K_2Cr_2O_7$ 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 (Al_2O_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 K_α and the scan rate was normally 1 degree (2Θ) per minute. *d*(*pm*) spacings calculated from 2Θ angles are estimated to be ±1%.

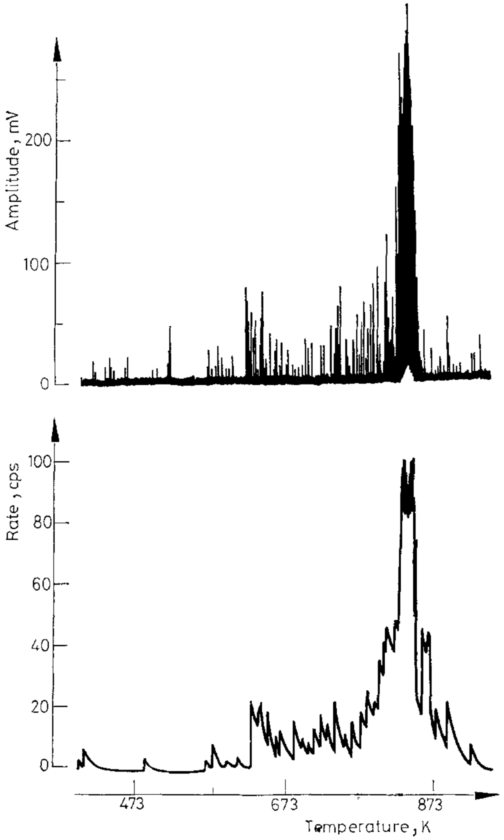

Fig. 1. Thermosonimetric curves of quartz crystals. Top: amplitude (mV), bottom: rate (cps), crystal dimensions: 1–2 mm, heating rate: 10 K min^{-1}

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 essence the measuring system is a silica glass stethoscope or "sounding rod" (200 mm long by 4 mm diameter) standing vertically on a pressure transducer. One end of the stethoscope is shaped in the form of a bell and contains the sample (approximately 1 g), the other end is polished to achieve good coupling with the transducer crystal (163° rotated Y-cut $LiNbO_3$ [8]). The stethoscope is held firmly in the vertical position by two radial groups of ball-bearings 5 mm and 20 mm from the polished end. Samples were heated by means of a small vertical nichrome wound furnace controlled at rates up to 40 K min^{-1}) by a Stanton Redcroft fast cycling linear temperature variable rate programmer. Signals emitted from the sample and focussed by the stethoscope on to the transducer were amplified by a Brookdeal LA 350 100 dB amplifier. Direct passage of the amplified signals (after rectification) to one channel of a Servoscribe RE 571.20 recorder provided curves of the average amplitudes (mV) of individual sonic emissions versus temperature. The average rate (cps) at which the sonic emissions (of amplitude above a preselected threshold) reached the transducer was recorded as a function of temperature by passing the amplifier output to an Isotope Developments 1700 Scaler whose output fed the second channel of the Servoscribe recorder. Temperature was continuously monitored with a chromel-alumel thermcouple located directly above the sample and connected to a Bryans 27000 Series recorder. This recorder was run at the same rate as the Servoscribe recorder, hence providing simultaneous monitoring of rate (cps), amplitude (mV) and temperature.

The form of the two types of thermosonimetric curve is shown in Figure 1 for a sample of small ($\sim 1-2$ mm) natural quartz crystals heated at 10 K min^{-1}. Both the amplitude and rate curves, which are in excellent agreement with those of similar material obtained by Lønvik [7, 9], show peak activity in the region of the $\alpha-\beta$ quartz inversion at 846 K. The precursor activity commencing at approximately 600 K is associated with the breakdown of fluid bubbles and pores within the quartz crystals [9].

