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Effect of Rare Earth Ions on the Phase Transition of Na_2SO_4 Crystals

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The V $\rightleftarrows$ I phase transition of Na_2SO_4 crystals was investigated on a sample of pure Na_2SO_4 and on rare-earth-ion ($Ln^{3+} = La^{3+}, Eu^{3+}, Tm^{3+}$)-doped Na_2SO_4 samples in various ambient gases (O_2, N_2, NH_3) with high temperature X-ray diffraction and differential thermal analysis. On heating in N_2 flow, the initiating temperature for the V → I transition was lowered by doping with Ln^{3+} ion and the doping effect was enhanced by an increase in the ionic size ratio $r_{Ln^{3+}}/r_{Na^+}$. The low temperature form of the solid solution (LSS) Na_2SO_4 and rare earth sulfate, which was a by-product in the preparation of the Ln^{3+}-doped samples, transformed to a high temperature form (HSS) after the V → I transition, and the initiating temperature for the LSS → HSS transition was highest in the Eu^{3+}-doped sample ($r_{Ln^{3+}}/r_{Na^+} \simeq 1$). On the other hand, on cooling in N_2 flow, the HSS was stable until room temperature in the La^{3+}- or Eu^{3+}-doped sample ($r_{Ln^{3+}}/r_{Na^+} \geqq 1$), but transformed to LSS in the Tm^{3+}-doped sample ($r_{Ln^{3+}}/r_{Na^+} < 1$). The results obtained in other ambient gas flows (O_2, NH_3) were considerably affected by the sorption of ambient gas into Na_2SO_4 crystals and/or the reaction between ambient gas and Na_2SO_4 and were different from those obtained in N_2 flow. © 1991 Academic Press, Inc.

Na_2SO_4 crystals are known to exhibit five polymorphisms (phases I, II, III, IV, and V). Many workers (*1–4*) have found that the phase transition is affected by the coexistence of a foreign sulfate and/or an ambient gas. Eysel *et al.* (*1*) found that divalent ion-doped Na_2SO_4 was stable in phase I even at room temperature. Saito *et al.* (2) reported that the III → I transition of Y-doped Na_2SO_4 depended on the amount doped of $Y_2(SO_4)_3$. In alkali metal ion- or alkaline earth ion-doped Na_2SO_4, we (*3, 4*) have found that the V → I and I → III transitions depend on the crystal structure of the dopant or product (compound or solid solution) made from Na_2SO_4 but the III → V transition is mainly affected by the ambient gas (especially water vapor).

In this study, the effect of ambient gas on the V $\rightleftarrows$ I transition of Na_2SO_4 crystals for a pure Na_2SO_4 sample and rare earth ion (Ln^{3+})-doped Na_2SO_4 samples was investigated with the high temperature X-ray diffraction (high temp-XRD) and differential thermal analysis (DTA).

Experimental

The pure and doped Na_2SO_4 samples used were prepared by evaporating to dryness aqueous solutions of Na_2SO_4 to which were added given amounts (0 to 20 mol%) of $Ln_2(SO_4)_3$ (Ln = La, Eu, Tm). This was followed by vacuum drying at 130°C for 2 hr. N_2 and O_2 were obtained by evaporation of pure liquid of N_2 and O_2, respectively, followed by a further purification by passage through a glass tube containing molecular

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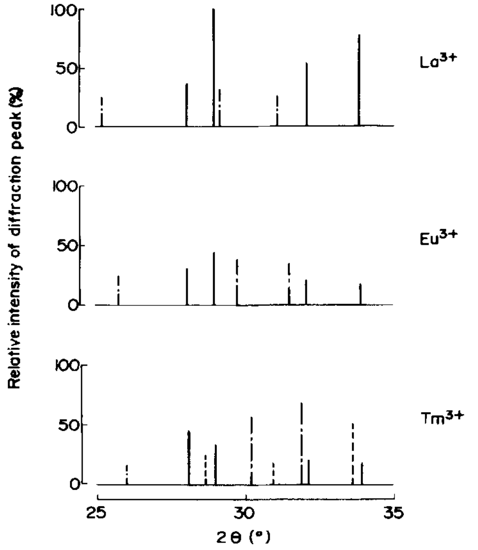

