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A DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF PHASE TRANSITIONS IN Na_2SO_4

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The results of a differential scanning calorimetric study of the transitions involving the various polymorphs of Na_2SO_4 are described. They are discussed in the light of their crystal structures and also in conjunction with more recently published data regarding these transitions.

Kracek [1] reported that Na_2SO_4 at atmospheric pressure exists in three crystalline forms, and designated them as V, III and I. Polycrystalline V separates from aqueous solution at 305.5 K. This, on heating, transforms into III which, in turn, at elevated temperatures goes over to I. The crystal structures of these three modifications have either been worked out from single-crystal X-ray data or by inference from the completely elaborated structures of other, isomorphic compounds.

DTA studies [1, 2] have indicated that these polymorphs interconvert according to the following scheme:

$$\underset{\text{Orthorhombic}}{\mathrm{V}} \xrightarrow{480\ \mathrm{K}} \underset{\text{Orthorhombic}}{\mathrm{III}} \xrightarrow{521\ \mathrm{K}} \underset{\text{hexagonal}}{\mathrm{I}}$$

Some interesting aspects of the influence of grinding on these transformations, and especially the V → III transition, were reported by Goyal et al. [2]. They showed that in a well-ground sample the V → III transition is totally absent, as observed in a DTA study, and concluded that V had transformed to III on grinding.

We report here our observations on these transformations as studied by differential scanning calorimetry (DSC).

Experimental

The Na_2SO_4 sample was of BDH ANALAR quality. However, as discussed later, this material could not be used as such, and fresh crystals had to be grown from an aqueous solution of this Na_2SO_4. The calorimeter used was the Perkin Elmer DSC-1B. The sample size was about 10 mg.

Results

The DSC scans of the Na_2SO_4 powder taken from the original packing gave peaks which were not reproducible. Hence, single-crystals were grown from an aqueous solution. It was observed that at 308 K predominantly prisms were obtained, although a few needle type crystals were also formed. On crystallizing at elevated temperatures, the proportion of the needles increased considerably, but at all temperatures in the range 308 – 368 K both types of crystals separated out. From X-ray powder patterns as well as single-crystal studies of the prisms and needles, it was established that these were phases V and III, respectively. A photograph of these crystals is shown in Fig. 1. The DSC scans at 8°/min are shown in Fig. 2. The DSC observations can be summarized as follows:

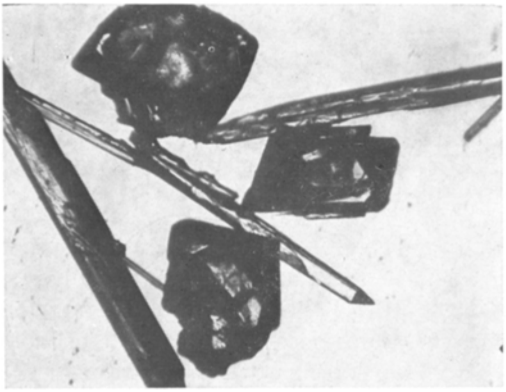

Fig. 1. Optical microscopic photograph of the two types of crystals of Na_2SO_4 with magnification × 300

Prisms

(1) The prisms hand-picked from the crystallized material gave a transition at 477 K (Fig. 2a), which is consistent with the earlier known V → III transition [1, 2, 6]. The heat of this transition is calculated to be 3.6 ± 0.4 cal/g. This is at variance with the reported [6] value of $\Delta H = 5.2 \pm 0.8$ cal/g for this transition. The observation of this peak at 477 K is consistent with the fact that needles of III do not exhibit this peak. Hence the assignment of the peak to the V → III transition is confirmed.

(2) During the first heating of V, in addition to the 477 K peak, another broad peak (Fig. 2b) at 523 K, with a total heat of transition of 8.5 ± 0.5 cal/g, was observed.

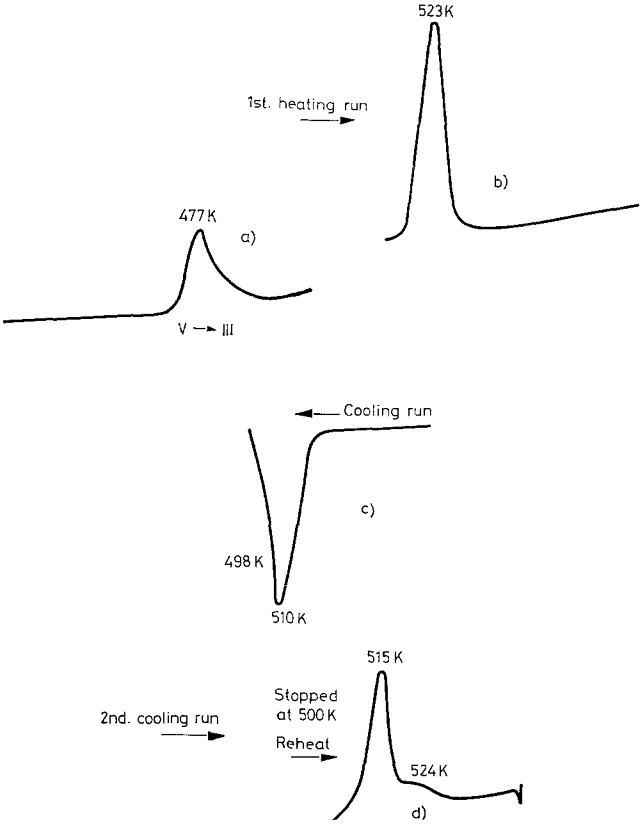

Fig. 2. Heating and cooling run of Na_2SO_4

(3) On first cooling from about 550 K, a doublet (Fig. 2c) at 501 K and 498 K, attributed to the I → III transition, with a combined $\Delta H = 8.8 \pm 0.8$ cal/g, was obtained. No other peak was observed during the first or subsequent cooling cycles down to room temperature.

