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A MODEL PROPOSED FOR THE INTERPRETATION OF DTA AND X-RAY DATA OF THE III ↔ I TRANSITION IN SODIUM SULFATE

KURIMA KOBAYASHI and YASUTOSHI SAITO *

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

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ABSTRACT

The transition between phase I and phase III in sodium sulfate (Na_2SO_4) was studied by high temperature X-ray diffraction and the calculation of diffraction patterns. An intermediate phase (phase II) was detected on cooling in the undoped and 1.7 at.% yttrium-doped Na_2SO_4, but not observed in the 3.8 at.% Y-doped sample. The DTA and X-ray diffraction results of the III ↔ I transition were explained well by a proposed model which consisted mainly of the following steps: (i) the rotation of the SO_4 tetrahedra, and (ii) the disappearance of interfaces among the transformed domains.

INTRODUCTION

In an earlier paper [1] on the phase transition in sodium sulfate (Na_2SO_4), it was pointed out that only the III ↔ I transition was detected by differential thermal analysis (DTA) and X-ray diffraction after several cycles of heating and cooling regardless of the method of sample preparation. During the III ↔ I transition, an intermediate phase assigned to phase II was observed only on cooling.

The mechanism of the III ↔ I transition has been mainly investigated by X-ray diffraction. The powder diffraction patterns of phases I, III and V were first recorded by Kracek and Ksanda [2]. Fischmeister [3] observed the more detailed pattern of phase III, and later he measured the changes in lattice constants over the range from room temperature to the melting point through the III ↔ I transition, and discussed the crystal structures of phases I and III [4]. A slightly modified structure of phase I was proposed by Höfer et al. [5]. In the studies on polymorphism of Na_2SO_4 using a single crystal of phase III, Mehrotra et al. [6] determined the lattice constants of phases II and III, and recognized that the *c*-axis was common in both phases during the I → III transition. By Weissenberg camera method with a single crystal, Amirthalingam et al. [7] revealed that the *c*-axis remained the same in phases I and III during the topotaxic III ↔ I transition.

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* To whom correspondence should be addressed.

Cody et al. [8] studied the III ↔ I transition by Raman spectroscopy and differential scanning calorimetry (DSC), and pointed out the similarity between the Raman spectrum of phase II and that of phase III.

In spite of numerous studies, the mechanism of the III ↔ I transition has not yet been understood. Especially, it has not been explained why the III ↔ I transition proceeds in one stage on heating and the reverse transition in two stages on cooling. In the present study, the III ↔ I transition in the undoped, 1.7 and 3.8 at.% yttrium-doped samples was studied by high temperature X-ray diffraction, and a possible transition model was proposed for the III ↔ I transition in the undoped Na_2SO_4.

EXPERIMENTAL AND PROCEDURE

The samples used in the present study were undoped sample (A), and 1.7 and 3.8 at.% yttrium-doped Na_2SO_4 used previously [1].

X-ray diffraction patterns were recorded at heating and cooling rates of 0.625°C min^{-1} and a scanning speed of 2° 2θ/min with a Rigaku Geigerflex high temperature X-ray diffractometer using Ni-filtered CuK_α radiation. The diffraction patterns of the samples could not be observed around $2\theta = 41$, 47 and 68°, because platinum used for the sample holder showed strong reflections at these angles. The measurement started at about 200°C after heating the sample up to about 760°C and the subsequent cooling.