FIG. 1. The XRD pattern of Ln^{3+} (10 mol%)-doped Na_2SO_4 samples before heating; (——) phase V of Na_2SO_4, (---) $Ln_2(SO_4)_3$, (–·–) LSS.

sieve 5A at 0°C. NH_3 was obtained by drying a cylinder of highly pure NH_3 through a soda lime tube at 25°C.

The progress of the phase transition reaction was measured by an apparatus which enabled a simultaneous measurement of high temp-XRD and DTA (Rigaku Denki Company, Limited: Geigerflex Type 2035) as described in the previous paper (*3*). The temperature was varied at the rate 5°C/min.

Results

Figure 1 shows the XRD patterns of the Na_2SO_4 samples doped with 10 mol% of $Ln_2(SO_4)_3$ before heating. All samples consisted of the phase V of Na_2SO_4 and the low temperature form of solid solution (LSS) between Na_2SO_4 and rare earth sulfate. The Tm^{3+}-doped Na_2SO_4 sample alone, furthermore, contained $Tm_2(SO_4)_3$ crystals. The diffraction peak height of Na_2SO_4 crystals in the La^{3+}-doped Na_2SO_4 sample was much higher than that in the Eu^{3+}- or Tm^{3+}-doped Na_2SO_4 sample.

The V → I transition of Na_2SO_4 was measured on the La^{3+}-doped Na_2SO_4 sample in N_2 flow by means of the high temp-XRD and DTA (Fig. 2). The diffraction peak of the phase V became low, while that of the phase I grew at 188°C with a simultaneous endothermic effect on the DTA curve (A in Fig. 2). Then, the diffraction peaks of both phase I and the LSS began to decrease, while that of the high temperature form of solid solution (HSS), the crystal system of which is similar to that of phase I Na_2SO_4, began increasing at 222°C with a simultaneous endothermic effect on the DTA curve (B in Fig. 2).

Similar examinations were carried out on a pure Na_2SO_4 sample and the La^{3+}-, Eu^{3+}-, or Tm^{3+}-doped Na_2SO_4 samples in a gas flow of N_2, O_2, or NH_3. Figure 3 shows the effects of doping with Ln^{3+} ion and ambient gas on the initiation temperature for the transitions of both the V → I of Na_2SO_4 crystals and the LSS → HSS. The initiating temperature for the V → I transition was lowered with an increase in the cation size of dopant in any ambient gas, and the initiating temperature in N_2 flow was remarkably

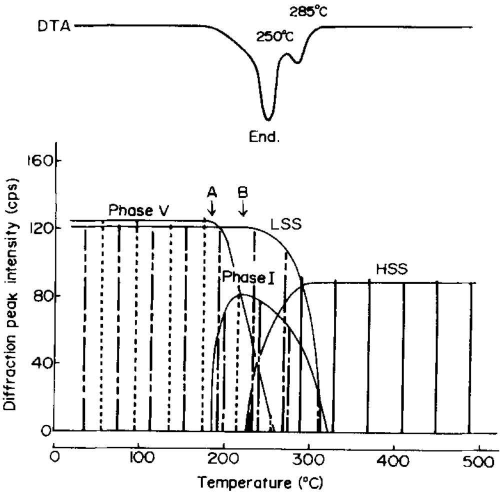

FIG. 2. High temp-XRD and DTA traces on the La^{3+} (10 mol%)-doped Na_2SO_4 sample in N_2 flow at heating rate of 5°C/min, (A) Initiating temperature of the V → I transition, (B) Initiating temperature of the LSS → HSS transition.