Results and discussion

The ambient temperature XRD pattern of triclinic $K_2Cr_2O_7$ was in excellent agreement both with that given in the ASTM index [10] and with the calculated d(pm) values based on the most recent single crystal refinement [3]. Increasing the temperature produced little change in the pattern until, at approximately 543 K, a new set of reflections appeared. During this transformation a few of the stronger reflections of the triclinic polymorph (e.g. 004 at 329.0 pm with $I_0/I = 100$) briefly became doubled as they decreased in intensity, otherwise there was a smooth but rapid transition. The pattern of the high temperature polymorph (at 573 K) is given in Table 1. Klement and Schwab [5] consider that this polymorph is monoclinic with $a = 755$ pm, $b = 752$ pm, $c = 1345$ pm, $\beta = 91° 41'$ probably isostructural with the $P2_1/n$ polymorph of $Rb_2Cr_2O_7$ [11] and the data of Table 1 are indexed on this basis. Although the agreement between the observed and calculated

d(pm) spacings is only reasonable and therefore does not fully verify the conclusions of Klement and Schwab [5], it is very similar to that between the observed and calculated spacings of $Rb_2Cr_2O_7$ for which full structural data are available [11]. On cooling the high temperature (monoclinic) polymorph, the diffraction pattern slowly reverted back over the range 510–480 K to that of the triclinic polymorph, again with some doubling of lines. After the completion of the reverse transformation, the intensities of some of the reflections of the triclinic polymorph were usually observed to have altered often by up to ±20%. However, no new reflections were ever evident and none of the original reflections ever disappeared. (For the explanation of these intensity variations – vide infra.) The X-ray evidence therefore points to a monotropic reversible transformation between the triclinic and monoclinic polymorphs progressing rapidly at 543 K in the forward direction and more slowly below 510 K in the reverse direction. No evidence was obtained for the formation of metastable polymorphs [4, 6].

Table 1

X-ray powder diffraction data for $K_2Cr_2O_7$ at 573 K.

d_{obs}(pm)	I_0/I	‡d_{calc} (pm)	hkl	d_{obs}(pm)	I_0/I	‡d_{calc}(pm)	hkl
671.9	11	672.4	002			327.0	$12\bar{1}$
		663.1	$10\bar{1}$			326.7	202
655.5	2	656.3	011			326.0	211
		653.4	101	321.3	11	325.9	121
		532.7	110	307.2	6	306.9	014
507.6	2	501.2	012			303.3	$21\bar{2}$
		497.3	$11\bar{1}$			301.8	$12\bar{2}$
487.9	8	493.2	111			300.0	122
425.2	1	420.0	$11\bar{2}$	298.3	4	299.6	212
		415.1	112	288.5	2	288.0	023
		388.3	$10\bar{3}$			285.8	$11\bar{4}$
		385.0	013			282.7	114
		382.5	103			271.5	$21\bar{3}$
		377.4	200			270.1	$12\bar{3}$
375.8	37	376.0	020			268.1	123
362.0	3	362.1	021			267.5	213
351.8	3	345.0	$11\bar{3}$	266.0	2	266.3	220
		340.9	113	263.1	3	261.9	$22\bar{1}$
		337.3	210	257.8	1	260.7	221
336.4	100	336.5	120			254.7	$10\bar{5}$
		336.2	004	250.9	5	253.2	015
		331.5	$20\bar{2}$			251.9	105
328.2	4	328.3	$21\bar{1}$	250.3	5	250.6	024, 030
		328.1	022				

+ calculated from $P2_1/n$ $a = 755$ pm; $b = 752$ pm; $c = 1345$ pm; $\beta = 91°41'$ [5].