A computation of X-ray diffraction patterns was carried out to confirm the crystal structures of phases I and III and to evaluate the validity of a proposed model for the III ↔ I transition. Because the space groups of phase I and the intermediate phase which appears on cooling are not known, the ordinary program is not available for the calculation of the diffraction patterns. In addition to the calculation, the mechanism of the III ↔ I transition is discussed with emphasis on the change in the arrangement of atoms in the present study. Therefore, the X-ray diffraction patterns of the phases were computed using the following equations

$$I_{hkl} = jPL|F_{hkl}|^2 \quad (1)$$

with

$$F_{hkl} = A_{hkl} + iB_{hkl} \quad (2)$$

$$A_{hkl} = \sum_n f_n \cos(hx_n + ky_n + lz_n) \quad (3)$$

$$B_{hkl} = \sum_n f_n sin(hx_n + ky_n + lz_n) \quad (4)$$

In eqns. (1)–(4), I_{hkl} is the intensity of the (hkl) reflection, j is the multiplicity factor, P is the polarization factor, L is the Lorentz factor, F_{hkl} is the structure factor of the (hkl) reflection, f_n is the scattering factor of n-th atom, and x_n, y_n and z_n are the positional parameters of n-th atom.

RESULTS AND DISCUSSION

Figure 1 schematically shows the structure of phase III indicated by Wyckoff [9] and that of phase I proposed by Höfer et al. [5]. The systems of phases III and I are orthorhombic and hexagonal, respectively. The lattice constants and the positional parameters of atoms in phase I were calculated assuming an orthorhombic unit cell for convenience of the calculation. Table 1 lists the calculated positional parameters of atoms based on the illustrations shown in Fig. 1 with the published lattice constants and space group of phase III.

Figure 2 presents the observed and calculated X-ray diffraction patterns of phases I and III. The calculated patterns were in good agreement with the observed patterns reported in the preceding paper [1] except the intensities of some reflections. This result indicates that the arrangements of atoms illustrated in Fig. 1 are fundamentally correct in both phases. However, the parameters and the calculaton based on eqns. (1)–(4) are not accurate enough to reproduce the intensities of reflections. Since the discussion is focused on the change in the arrangement of atoms during the III ↔ I transition in the present study, it is valid to employ the computed parameters for the analysis of the transition mechanism.

In the preceding paper [1], the doping of yttrium in Na_2SO_4 showed two different effects on the transition temperatures. Compared with the III → I transition temperature of about 250°C on heating in the undoped Na_2SO_4, the transition temperatures lowered in the samples containing less than about 2 at.% Y. For example, the transition temperature was 170°C on heating in the 0.8 at.% Y-doped sample. On the contrary, the transition temperatures increased up to about 320°C on heating in

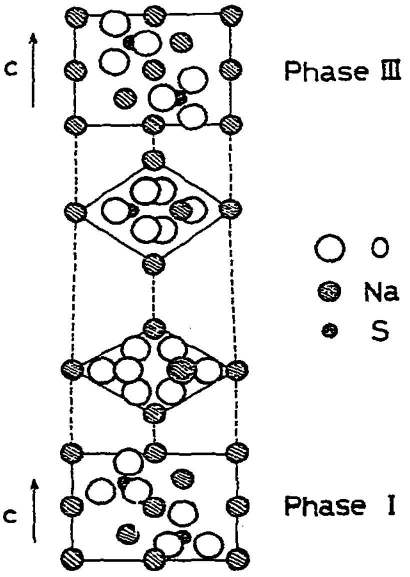


Fig. 1. Schematic representation of the structures of phases I and III projected on (011). Phase III was indicated by Wyckoff [9] and phase I was proposed by Höfer et al. [5].

TABLE I

Crystal data of phases I and III (The positional parameters of atoms were calculated by the authors.)

