Thermochimica Acta, 29 (1979) 243–246

THERMOSONIMETRY OF SOME ALKALI METAL DICHROMATES

K. LØNVIK
Institutt for eksperimentalfysikk, NTH, Trondheim.

INTRODUCTION

Thermosonimetry (TS) (ref.1) is basically a technique for detecting mechanical vibrations induced by volumetric changes in solids. The preliminary aim of this work was to compare results, using this method, with known data on structural phase transitions in alkali metal dichromates (ref.2). From a purely structural point of view, these substances are extremely interesting, due to their polymorphism. The TS temperature spectroscopy was performed on available analogous substances such as potassium, sodium and cesium-dichromate. The results presented are in agreement with those of other methods.

EXPERIMENTAL PROCEDURE

The TS-measurements were carried out with a commercial P.A. analytical reagent grade of specimen. At the start of the experiment the crystalline powder was loosely packed in the open sample holder of the stethoscope (ref.1), and then heated in an open-air atmosphere to a temperature level well above melting point. The molten sample was then immediately cooled down to a certain pre-determined temperature and subsequently reheated a second time. The rate of TS-activity was then recorded as a function of the temperature measured in a dummy sample placed near the sample holder with the dichromate.

RESULTS

The recordings of the primary rate of TS-activity versus the reference temperature for each of the three different crystalline samples are given in Figs. 1,2 and 3. The onset temperatures (corrected according to calibration) of the prominant processes of $K_2Cr_2O_7$ are summarized in Table 1. They are in good agreement with known transitions.

TABLE 1

State of sample	Starting temp.	Onset temp. of p.t. structural	Onset temp. of p.t. fusion	Processing
Orig.crystalline powder	20°C	262°C	395°C	1. heating
		245	388	cooling
Prev.melted sample	200°C	262	395	2. reheating
		261	388	cooling
	20°C	247	395	3. reheating
		262	390	cooling

