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DTA AND X-RAY STUDIES ON THE PHASE TRANSITION IN UNDOPED AND YTTRIUM-DOPED SODIUM SULFATES

YASUTOSHI SAITO *, KURIMA KOBAYASHI and TOSHIO MARUYAMA

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227 (Japan)

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ABSTRACT

Phase transitions in undoped and yttrium-doped sodium sulfates (Na_2SO_4) were studied by differential thermal analysis (DTA) and X-ray diffraction. After several cycles of heating and cooling, the undoped Na_2SO_4 finally exhibited one endothermic peak at 250°C on heating and two exothermic peaks around 230°C on cooling, regardless of the method of sample preparation. These peaks corresponded to the transitions between the high temperature stable phase (phase I) and the low temperature metastable phase (phase III). On cooling, the I → III transition accompanied the formation of an intermediate phase (phase II), which was composed of the reversible I ↔ II and irreversible II → III transitions. The transition temperatures lowered in samples containing less than about 1.7 at.% yttrium, e.g., down to about 170°C on heating in the 0.8 at.% Y-doped sample. The doping of more than about 2.0 at.% Y raised the transition temperatures, e.g., up to about 320°C on heating in the 3.8 and 5.3 at.% Y-doped samples. High temperature X-ray diffraction revealed that the transition in the yttrium-doped samples was basically the same as the III ↔ I transition in the undoped Na_2SO_4.

INTRODUCTION

It is known that anhydrous sodium sulfate (Na_2SO_4) exhibits five polymorphisms referred to as phases I to V. Since distinguished works by Kracek et al. [1–4], numerous studies [5–17] have been made on the phase transitions of Na_2SO_4 by means of differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction, dilatometry, Raman spectroscopy and heat capacity measurement. Phase V, which is named thenardite, is the stable modification at ordinary temperatures, and it finally transforms into phase I on initial heating through different routes depending on the method of preparation, thermal history, water or acid contamination, and so forth. The high temperature modification, phase I, transforms into phase III on cooling. Phase III is metastable at room temperature, as pointed out in equilibrium diagrams by Kracek [1] and Brodale and Giauque [10], and it converts to phase V over a period of days to months only in

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* To whom correspondence should be addressed.

undried air. Upon second and the subsequent heating and cooling, the III ↔ I transition reversibly occurs with a hysteresis accompanying the formation of an intermediate phase (phase II) on cooling. The transition behavior stated above is generally consistent among the quoted papers, whereas the transition mechanism and the formation of intermediate phases have not yet been fully established.

In recent years, the high temperature modification, phase I, has become an interesting material as a solid electrolyte with the Na^+ ion conduction. Jacob and Rao [18] showed the possibility of using phase I of Na_2SO_4 as a solid electrolyte in a galvanic cell for the detection of sulfur oxides in a gaseous phase. The substitution of Na^+ ions by the divalent or trivalent ions in the cation sublattice of phase I is expected to cause an increase in the cation vacancy concentration and thereby high ionic conductivity. It has been recognized by Höfer et al. [19,20] that the Na^+ ions can be replaced by Y^{3+} ions up to 15% corresponding to 30% cation vacancies in phase I, which results in an increase of electrical conductivity.

In spite of crystal chemical and electrochemical studies on the solid solution in Na_2SO_4–$Y_2(SO_4)_3$ system [15,19,20], the effect of yttrium-doping on the phase transition in Na_2SO_4 has not yet been clarified. The purpose of the present paper is to attempt to elucidate the phase transition of undoped Na_2SO_4 prepared by various methods and the effect of yttrium-doping on the III ↔ I transition in Na_2SO_4 by DTA and X-ray diffraction techniques. Further work will describe the proposed mechanism of the III ↔ I transition for interpreting the DTA curves obtained here.

EXPERIMENTAL

Materials

Four samples of undoped Na_2SO_4, including its hydrates, were used for DTA measurements and referred to as samples (A) to (D) as follows.

Sample (A): powdered anhydrous Na_2SO_4 of 99.99% purity was used without any treatment.

Sample (B): decahydrate ($Na_2SO_4 \cdot 10\ H_2O$) crystals of 99.99% purity were ground to powders with an agate mortar.

Sample (C): transparent monocrystals of Na_2SO_4 were crystallized on slow cooling from the melt of sample (A) held at 1090°C for 2 h in a platinum crucible.

Sample (D): transparent crystals (1–8 mm in size) were crystallized out of a saturated aqueous solution of sample (A) at about 60°C.