	Phase III				Phase I [a]		
	$a=5.592$ Å	System: orthorhombic			$a=5.350$ Å	System: hexagonal	
	$b=8.926$	Space group: Cmcm			$b=9.266$	space group:?	
	$c=6.953$				$c=7.120$		
Na	$x=0.5000$	$y=0.0000$	$z=0.0000$	Na	$x=0.5000$	$y=0.0000$	$z=0.0000$
	$x=0.5000$	$y=0.0000$	$z=0.5000$		$x=0.5000$	$y=0.0000$	$z=0.5000$
	$x=0.0000$	$y=0.2000$	$z=0.7500$		$x=0.0000$	$y=0.1667$	$z=0.7500$
	$x=0.5000$	$y=0.3000$	$z=0.2500$		$x=0.5000$	$y=0.3333$	$z=0.2500$
	$x=0.0000$	$y=0.5000$	$z=0.5000$		$x=0.0000$	$y=0.5000$	$z=0.5000$
	$x=0.0000$	$y=0.5000$	$z=0.0000$		$x=0.0000$	$y=0.5000$	$z=0.0000$
	$x=0.5000$	$y=0.7000$	$z=0.7500$		$x=0.5000$	$y=0.6667$	$z=0.7500$
	$x=0.0000$	$y=0.8000$	$z=0.2500$		$x=0.0000$	$y=0.8333$	$z=0.2500$
S	$x=0.0000$	$y=0.1500$	$z=0.2500$	S	$x=0.0000$	$y=0.1667$	$z=0.2500$
	$x=0.0000$	$y=0.8500$	$z=0.7500$		$x=0.0000$	$y=0.8333$	$z=0.7500$
	$x=0.5000$	$y=0.3500$	$z=0.7500$		$x=0.5000$	$y=0.3333$	$z=0.7500$
	$x=0.5000$	$y=0.6500$	$z=0.2500$		$x=0.5000$	$y=0.6667$	$z=0.2500$
O	$x=0.7824$	$y=0.0500$	$z=0.2500$	O	$x=0.7725$	$y=0.0909$	$z=0.1804$
	$x=0.2176$	$y=0.0500$	$z=0.2500$		$x=0.2275$	$y=0.0909$	$z=0.1804$
	$x=0.7824$	$y=0.9500$	$z=0.7500$		$x=0.7725$	$y=0.9091$	$z=0.6804$
	$x=0.2176$	$y=0.9500$	$z=0.7500$		$x=0.2275$	$y=0.9091$	$z=0.6804$
	$x=0.0000$	$y=0.2500$	$z=0.4250$		$x=0.0000$	$y=0.1667$	$z=0.4593$
	$x=0.0000$	$y=0.7500$	$z=0.9250$		$x=0.0000$	$y=0.8333$	$z=0.9593$
	$x=0.0000$	$y=0.2500$	$z=0.0750$		$x=0.0000$	$y=0.3183$	$z=0.1804$
	$x=0.0000$	$y=0.7500$	$z=0.5750$		$x=0.0000$	$y=0.6817$	$z=0.6804$
	$x=0.5000$	$y=0.2500$	$z=0.5750$		$x=0.5000$	$y=0.1817$	$z=0.6804$
	$x=0.5000$	$y=0.2500$	$z=0.9250$		$x=0.5000$	$y=0.3333$	$z=0.9593$
	$x=0.7176$	$y=0.4500$	$z=0.7500$		$x=0.7275$	$y=0.4091$	$z=0.6804$
	$x=0.2824$	$y=0.4500$	$z=0.7500$		$x=0.2725$	$y=0.4091$	$z=0.6804$
	$x=0.2824$	$y=0.5500$	$z=0.2500$		$x=0.2725$	$y=0.5909$	$z=0.1804$
	$x=0.7176$	$y=0.5500$	$z=0.2500$		$x=0.7275$	$y=0.5909$	$z=0.1804$
	$x=0.5000$	$y=0.7500$	$z=0.4250$		$x=0.5000$	$y=0.6667$	$z=0.4593$
	$x=0.5000$	$y=0.7500$	$z=0.0750$		$x=0.5000$	$y=0.8183$	$z=0.1804$

[a] Lattice constants and positional parameters were calculated assuming an orthorhombic unit cell.

the samples containing 2.7–5.3 at.% Y. The electrical conductivity of Na_2SO_4 was also affected by the doping of yttrium in two different ways depending on the yttrium concentration, which was consistent with the changes in the transition temperatures [10]. In the present study, high temperature X-ray diffraction was performed on the samples doped with 1.7 and 3.8 at.% Y which were selected from two ranges below and above the yttrium concentration of 2 at.%.