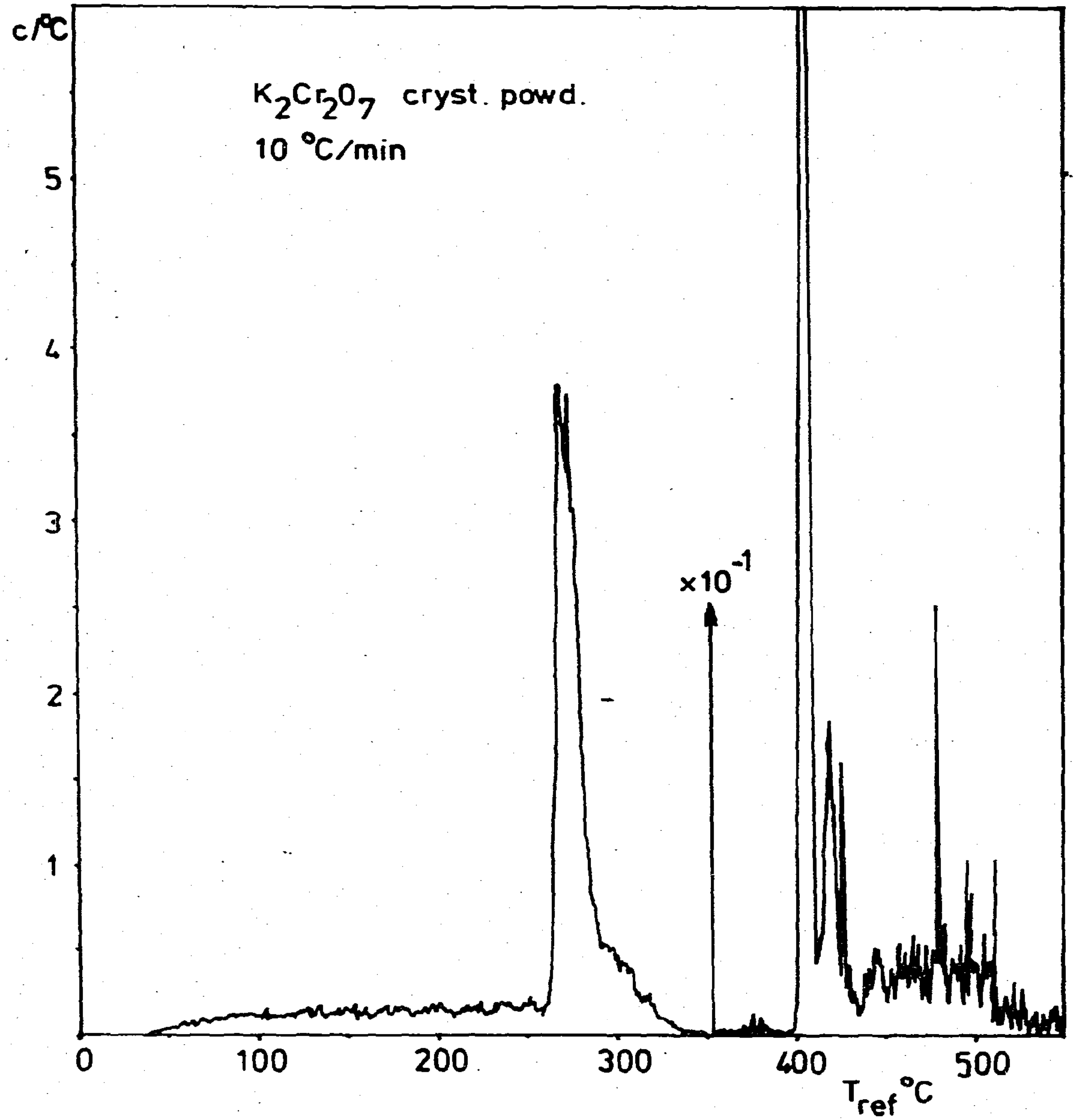

Fig. 1. A complete registration of a sample of $K_2Cr_2O_7$-crystalline powder showing the phase transitions. Additional TS-information is found at 503, 599, 620 and 630 and precursing effects at 648 K.

The thermal pre-history and the state of the sample obviously have an effect on the temperature instability of the structural change.

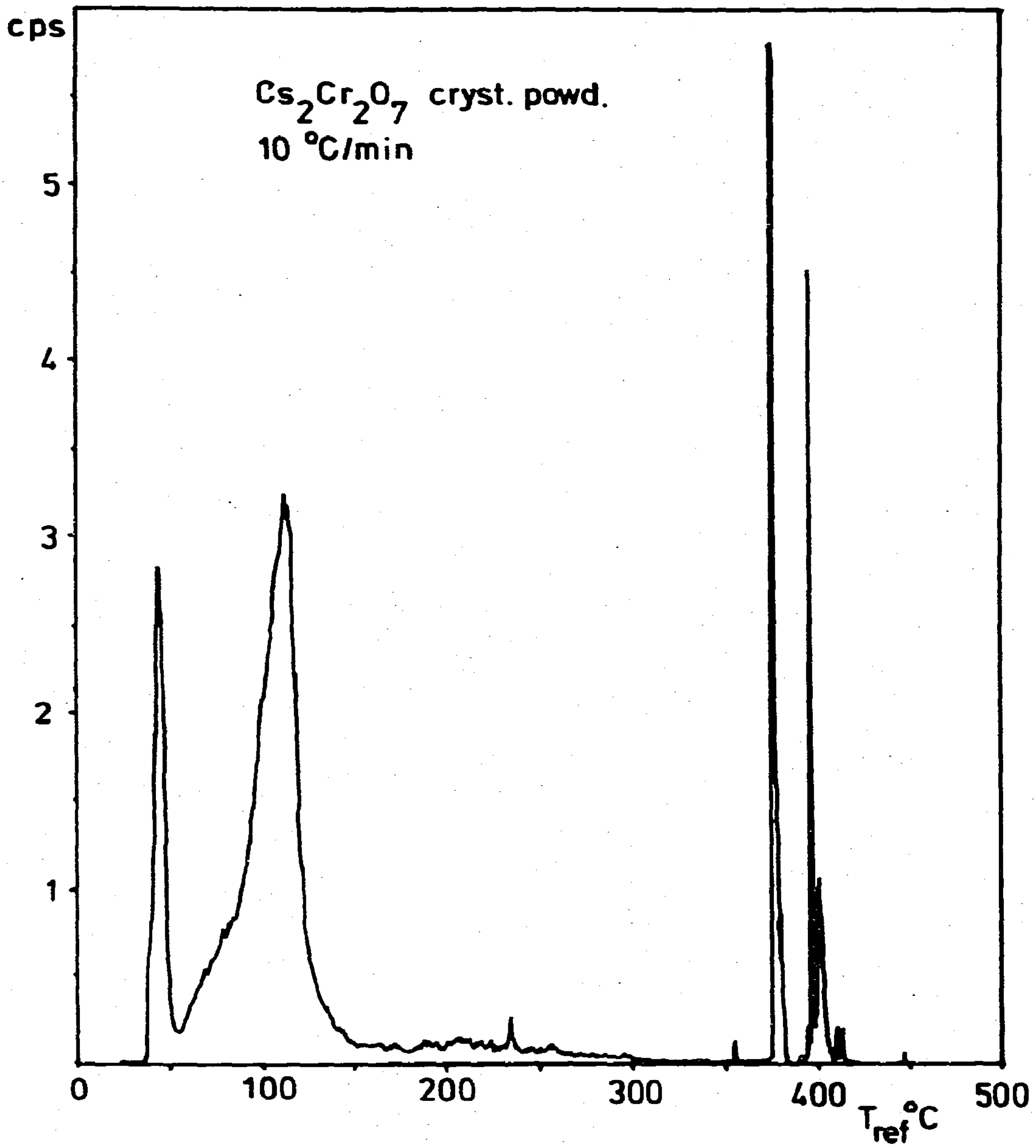

Fig. 2. Rate of TS-activity in a sample of $Cs_2Cr_2O_7 \cdot 2H_2O$ - crystalline powder giving the effect of release of crystal water and the temperatures of phase transitions; structural 636 and by reheating 626, fusion 657 K. Extra TS-lines are observed at 469, 504, 636 and a change in the general TS-level at 573 K.