(4) On second heating from room temperature (or during subsequent heating) the 477 K peak due to V → III was absent, which indicated that the sample once heated beyond 477 K did not revert immediately to V on cooling to room temperature. This is consistent with earlier DTA data [1, 2, 6]. This observation was interpreted as due to the metastability of phase III. We find that single-crystals of III can be grown at room temperature and are stable over P_2O_5 in a desiccator for at least four months.

During second and subsequent heating cycles, the III → I transition is observed with a slight shift in the temperature of transition (530 K). The ΔH of this transition is about 8.0 ± 0.8 cal/g.

(5) Second and subsequent cooling cycles gave the same results as in (3) above.

(6) A new feature hitherto not reported regarding these transitions is that if the cooling cycle is terminated at 500 K, i.e. after passing through the 501 K peak but not the 498 K peak, and the sample is reheated, a very well resolved doublet (Fig. 2d) at 515 K and 524 K, with a combined $\Delta H = 6.2 \pm 0.6$ cal/g, is obtained. On cooling back, the doublet at 501 K and 498 K is obtained once again, with a total $\Delta H = 8.4 \pm 0.8$ cal/g. Terminating cooling at 500 K and reheating gave the same results as above. Also, if the cooling was continued below 500 K, the 498 K peak was observed. Once the sample was cooled below the 498 K peak, further reheating gave back the unresolved 523 K peak, with $\Delta H = 8.0 \pm 0.8$ cal/g. Kracek and Gibson [6] gave a value of 12.6 cal/g for the III → I transition.

Needles of III

Needles of III gave identical results as described above for prisms of V. Naturally, the 477 K peak due to the V → III transition was absent.

Discussion

These results indicate that the V → III transition is a single-stage process, and is irreversible in the sense that once III is formed it does not revert to V even after cooling to room temperature. An examination of the crystal structures proposed for these polymorphs suggests that probably the V → III transition is of reconstructive type, in which all bonds are broken and remade within a narrow temperature interval.

Amirthalingam et al. [3] have shown that the III → I transition is a truly topotactic transformation, and involves minor shuffles and rearrangement of atoms in the structure. The orthorhombic III can be visualized in terms of a pseudo-hexagonal cell to start with, and on transformation to I it becomes truly hexagonal. Our DSC results mentioned above involved more than one step for the III → I transformation.

Such a possibility finds support in the work of Mehrotra et al. [4], who interposed a phase II between III and I in their scheme of transitions. Pistorius [5] in his work on high-pressure polymorphic changes of Na_2SO_4 does not include phase II right up to 60 Kbar and 723 K. Nevertheless, Kracek and Gibson [6] mentioned that if the I → III transition is inhibited during cooling, then I goes over to II reversibly at 509 K.

In the light of this, the present DSC data can be explained on the basis of the following scheme:

(a) Complete heating and cooling cycling:

$$\mathrm{V} \xrightarrow{477} \mathrm{III} \xrightarrow{523} \mathrm{(II)} \xrightarrow{523} \mathrm{I} \quad \text{FIRST HEATING}$$

$$\mathrm{III\ (RT)} \longleftarrow \mathrm{III} \xleftarrow[498]{} \mathrm{II} \xleftarrow[501]{} \mathrm{I} \quad \text{COOLING}$$

Probably metastable

(b) Heating up to 23 K and partial cooling to 501 K:

$$\text{Partly (III)} + \text{II} \xrightarrow{501} \text{I}$$

$$\text{Reheat III} \xrightarrow{515} \text{II} \xrightarrow{525} \text{I}$$

Thus, a revised scheme of phase transitions is suggested, as follows:

$$\text{V} \xrightarrow{477} \text{III} \xrightarrow{515} \text{II} \xrightarrow{523} \text{I}$$

$$\text{III} \xleftarrow[498]{} \text{II} \xleftarrow[501]{} \text{I}$$

This shows that pure phase III can be superheated and goes over to I directly, without an intermediate step. However, if II co-exists with it (as in the case of observation (6) above), III goes first to II and only then to I. In this way one could obtain the transformation temperatures for III → II and II → I steps without ambiguity.

In view of the metastability of some of the phases, and the sluggishness in the transformations, no undue importance should be attached to the actual heats of transition. This partly explains the wide discrepancy between the value for ΔH for the transitions reported in the literature by different authors.

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Résumé — On décrit les résultats de l'étude, effectuée par analyse calorimétrique différentielle, des transitions mettant en jeu les diverses formes polymorphes de Na_2SO_4. Les résultats sont discutés en tenant compte des données récemment publiées sur ces transitions.

Zusammenfassung – Die Ergebnisse einer mit Differentialabtastkalorimetrie durchgeführten Untersuchung der Übergänge verschiedener Polymorphe von Na_2SO_4 werden beschrieben. Sie werden im Hinblick ihrer Kristallstrukturen und im Zusammenhang mit verschiedenen unlängst veröffentlichten Daten bezüglich dieser Übergänge diskutiert.

Резюме — Описаны результаты изучения переходов и различных полиморфных форм для сульфата натрия с помощью дифференциальной сканирующей калориметрии. Результаты обсуждены на основе их кристаллических структур, а также в связи с недавно опубликованными данными для этих переходов.