Figure 3 shows the changes in the interplanar spacings of the (002), (021) and (111) reflections in the undoped, 1.7 and 3.8 at.% Y-doped samples during heating and cooling through the III ↔ I transition. The reflections in the 1.7 and 3.8 at.%

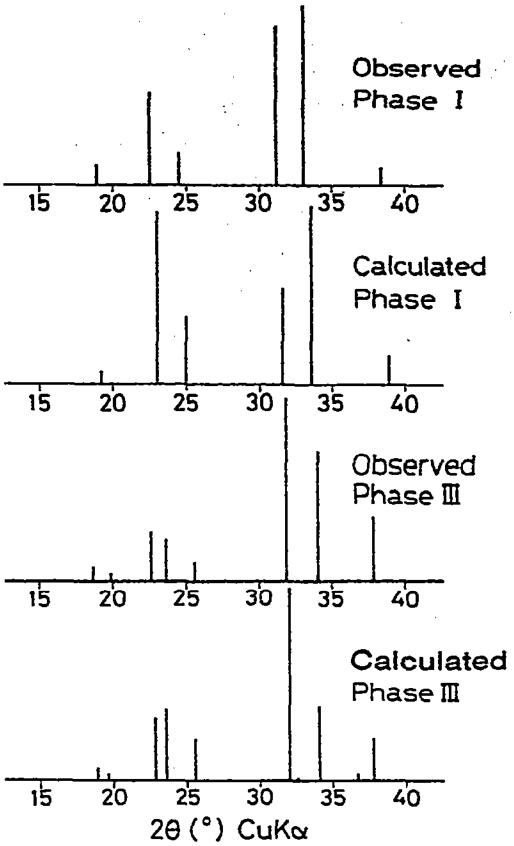


Fig. 2. Observed and calculated X-ray diffraction patterns of phases I and III.

