Thermochimica Acta, 58 (1982) 107–109
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THE THERMAL EXPANSION AND CRYSTALLOGRAPHIC PHASE TRANSFORMATION OF Na_2CrO_4

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(Received 10 March 1982)

In continuation of earlier studies on the nature of phase transformation in Na_2SO_4 and $NaBF_4$ [1,2], we report here the work done on the thermal expansion and nature of thermal phase transformation in anhydrous Na_2CrO_4. It is known that at room temperature Na_2CrO_4 is isomorphous with Na_2SO_4(III) and that it is transformed from orthorhombic to hexagonal when heated beyond 413°C [3]. Two factors prevented single crystal work as in the case of Na_2SO_4(III) [1]: (1) The crystals were hygroscopic; and (2) the transition temperature being 413°C, the enormous heat conduction affects the X-ray film in the Weissenberg set-up. A maximum of 300°C alone could be reached previously [1].

EXPERIMENTAL

X-Ray powder patterns of anhydrous Na_2CrO_4 were obtained using CuK_α radiation in conjunction with the M.R.C. high temperature assembly fitted to the Philips wide-angle goniometer. The temperature measurements are in error of about 1°C (in the range studied). The *d* values obtained at room temperature, 152, 254, 305, 352, 405, 452, 504 and 552°C were least squares fitted to deduce the lattice parameter values before and after the phase transition. Before starting the work, the sample was kept in the camera at 120°C for 2 h while a stream of N_2 gas was flushed through the camera to remove all the water vapour. The E.S.Ds found in the lattice parameters are indicated in Fig. 1.

RESULTS AND DISCUSSION

The lattice parameters *a*, *b* and *c* of the orthorhombic form (space group *C mcm*) and the *a* and *c* values of the hexagonal form vs. temperature are

0040-6031/82/0000–0000/$02.75

plotted in Fig. 1. It is seen that within the temperature range studied and the errors involved in the experiment, the thermal expansion is linear. Least squares straight lines were fitted as shown in Fig. 1. It is found that while for

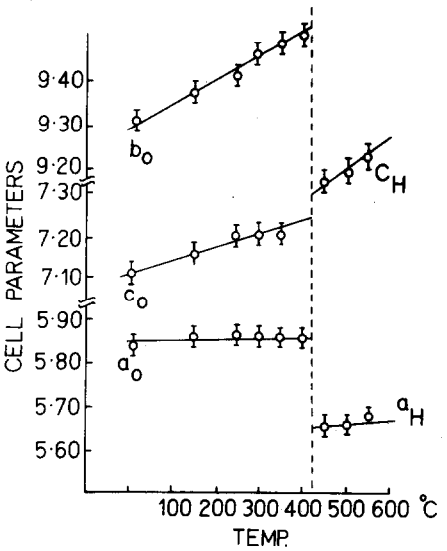

Fig. 1. Thermal expansion of $Na_2Cr_2O_4$ (isomorphous with Na_2SO_4 III).

the *a* axis there is practically no expansion before and after the transition, a maximum expansion is found for the *b* axis. The values obtained for the thermal expansion coefficients using the slope of the least squares fitted straight lines are $\% B_{b,\text{ortho}} = 5.22 \times 10^{-3}$ and $\% B_{c,\text{ortho}} = 4.21 \times 10^{-3}$. These values and the nature of the thermal expansion behaviour are very similar to those of Na_2SO_4(III) [4]. Hence it is concluded that the nature of the phase transformation in anhydrous Na_2CrO_4 is akin to that of Na_2SO_4(III), i.e., topotactic, and that here also the pseudo-hexagonal cell at room temperature converts to the regular hexagonal cell as was found in the lattice relations during the phase transformation of Na_2SO_4(III) [1].

ACKNOWLEDGEMENT

The authors wish to thank Dr. A.C. Momin for his help in collecting the X-ray data.

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