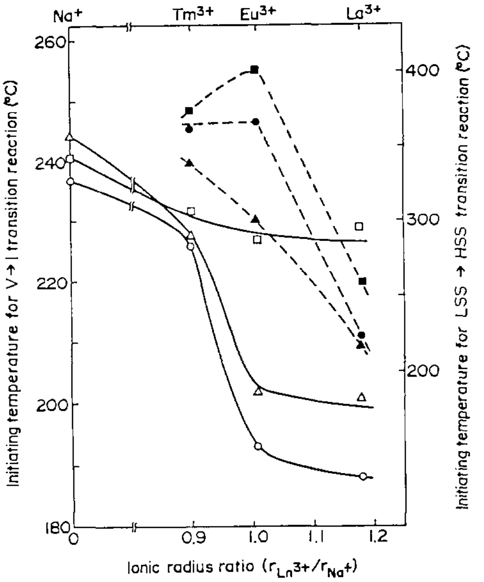

FIG. 3. The V → I transition (solid line) of Na_2SO_4 crystals and the LSS → HSS transition (dotted line) of pure and Ln^{3+} (10 mol%)-doped Na_2SO_4 samples, in (○,●) N_2, (△,▲) O_2, (□,■) NH_3 (flow rate: 100 ml/min).

lower in any sample than that in O_2 flow or NH_3 flow. The initiating temperature for the LSS → HSS transition in N_2 flow became lower in the order Eu^{3+}-doped ≃ Tm^{3+}-doped ≫ La^{3+}-doped, and it was considerably higher or lower than that in O_2 or NH_3 flow, respectively, in any Ln^{3+}-doped Na_2SO_4 sample.

Figure 4 shows the effect of amount doped with Ln^{3+} on the V → I transition for the Ln^{3+}-doped Na_2SO_4 samples in N_2 flow. The transition was further promoted with an increase in the doping amount of La^{3+} or Eu^{3+} ($r_{Ln^{3+}}/r_{Na^+} \geqq 1$), but it was hardly affected by doping with Tm^{3+} ($r_{Ln^{3+}}/r_{Na^+} < 1$).

On cooling in the case of the pure Na_2SO_4 sample, the initiating temperature for the I → III transition became lower in the order N_2 flow > NH_3 flow > O_2 flow, contrary to the V → I transition. However, no III → V transition was observed in any ambient gas. On the other hand, in the case of the Ln^{3+}-doped Na_2SO_4 samples, the HSS produced on heating in any ambient gas was stable until room temperature in the La^{3+}- or Eu^{3+}-doped Na_2SO_4 sample but it transformed to the LSS in the Tm^{3+}-doped Na_2SO_4 sample.

Discussion

The crystallographic patterns of the Ln^{3+}-doped Na_2SO_4 samples before heating (Fig. 1) are thought to be closely related to the solubilities of Na_2SO_4, $Ln_2(SO_4)_3$, and LSS in water under the preparation conditions of Ln^{3+}-doped Na_2SO_4 samples.

The solubilities of $Ln_2(SO_4)_3$ and LSS are known to be much less than that of Na_2SO_4 (5). It is also known that the solubility of $Ln_2(SO_4)_3$ decreases in order $La_2(SO_4)_3$ > $Eu_2(SO_4)_3$ ≫ $Tm_2(SO_4)_3$ and the solubility of LSS decreases in the order (Tm,Na)SO_4 > (Eu,Na)SO_4 ≫ (La,Na)SO_4 (5). From these facts and the results shown in Fig. 1, Na_2SO_4 would precipitate on the produced (La,Na)SO_4 particles in an La^{3+}-doped Na_2SO_4 sample, and it would coprecipitate with (Eu,Na)SO_4 on (Eu,Na)SO_4 particles which had precipitated partially in the Eu^{3+}-doped Na_2SO_4 samples. However in a Tm^{3+}-doped Na_2SO_4 sample, Na_2SO_4 and (Tm,Na)SO_4 would coprecipitate on $Tm_2(SO_4)_3$ particles.