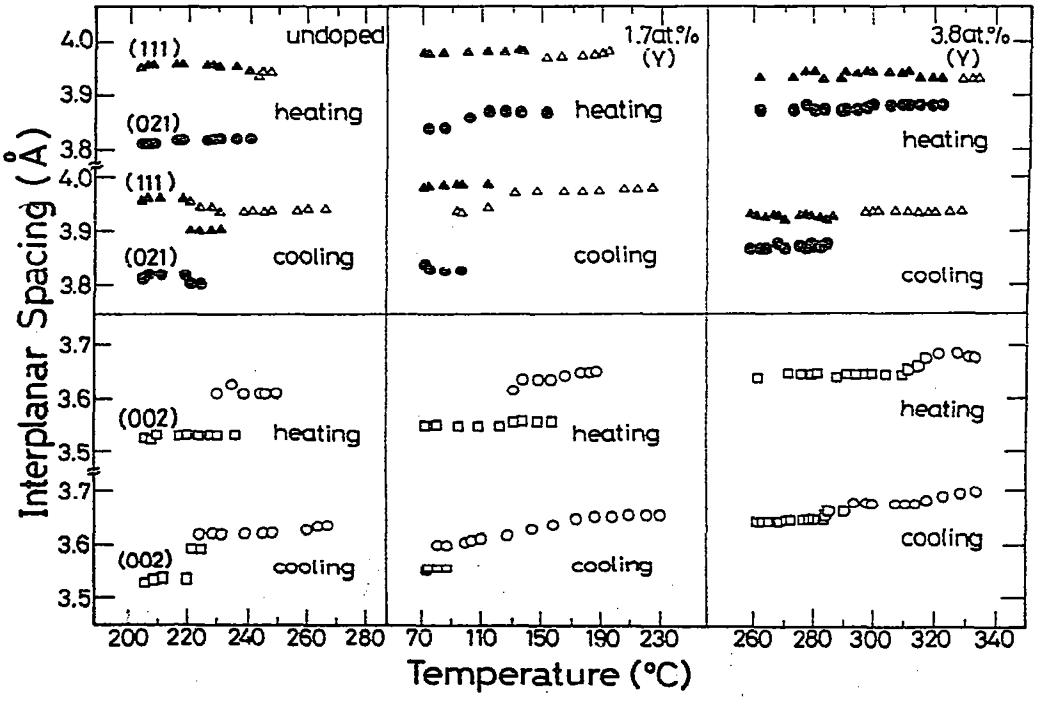


Fig. 3. Changes in the interplanar spacings around the transition temperatures in the undoped, 1.7 and 3.8 at.% Y-doped samples.

Y-doped samples basically correspond to those in the undoped sample. Therefore, the reflections were indexed on the basis of indexing in the undoped Na_2SO_4.

In the undoped Na_2SO_4, the III ↔ I transition occurred at about 240°C on heating and around 220–230°C on cooling. The (111) reflection at about 3.95 Å remained through the transition with a slight change in the spacing. However, the reflection at about 3.90 Å was separated from the reflection at about 3.95 Å during the transition on cooling. The (021) reflection at about 3.81 Å disappeared above 240°C on heating, and reappeared below 220–230°C on cooling. The spacing of the (002) reflection abruptly changed between about 3.53 Å and about 3.62 Å at the transition temperatures.

The transition temperatures of the 1.7 at.% Y-doped sample lowered to about 150°C on heating and to around 90–110°C on cooling. The changes in diffraction angles were similar to those for the undoped sample accompanying a slight expansion of the spacings. The reflection at about 3.95 Å was separated from the (111) reflection during the transition on cooling.

In the 3.8 at.% Y-doped sample, the transition temperature increased up to about 320°C on heating and about 285°C on cooling. The reflection which appeared only during the transition was not observed in this sample. The spacing of the (002) reflection continuously changed between about 3.65 Å and 3.70 Å through the transition.

The X-ray measurements suggested that the intermediate phase (phase II) existed in the undoped and 1.7 at.% Y-doped samples during the I → III transition on cooling. This result was consistent with that obtained by DTA in the preceding study [1].

The X-ray diffraction pattern of the intermediate phase in the undoped Na_2SO_4 was recorded at about 230°C on cooling. Figure 4 shows the observed pattern of the intermediate phase and the calculated patterns of phases I and III. From a compari-

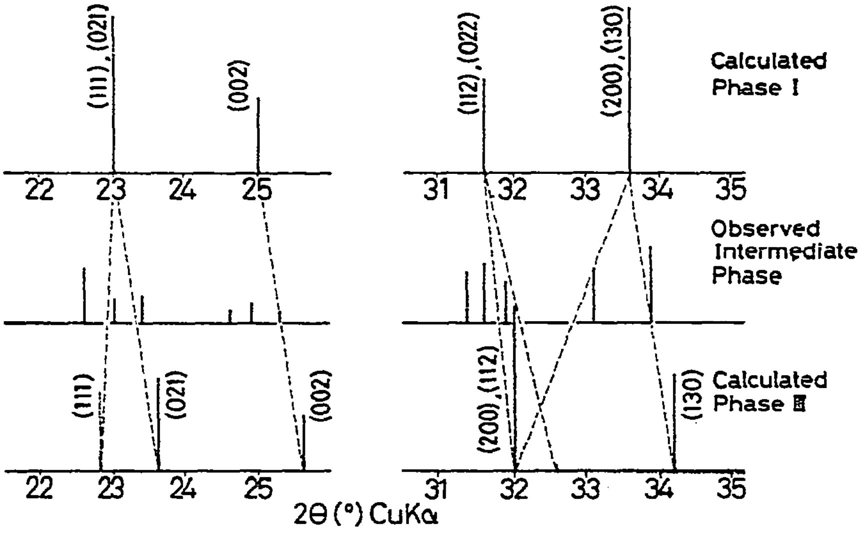


Fig. 4. Calculated and observed patterns during the III↔I transition in the undoped Na_2SO_4.