The DTA peaks associated with the triclinic → monoclinic transformation of $K_2Cr_2O_7$ obtained by successively heating (at 10 K min^{-1}) and cooling (at 5 K min^{-1}) a sample consisting of 500 μm crystallites are shown in Figure 2(a). The first heating endotherm (at 543 K) is approximately twice the area of the subsequent cooling exotherms (at 508 K) and heating endotherms (at 528 K) – these latter peaks being approximately equal in area if allowance is made for the different heating and cooling rates. Thermosonimetric amplitude (mV) curves of the same sample cycled through the transformation at the same heating and cooling rates are shown in Figure 2(b). In these curves the heating peaks successively decrease in amplitude (becoming constant after 3 or 4 heatings) and the cooling peaks show a considerably more prolonged activity than do the heating peaks. The observed decrease in heating peak amplitude suggests that successive cycling through the transition produces crystal strain which is released by thermal shock processes resulting in reduction of crystallite size. The influence of particle size on

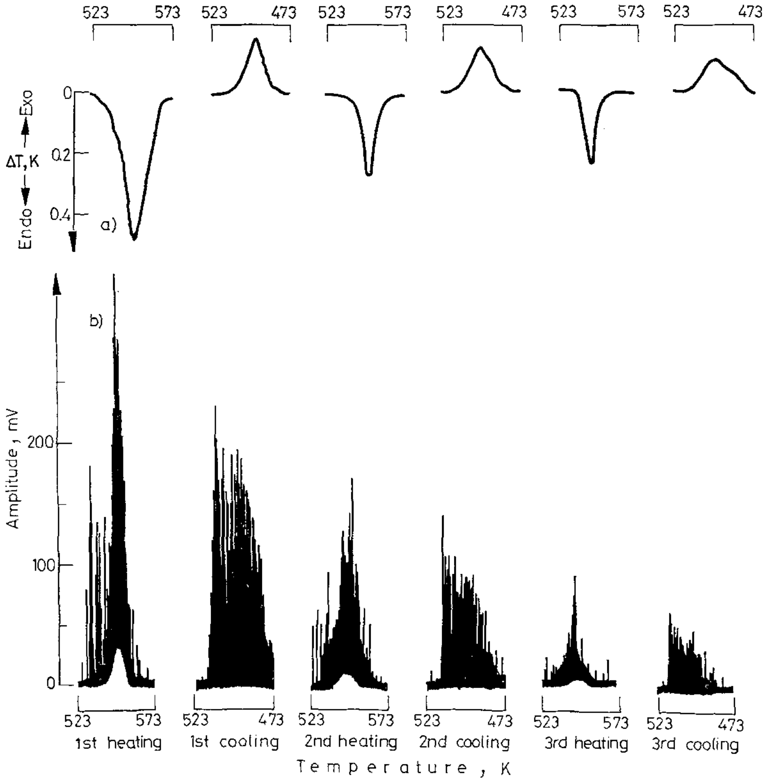

Fig. 2. Successive $K_2Cr_2O_7$ heating and cooling curves. a): DTA; b): TS amplitude. Initial particle size: 500 μm, heating rate: 10 K min,$^{-1}$ cooling rate: 5 K min^{-1}

the thermosonimetric amplitudes and on the DTA peaks obtained on heating various $K_2Cr_2O_7$ samples at 10 K min^{-1} through the triclinic → monoclinic transformation is shown in Figure 3. The thermosonimetric curves show a marked increase in amplitude with increasing particle size, presumably because the low thermal conductivity of $K_2Cr_2O_7$ causes steeper thermal gradients within the larger particles resulting in more catastrophic strain release. The DTA endotherms also show an increase in peak area with increasing particle size. Peak area in DTA is primarily a function of the thermal diffusivity, α, of the sample including its air spaces. (It can be assumed that radiation transfer is a small factor in the total heat transfer function at the temperature of this peak). α is given by the expression [12]:

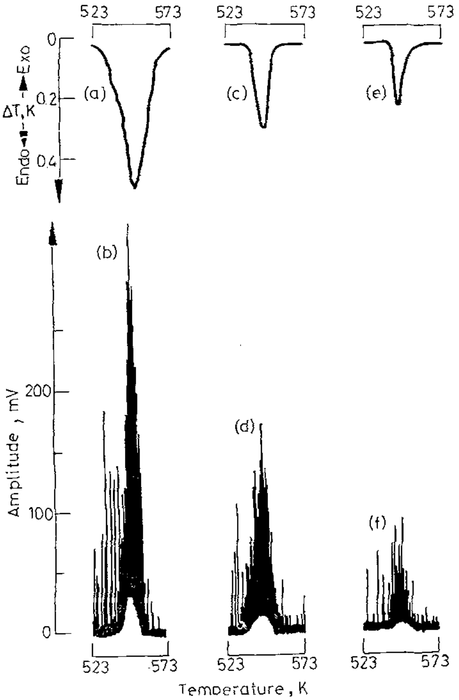

Fig. 3. The influence of particle size on the heating curves of $K_2Cr_2O_*$. Top: DTA, bottom: TS amplitude. Particle sizes: a) and b) 500 μm, c) and d) 200 μm, e) and f) 100 μm.

$$\alpha = \frac{\lambda}{\rho c}$$

where λ = thermal conductivity of sample, ρ = bulk density of sample and c = specific heat of sample.

The influence of particle size on both λ and c will be small and will tend to be compensatory in the case of $K_2Cr_2O_7$ therefore the major influence of particle size on α will be its inverse proportionality with ρ. Since the bulk density certainly increases with decrease in particle size it is to be expected that the area of the transition endotherm will decrease with particle size, in agreement with the observed results, Figure 3.

Since both thermosonimetry and DTA indicated that decreases in crystallite sizes occur during the triclinic → monoclinic transformations, a sample of $K_2Cr_2O_7$ consisting of a mixture of particle sizes was observed on the hot-stage microscope. On heating through 543 K the crystals suddenly crazed over their surfaces and on cooling, the reverse transformation at 510–480 K was accompanied by splitting of many of the larger crystals into smaller fragments. Whether this physical fracturing is purely a thermal shock effect or is associated with the monoclinic → triclinic transformation itself is not clear, but experiments showed that neither the DTA peaks nor the thermosonimetric peaks associated with the second heating were influenced by the rate of cooling after the first heating even when the cooling rate was reduced to 0.5 K $\min^{-1}$. The evidence, therefore, indicates that the physical fracturing is associated with the transition itself.

Vesnin and Khripin [4] report small endothermic events in their DTA curves of $K_2Cr_2O_7$ at 618 K and 653 K which they attribute to further polymorphic transformations. In this work we also occasionally observed small events at temperatures above the 543 K endotherm. However, these were not repeatable and we attribute them to sample settling after the physical disturbances which occur at the 543 K transformation. Settling effects are also noticeable in Figure 2(a) where some peaks are indented with small irregularities. Also of interest is the apparent structuring, in the form of a shoulder, on the second cooling exotherm (more pronounced on the third cooling exotherm) indicating that the monoclinic → triclinic transformation may be complex and may involve an intermediate phase. However, apart from the previously noted doubling of some X-ray reflections, no further evidence of intermediate formation was obtained.

The physical fracturing which predominantly occurs during cooling also accounts for the unpredictable X-ray intensity variations which occur in triclinic $K_2Cr_2O_7$ which has been cycled through its 543 K transformation. Thus, there is sufficient physical disturbance of the sample surface and fracture damage to individual crystallites during the transformation to create intensity inconsistencies which are clearly observable even when a spinner attachment is used. Presumably, the magnitude of these unusual effects was contributory to the previous reports of metastable phase formation during cooling [4, 6]. Presumably, also contributory was the observation that the onset temperatures of the first heating, first cooling and second heating DTA peaks occur at 543 K, 508 K and 528 K, respectively. A heating/cooling temperature hysteresis is not unusual, particularly in compounds containing $[X_2O_7]^{n-}$ diortho-anions (X = Cr, V, P, Si) for which up to 100 K hystereses have been reported [13] and 20 K hystereses are common [14]. Similarly, the rates of forward and reverse transitions in these compounds commonly are considerably different, the reverse transformation normally being the more sluggish [15, 16].