Samples (A) and (B) were purchased from Wako Pure Chemical Industries Ltd., Japan.

Yttrium-doped samples (0.3–5.3 at.% Y) were prepared using the following procedure. Weighed Y_2O_3 of 99.99% purity was dissolved in sulfuric acid. The desired amount of sample (A) was added to the solution and diluted with distilled water for the complete dissolution of Na_2SO_4. After evaporation of the solution to dryness, the remaining white solid was heated at 400°C for 6 h, and then pulverized by grinding. The powder thus obtained was calcined at 800°C for 6 h, pressed into pellets at 2 ton cm^{-2} and sintered at 800°C for 48 h. The sintered pellets were finally ground to powders. The yttrium content in the doped samples was determined by X-ray fluorescence analysis, and was defined as the atomic fraction of yttrium in all cations, i.e., $Y/Na+Y\%$.

Apparatus and Procedure

DTA curves in air were recorded with Rigaku Thermoflex M 8075 (TG–DTA) and Shinku Riko DSC-1500 (DSC–DTA) using samples of 5–20 mg with α-Al_2O_3 as reference material. The temperature was raised and lowered at a rate of 2.5°C min^{-1} in samples (A) and (B), and 2°C min^{-1} in samples (C) and (D). The rates employed seemed to be slow enough to detect the formation of an intermediate phase during the transition. In yttrium-doped samples, the temperature was varied at a rate of 2.5°C min^{-1}.

X-Ray powder diffraction patterns were obtained using a Rigaku Geigerflex high temperature X-ray diffractometer using Ni-filtered Cu K_α radiation in the range room temperature to 760°C. The platinum sample holder was used as a heater, on which the 5–20 mg sample was coated. Platinum showed strong reflections at $2\theta \approx 41$, 47 and 68°, so the reflections of the samples could not be observed around these angles. On account of the geometrical condition, it was impossible to determine exact values of interplanar spacings.

RESULTS AND DISCUSSION

Undoped Na_2SO_4

Figure 1 shows DTA curves of four undoped samples. Sample (A) exhibited a broad endothermic peak between 235 and 270°C on first heating. As seen in Fig. 1, this peak is asymmetric and appears in the form of multiple peaks over a wide range of temperature. By X-ray diffraction sample (A) was identified to be phase V, and the high temperature phase after the peak to be phase I. On the basis of earlier studies [1,13,16], phase V finally transforms into phase I on heating through the successive or simultaneous formation of intermediate phases depending on atmosphere and conditions of the sample preparation. The asymmetry and multiple splitting of the DTA curve may be attributed to several transformations between phases.

Phase I thus obtained is stable up to the melting point. Cooling phase I yielded two exothermic peaks around 235 and 227°C. These peak temperatures are in good agreement with the reported values [1,16] for the I → II and II → III transitions, respectively. No other peaks were detected down to room temperature, and the end product was identified as phase III by X-ray diffraction.

On second heating, however, only one endothermic peak was observed around

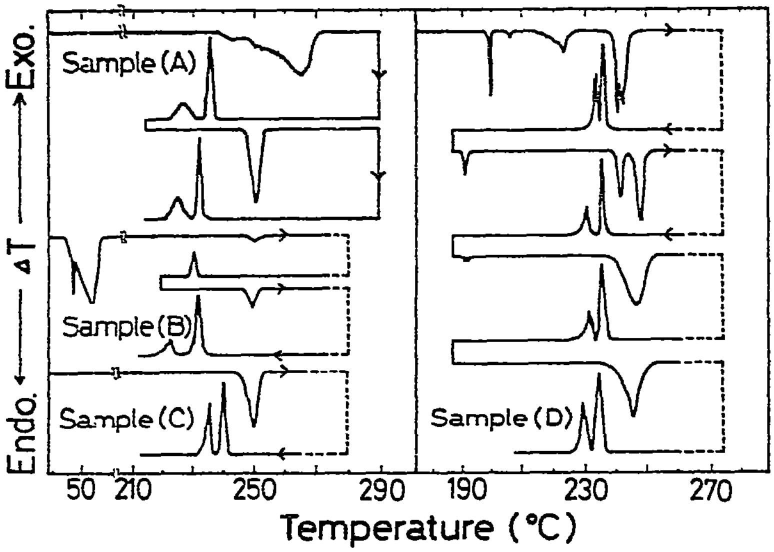


Fig. 1. DTA curves of the undoped Na_2SO_4 prepared by various methods.