son with the calculated patterns, the pattern of the intermediate phase seems to be composed of the reflections of phases I and III. The calculation reveals that some reflections in both phases are composed of a few different reflections. For example, the reflection at about $2\theta = 23°$ in phase I consists of the (111) and (021) reflections. Consequently, the separated reflections of phase I or phase III may be observed in the pattern of the intermediate phase.

On the other hand, a comparison of the crystal structure of phase I with that of phase III reveals that the structure of the phase I results from the rotation of SO_4 tetrahedra and a slight expansion of the lattice in phase III, as shown in Fig. 5. The changes in the atomic positions are considered to occur during the III ↔ I transition. This transition model is also supported by the results of Mehrotra et al. [6] and Amirthalingam et al. [7], i.e., phases I, II and III have the *c*-axis in common. To check the structural model of the transition with the observed data, the patterns of the intermediate states during the transition were calculated in the following procedure:

(1) the rotation angle of SO_4 tetrahedra and the lattice constants in phase I are shifted stepwise to those in phase III;

(2) the diffraction patterns of the intermediate states are calculated using the positional parameters obtained in each step of the shift.

Since the lattice constants cannot be determined accurately with the diffraction angles observed by the high temperature X-ray diffractometer, the values listed in Table 1 are used in the calculation. Dashed lines in Fig. 4 indicate the changes in the calculated angles of the reflections. Some reflections of phase I are gradually separated into those of phase III with a shift of the positions of the atoms as the I → III transition proceeds. If the arrangement of atoms in the intermediate phase exists in the course of the shift mentioned above, the dashed lines show the diffraction angles for the phase. A comparison of the calculated patterns with the observed pattern indicated that the intermediate phase should be a mixed phase of phases I and III, or a coexisting phase of phases I, III and the intermediate phase.

Figure 6 represents this transition model projected on the *a*–*b* plane. In phase III, the SO_4 tetrahedral rotate in direction A and the III → I transition proceeds in one

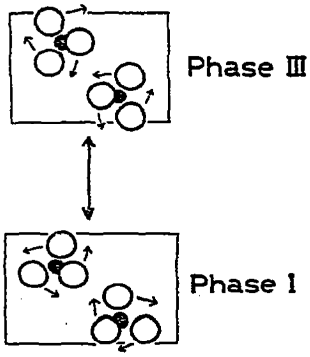
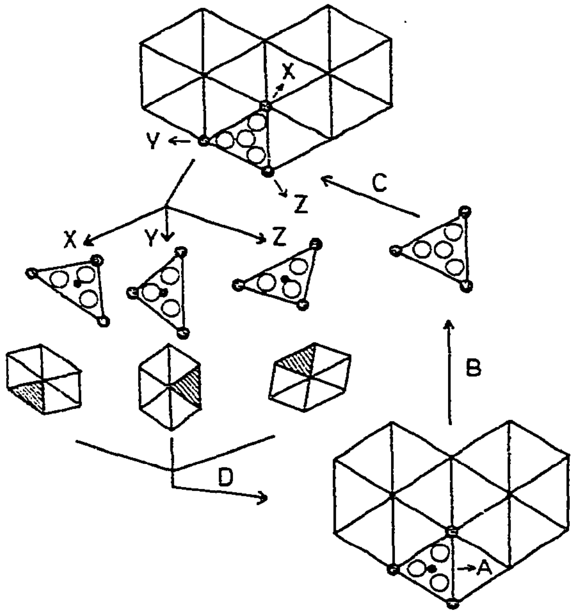


Fig. 5. Schematic representation of the III↔I transition model projected on (011).