The unusual feature of the $K_2Cr_2O_7$ transformation is that the onset of the first heating endotherm is consistently found at 543 K, whereas the onsets of the second and subsequent heating peaks are found at approximately 528 K. The reason for this is not clear but three possibilities are given here.

(i) Crystals of $K_2Cr_2O_7$ grown from solution always release a small ($<0.1\%$) but variable quantity of water vapour during the triclinic → monoclinic transformation at 543 K [17]. This does not occur during subsequent heatings, thus the pressure exerted by this gas within the crystal may stabilise the triclinic polymorph.

(ii) The unusual external morphology of triclinic $K_2Cr_2O_7$ has been attributed to monoclinic stacking faults [18]. Also a metastable monoclinic polymorph (not the high temperature monoclinic polymorph) has been grown from aqueous solution [5]. Although no X-ray reflection which cannot be indexed on the basis of the triclinic cell has been observed, it is possible that small amounts of these overgrowths, present in solution grown crystals but perhaps not present in crystals formed by cooling the high temperature polymorph, have a stabilising influence on the triclinic polymorph.

(iii) The physical damage which occurs even during slow cooling may extend to the crystalline structure itself. Thus, triclinic $K_2Cr_2O_7$ crystals formed by cooling the high temperature monoclinic polymorph may not only contain an increased quantity of structural and surface defects but may also be positionally and conformationally more disordered than solution grown crystals. The consequent lower lattice energy and higher entropic contributions to the total free energy of the triclinic polymorph formed during cooling from high temperature may be sufficient to lower the transition temperature from 543 K to 528 K.

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RÉSUMÉ — On a étudié le comportement thermique de $K_2Cr_2O_7$ par thermosonimétrie, ATD, diffraction des rayons X à haute température et microscopie avec platina chauffante. Une transformation rapide de la phase triclinique à la phase monoclinique a lieu à 543 K et est lentement réversible à 508 K. Un fractionnement important des cristallites est associé à la transition inverse et se manifeste par des intensités anormales des raies de diffraction X, ce qui a été préalablement interprété comme la formation d'une phase métastable. Lors d'un nouvel échauffement, la transformation a lieu à 528 K. Diverses interprétations possibles de l'hystérèse de température sont proposées.

ZUSAMMENFASSUNG — Thermosonimetrie, DTA, Hochtemperatur-XRD und Mikroskopie in heißem Zustand wurden zur Untersuchung des thermischen Verhaltens von $K_2Cr_2O_7$ eingesetzt. Eine schnelle Phasenänderung von der triklinen zur monoklinen Form findet bei 543 K statt, welche bei 508 K langsam reversibel ist. Der schwere Kristallbruch ist mit dem umgekehrten Übergang verbunden und weist anomale Röntgenstrahlen-Intensitäten auf, welche früher als Bildung einer metastabilen Phase gedeutet wurden. Bei wiederholtem Aufheizen geht die Änderung bei 528 K vor sich. Mögliche Deutungen der Temperaturhysterese werden gegeben.

Резюме — Для изучения термического поведения $K_2Cr_2O_7$ были использованы термоультразвукометрия, ДТА, высоко-температурная рентгеновская дифрактометрия и горячая ступенчатая микроскопия. При 543 К происходит быстрое фазовое превращение от триклинной до моноклинной системы, которое медленно обратимо при 508 К. Разрыв фрактурированных кристаллитов связан с обратным переходом и проявляется в аномальной интенсивности рентгеновских линий, что ранее было интерпретировано как образование метастабильной фазы. При повторном нагреве превращение наблюдается при 528 К. Дана возможная интерпретация этого температурного гистерезиса.