250°C corresponding to the III → I transition. The subsequent cooling from phase I gave two exothermic peaks at slightly lower temperatures than those obtained on first cooling. A minor shift in peak temperatures disappeared after several repetitions of heating and cooling.

Sample (B) showed two prominent endothermic peaks in the temperature range 25–70°C and a small endothermic peak at about 255°C on first heating. Thermogravimetry and X-ray diffraction suggested that the first two peaks corresponded to the dehydration and the small peak to the V → I transition. On first cooling, a small exothermic peak was observed at about 230°C. Second heating gave an endothermic peak at 252°C, and two exothermic peaks appeared around 231 and 222°C on second cooling. All the peaks after the dehydration grew with the repetition of heating and cooling, which suggested an increase in crystallinity of each phase.

Sample (C) showed one endothermic peak at 250°C on first heating from room temperature, and two exothermic peaks around 232 and 228°C on subsequent cooling. The DTA curves obtained in sample (C) were almost the same as those in sample (A) subjected to several cycles of heating and cooling. Therefore, sample (C) should be phase III of Na_2SO_4. Actually the X-ray diffraction pattern of sample (C) was in good agreement with that of phase III observed at room temperature in the present study. This result indicates that sample (A) should finally convert to phase III on cooling after the crystallization from the melt in a platinum crucible.

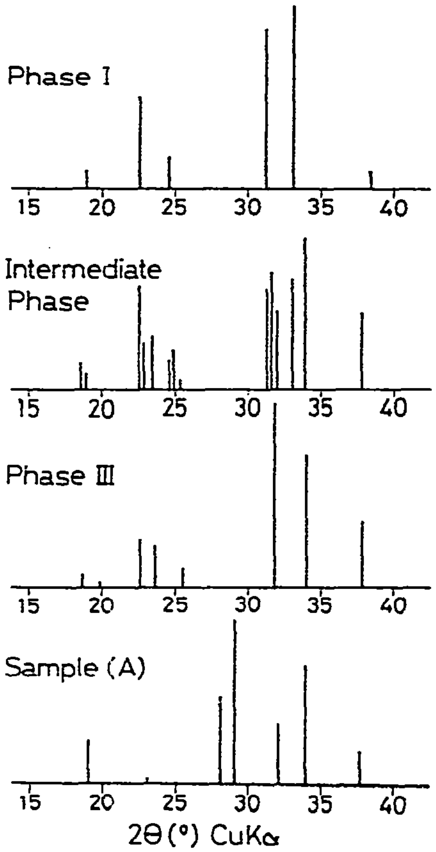
DTA curves of sample (D) were more complicated, especially on initial heating in which several endothermic peaks appeared. On first cooling, two exothermic peaks were observed around 236 and 235°C. Three endothermic peaks existed at 195, 245 and 251°C on second heating. On second cooling, two exothermic peaks were recognized at 235 and 230°C, which was almost the same in the subsequent cooling cycles. Upon third heating, the endothermic peak around 195°C became extremely small, and the peaks at 245 and 251°C combined into one peak. It has been reported that phase V transforms into phase I through the transitions between polymorphs in sequence [1,13,16]. The complex DTA curves observed on initial heating and cooling in sample (D) may result from these transitions. As generally noted [1,10], the transitions in Na_2SO_4 are affected by moisture in the atmosphere. Brodale and Giauque [10] have stated that it is very difficult to remove water completely from Na_2SO_4 by heating at 350°C. They have also mentioned that Na_2SO_4 may contain many nuclei of phase V even if it is held at temperatures in which phase I is stable. Mehrotra et al. [13] have pointed out that the III ↔ V transition is very sluggish. These facts suggested that nuclei of phase V remained over the whole temperature range on initial heating and cooling. Consequently, the peaks detected on first to third heating and cooling in sample (D) may be attributed to the transitions which are influenced by the factors mentioned above, i.e., stepwise transitions between phases V and I, effect of moisture and slowness in some transitions. The complexity in DTA curves for sample (D) was eliminated by several cyclic heating and cooling, and finally only the III ↔ I transition was observed after the fourth cycle.

Samples prepared by various methods gave different DTA curves in the initial cycles of heating and cooling. However, all the samples finally exhibited one endothermic peak at about 250°C on heating and two exothermic peaks around 230°C on cooling after several cycles, which were caused by the III ↔ I transition. The effect of moisture on the III ↔ I transition was assumed to be negligible in the present study because heating and cooling cycles were confined to the temperature range above 200°C.