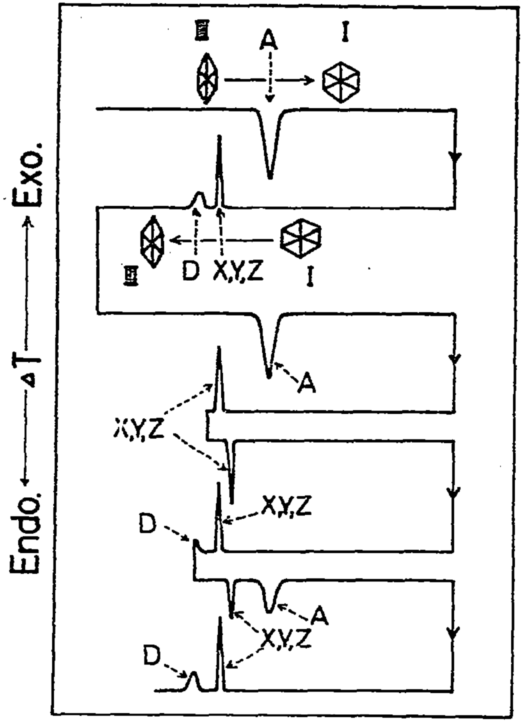


Fig. 6. Schematic representation of the III↔I transition model projected on (110).

Fig. 7. Interpretation of DTA curves for the III↔I transition on the basis of the proposed mechanism.

step (B → C). On the other hand, the rotation of the tetrahedra in phase I is equivalent in three directions (*X*, *Y*, *Z*). Accordingly, the I → III transition takes place in the following two steps.

First step: The nuclei of the transition are formed and grow to contact with one another by the rotation of the SO_4 tetrahedra in either of the three equivalent directions (*X*, *Y*, *Z*), which results in the formation of interfaces among the transformed domains.

Second step: The interfaces disappear with the growth of one domain at the expense of the other domains (D).

This transition model suggests that phase II consists of the domains of phase III with different orientations. There is no contradiction between the model and the experimental results obtained by Cody et al. [8], indicating the similarity in Raman spectra of phases II and III.

The model for the III ↔ I transition is schematically shown in Fig. 7 with DTA curves obtained in the preceding study [1]. DTA curves exhibited one endothermic peak at about 250°C on heating and two exothermic peaks around 230°C on cooling. The first exothermic peak on cooling corresponds to the I → II transition. This transition was reversible when reheating started before the completion of the second exothermic peak on cooling. Reheating in the course of the second exothermic peak yielded two endothermic peaks which corresponded to the II → I and

III → I transitions. On the basis of the proposed transition model, the endothermic peak at about 250°C on heating results from the rotation of the SO_4 tetrahedra and a slight expansion of the lattice in phase III. The first exothermic peak on cooling represents the first step, i.e., the I → II transition. The reversibility of this transition indicates that the SO_4 tetrahedra easily rotate in the reverse direction in each transformed domain on reheating. Since the second exothermic peak on cooling is attributed to the second step, it is suggested that the II → III transition is irreversible due to the lack of reversibility in the formation and disappearance of the interfaces among the transformed domains. Consequently the direct transformation of phase III into phase I on heating can be also explained by this transition model.

CONCLUSION

X-Ray diffraction revealed that an intermediate phase (phase II) existed during the I → III transition on cooling in the undoped and 1.7 at.% Y-doped Na_2SO_4, but not in the 3.8 at.% Y-doped sample. The structural transition model for the undoped Na_2SO_4 suggested that one endothermic peak for the III → I transition on heating in DTA was caused by the rotation of the SO_4 tetrahedra in one direction and a slight change in lattice constants. In contrast, two exothermic peaks for the I → II and II → III transitions on cooling were attributed to the rotation of the SO_4 tetrahedra in three equivalent directions with the change in lattice constants and to the disappearance of interfaces among the transformed domains. Phase II formed on cooling should consist of the domains of phase III with different orientations.

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