In the temperature regions outside the known peaks of the phase transitions, several additional TS-activities were observed of unidentified physical character. However, the most striking characteristic for all the dichromates investigated was definitely the numerous sub-peaks and peak splitting during the course of the melting process.

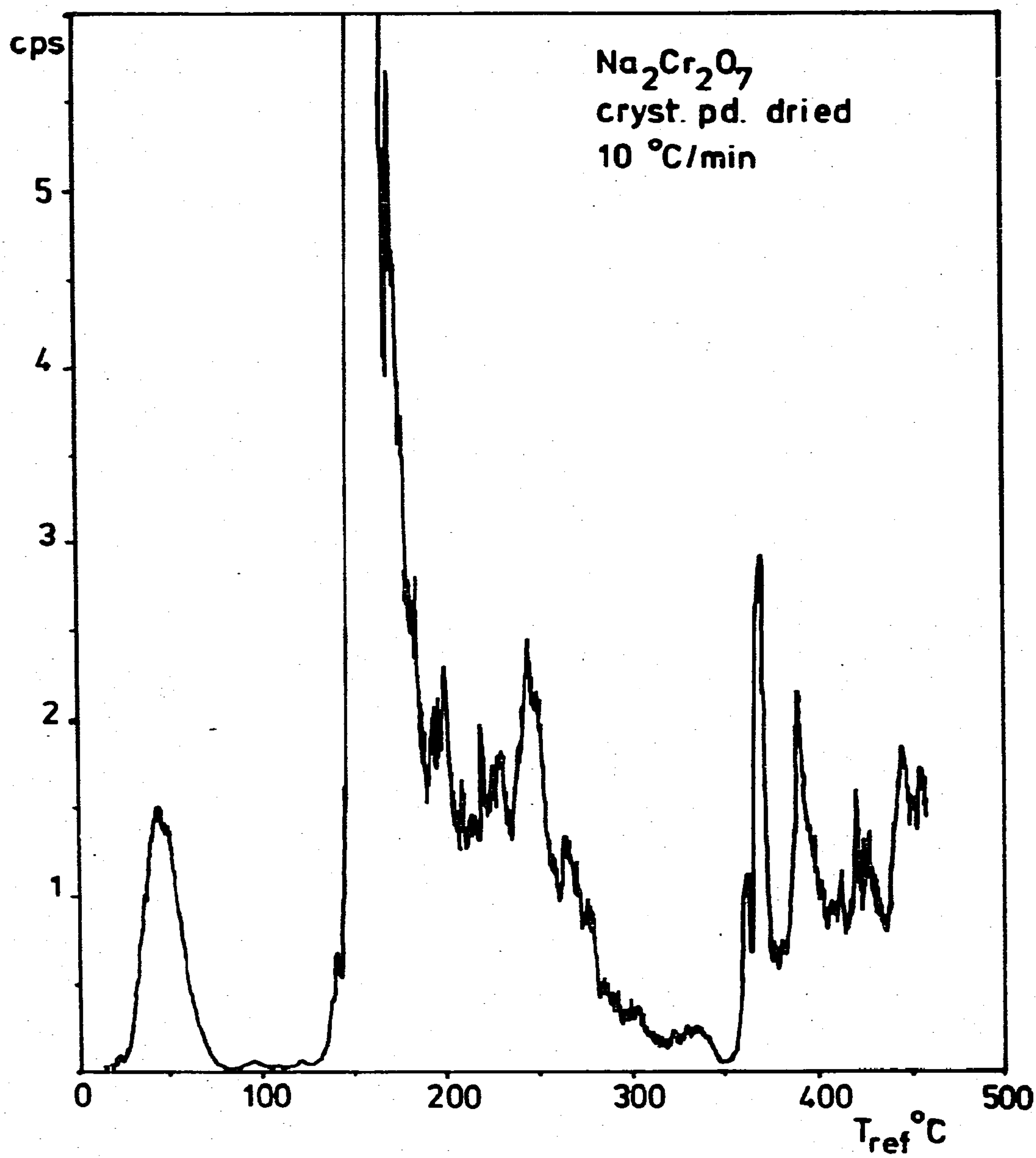

Fig. 3. The TS-recording of a sample of $Na_2Cr_2O_7 \cdot 2H_2O$-crystalline powder with the characteristic drop in the precursing TS-activity before the proposed onset of fusion at 628 K. Within the immediate broad range of continuously decreasing activity, the following peaks are recognized at 440, 521 and 602 K.

REFERENCES

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