Figure 2 shows the high temperature X-ray diffraction patterns of phases I, II, and phase III and untreated sample (A). The temperatures were selected on the basis of the DTA results. The pattern of phase II was first determined in the present study, and it remained unchanged during the measurement held at about 230°C for about 1 h on cooling. Kracek [1] found a new phase stable between 234 and 228°C on cooling, and assigned it as phase II. The patterns of phases I and III and untreated sample (A) agreed well with those observed by Kracek and Ksanda [4] and calculated by the simple computer program taking some basic corrections into consideration. The procedure for programming will be presented in another paper [21] with the discussion on the mechanism of the III ↔ I transition.

It is interesting to note that the III ↔ I transition accompanies two exothermic peaks on cooling compared to one endothermic peak on heating. Wiedemann et al. [16] have pointed out that phase II does not appear on heating during the III → I transition. In the I → III transition, the reason for the splitting of the DTA peak on cooling has not been fully known. In order to clarify the difference in the DTA peaks on heating and cooling, the following experiments were performed by interrupting cooling and the subsequent reheating before the complete conversion to phase III. The results obtained are shown in Fig. 3.

Reheating immediately after the end of the first peak on cooling gave a sharp endothermic peak around 235°C. This peak was not observed on heating after the completion of the second peak on cooling. When reheating started in the course of the second peak on cooling, the sharp endothermic peak around 235°C was followed



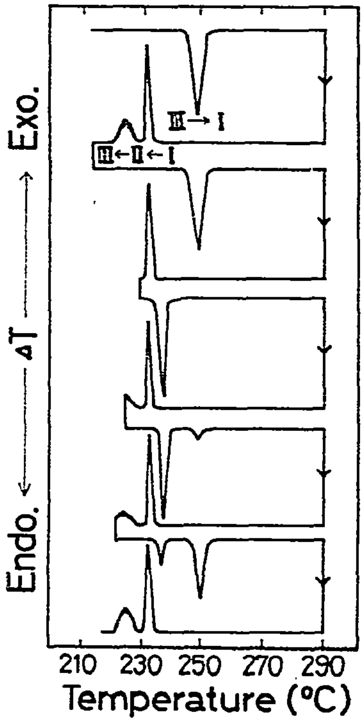


Fig. 2. X-Ray diffraction patterns of phase I, intermediate phase, phase III and untreated sample (A).

Fig. 3. DTA curves of the undoped Na_2SO_4.

by a small endothermic peak at about 250°C, of which the peak temperature corresponded to that for the III → I transition. The peak at 250°C grew larger as the starting temperature of reheating lowered. On the contrary, the peak at 235°C became smaller with the growth of the peak at 250°C. The X-ray diffraction patterns obtained at 230°C on cooling corresponded to that of phase II as described before.

These results suggest that upon cooling phase I transforms into phase II at the first exothermic peak and then into phase III at the second peak. Before the termination of the II → III transition, the remaining phase II converts to phase I on reheating. However, phase II does not appear on heating after the completion of the II → III transition. Phase II can easily revert to phase I, and thereby the hysteresis width is smaller in the II ↔ I transition than in the III ↔ I transition. Mehrotra et al. [13] have pointed out that the I ↔ II transition is very fast, whereas the II ↔ III transition is slower and the III ↔ V very sluggish. Phase III which is once formed on cooling directly transforms into phase I around 250°C on heating without the formation of phase II as an intermediate phase. Thus the I ↔ II transition is proved to be reversible and the II ↔ III transition to be irreversible.

Yttrium-doped Na_2SO_4

Figure 4 shows the effect of yttrium-doping on DTA curves of Na_2SO_4. Doping with less than 1.7 at.% Y lowered the temperature of the III ↔ I transition. The minimum peak temperature on heating was about 170°C in the 0.8 at.% Y-doped sample compared with 250°C in the undoped sample. On the cooling curves, the peak temperatures lowered, and the temperature interval between the two peaks became larger with increasing yttrium content. On the other hand, the transition temperatures increased in the samples containing yttrium between 2.7 and 5.3 at.%. The peak temperature was about 320°C on heating in both 3.8 and 5.3 at.% Y-doped samples. The separation of the two exothermic peaks on cooling became undistinguished in the 2.7 and 3.8 at.% Y-doped samples. In the 5.3 at.% Y-doped sample, only one exothermic peak was observed at about 300°C on cooling.