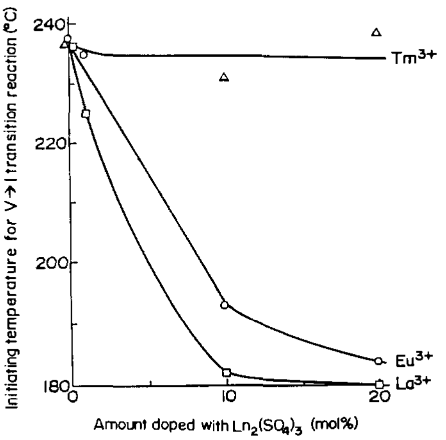

FIG. 4. The effect of amount doped with Ln^{3+} on the V → I transition of Na_2SO_4 crystals on the Ln^{3+}-doped Na_2SO_4 samples in N_2 flow.

Saito *et al.* reported that the III ⇄ I transition of Na_2SO_4 proceeds with the rotation of the SO_4^{2-} tetrahedron, and this transition model was supported by the results of Mehrotra *et al.* (*6*) and Amirthalingam *et al.* (*7*). Therefore the results obtained in N_2 flow (Fig. 3) suggest that the rotation of the SO_4^{2-} tetrahedron in Na_2SO_4 crystals becomes easy owing to the Na vacancy formed in Na_2SO_4 crystals due to the diffusion of Na^+ ions into the LSS, resulting in promotion of the V → I transition. The diffusion of Na^+ ions into the LSS in the La^{3+}-doped Na_2SO_4 sample ($r_{Ln^{3+}}/r_{Na^+} > 1$) would most easily occur among the samples used here (Figs. 3 and 4), resulting in promotion of the transition from LSS to HSS, which corresponds to the solid solution between the phase I of Na_2SO_4 and a small amount of foreign cation sulfate as pointed out by Eysel *et al.* (*8*).

We have found that Na_2SO_4 crystals rapidly sorb O_2 gas (*9*). It is well known that the chemical affinity between rare earth and oxygen is strong. In O_2 flow, the SO_4^{2-} tetrahedron of Na_2SO_4 crystals is thought to become considerably difficult to rotate due to the sorption of O_2 gas into Na_2SO_4 crystals, resulting in inhibition of the V → I transition in all Na_2SO_4 samples. In the Eu^{3+}- and Tm^{3+}-doped Na_2SO_4 samples ($r_{Ln^{3+}}/r_{Na^+} \leqq 1$), the diffusion of Na^+ into LSS and the diffusion of Ln^{3+} into Na_2SO_4 occur simultaneously and latter is promoted by oxygen sorbed into Na_2SO_4 due to the strong chemical affinity between rare earth and oxygen, resulting in the promotion of the LSS → HSS transition. In the La^{3+}-doped Na_2SO_4 sample ($r_{Ln^{3+}}/r_{Na^+} > 1$), the diffusion of Ln^{3+} into Na_2SO_4 cannot be expected, in which case the LSS → HSS transition could not be promoted even if in O_2 flow. In NH_3 flow, we think that the NH_3 complex formed on the crystal surface of Na_2SO_4 suppressed not only the rotation of the SO_4^{2-} tetrahedron of Na_2SO_4 crystals but also the diffusion of Na^+ ion and/or Ln^{3+} ion, resulting in a rise in the initiation temperature of both the V → I transition and the LSS → HSS transition. It could be thought that the I → III transition in pure Na_2SO_4 sample on cooling was also suppressed by the existences of oxygen sorbing into Na_2SO_4 crystals and of the NH_3 complex on the crystal surface of Na_2SO_4 as well as the V → I transition on heating.

Conclusion

The phase transition reaction of Na_2SO_4 crystals was promoted by the enhanced rotation of the SO_4^{2-} tetrahedron caused by Na vacancy in Na_2SO_4 crystals. However, the promotive effect of Na vacancies was suppressed by not only the Ln^{3+} ion diffusing into Na_2SO_4 crystals and but also by O_2 sorbing into Na_2SO_4 crystals and the NH_3 complex on the crystal surface of Na_2SO_4.

Acknowledgments

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