Figure 5 displays typical patterns taken by high temperature X-ray diffraction for the undoped, 1.7 and 3.8 at.% Y-doped samples at indicated temperatures. The transition temperatures observed by X-ray diffraction corresponded to those obtained by DTA. In the undoped sample, the patterns observed above 280°C agreed with the pattern of phase I which was reported by Kracek and Ksanda [4]. The high temperature phase could not be quenched to room temperature. In the 1.7 at.% Y-doped sample, the patterns of the low temperature phase was similar to that of

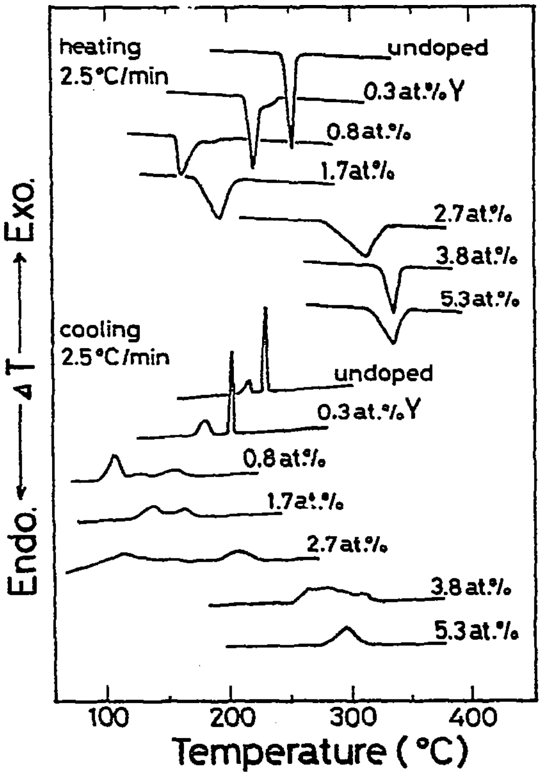


Fig. 4. DTA curves of the undoped and yttrium-doped Na_2SO_4.

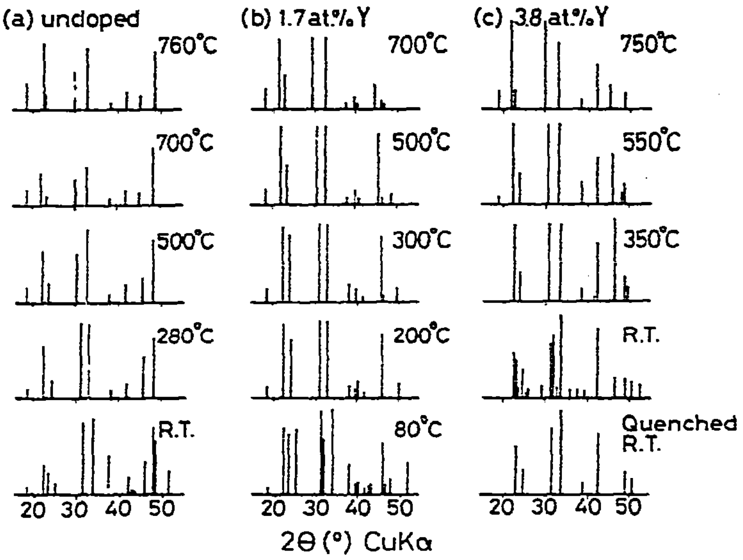


Fig. 5. High temperature X-ray diffraction patterns of the undoped, 1.7 and 3.8 at.% yttrium-doped samples.

phase III. The pattern observed at 200°C was different from those obtained below 200°C. For the high temperature phase, the intensities of reflections and the pattern around $2\theta = 35$–$50°$ were distinct from the pattern of phase I in the undoped sample. In spite of a high cooling rate of more than 100°C min^{-1}, the high temperature phase could not be quenched. In the 3.8 at.% Y-doped sample, a change in patterns was detected around 350°C. The pattern of the high temperature phase was in good agreement with that of phase I in the undoped Na_2SO_4. The pattern obtained below 350°C contained some reflections which could not be indexed, suggesting the phase separation in the lower temperature range. The high temperature phase was obtained at room temperature by quenching.

CONCLUSION

The transitions between polymorphs in the undoped Na_2SO_4 occurred in various ways depending on the method of sample preparation in the initial heating and cooling cycle. After several cycles of heating and cooling in all samples, only the III → I transition took place at about 250°C on heating, and the reversible I → II and irreversible II → III transitions were observed around 230°C on cooling.

The transition temperatures lowered in the samples containing less than about 1.7 at.% Y, whereas the doping of more than 2.0 at.% Y raised the transition temperatures. X-Ray diffraction revealed that the transitions in yttrium-doped samples were basically the same as the III ↔ I transition in the undoped Na_2SO_4.

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