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# Peculiarities of the structural phase transitions in $\text{Na}_2\text{SO}_4(\text{V})$ : a Raman scattering study

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## Abstract

The structural phase transitions occurring at the first heating of as-grown  $\text{Na}_2\text{SO}_4(\text{V})$  are so peculiar that there have been many controversial reports about them, especially with regard to the possible existence of several intermediate phases (II–IV) between the room-temperature (V) and high-temperature (I) phases. From this first detailed study of polarized Raman spectra based on oriented single crystals, we have obtained new results regarding the existence and nature of intermediate phases between phases V and I. We normally found that single-crystal  $\text{Na}_2\text{SO}_4(\text{V})$  transforms directly to phase I at 242 °C without any occurrence of an intermediate phase (type-1 transition), but occasionally it transforms to a mixed phase of II and III near 234 °C, and then the phase II regions transform to phase I near 240 °C, and finally the phase III regions transform to phase I near 250 °C (type-2 transition). These results were confirmed from single-crystal ionic conductivity measurements and thermal calorimetry studies. For polycrystalline powder, however, both of these two types of transition sequences occur simultaneously, resulting in a complex and sluggish behaviour with temperature change. Hence it is now evident for powdered samples why many authors have hitherto reported so many diverse and contradictory results regarding the structural transitions of phase V.

## 1. Introduction

Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) exhibits a number of unusual structural phase transitions between several phases often referred to as I–V [1–3]. Crystals of  $\text{Na}_2\text{SO}_4$  when grown from aqueous solution are in phase V, and on heating this phase transforms eventually to the high-temperature phase (I) at approximately 240 °C. Phase I occurs directly on cooling below the melting point

of  $\text{Na}_2\text{SO}_4$  (884 °C) and the resulting crystal then transforms from phases  $\text{I} \rightarrow \text{II} \rightarrow \text{III}$  on further cooling. Phase II is an intermediate phase that exists within a narrow temperature range near 230 °C and phase III is metastable at room temperature. On reheating, the transition from  $\text{III} \rightarrow \text{I}$  takes place without occurrence of an intermediate phase.

The crystal structure of phase V is orthorhombic, space group  $Fddd$  [4], and the high-temperature phase I is hexagonal,  $P6_3/mmc$  [5]. The other room-temperature phase (III) also has orthorhombic symmetry,  $Cmcm$  [6], and the structure of the intermediate phase II is thought to be orthorhombic,  $Pbnm$  [2]. Here we note that there are two well-characterized room temperature forms, V and III. Phase III was reported to be quite stable for more than one year at room temperature when the  $\text{Na}_2\text{SO}_4$  (III) sample was contained in dried air [7, 8]. However, in the normal atmosphere, phase III slowly reverts to phase V. The mechanism of this conversion in  $\text{Na}_2\text{SO}_4$  is entirely unknown, but it most likely involves water molecules.

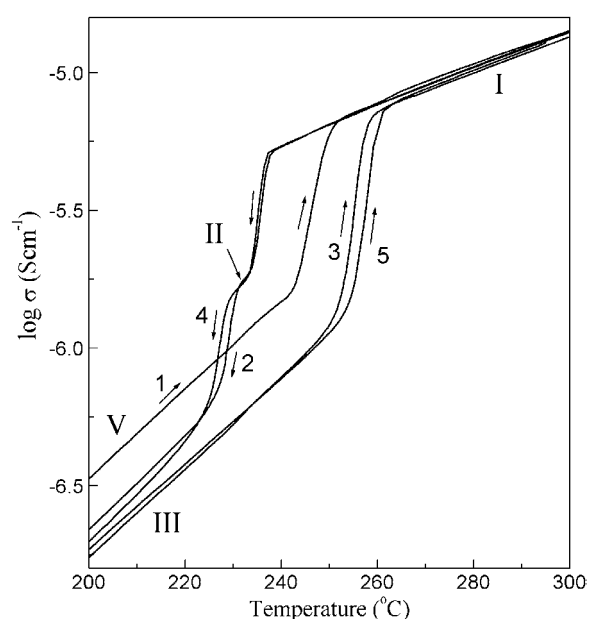
The transitions occurring at the first heating of as-grown  $\text{Na}_2\text{SO}_4(\text{V})$  are so peculiar that there have been many controversial reports about them, especially with regard to the existence of intermediate phases between V and I [1, 7–17]. The intermediate phase has been regarded frequently as phase III, and the reported values of the  $\text{V} \rightarrow \text{III} \rightarrow \text{I}$  transition temperatures are diverse, varying by as much as  $\sim 40$  °C. Sometimes it was reported that multiple transitions take place in between phases V and I [9, 10, 16]. Even the possibility of a direct  $\text{V} \rightarrow \text{I}$  transition without the occurrence of an intermediate phase under the conditions of extremely slow heating has been reported once [1]. Nearly all of these previous studies, which have been mainly thermal in nature, were performed on powders or pressed pellets of  $\text{Na}_2\text{SO}_4$ .

Here we have employed a dynamic technique, Raman spectroscopy, as well as differential scanning calorimetry (DSC) and ionic conductivity, to study oriented single crystals of  $\text{Na}_2\text{SO}_4$ , focusing on the transitions of phase V on the first heating process. We found entirely new results on the structural phase transitions of  $\text{Na}_2\text{SO}_4(\text{V})$  single crystals concerning the existence and nature of the intermediate phases between the room-temperature phase V and the high-temperature phase I. By comparison with analogous results obtained from powders, we uncover why such diverse results on the transition sequences have been reported previously.

## 2. Experimental details

Colourless single crystals of  $\text{Na}_2\text{SO}_4(\text{V})$  were grown from aqueous solution at 50 °C by slow evaporation of the solvent. Crystals of bipyramidal shape grew to a size of  $\sim 20 \times 30 \times 35 \text{ mm}^3$  with well-developed (110) and (111) faces. Sodium sulfate cleaves readily along (010) planes. We confirmed the crystallographic axis orientation by x-ray diffraction and we found that the unit cell dimensions of one  $\text{Na}_2\text{SO}_4(\text{V})$  sample were very similar to the structural data reported by Nord [4]. A number of oriented and polished samples of rectangular shape were prepared for the Raman study. The temperature of the sample was measured with a gold–iron/chromel thermocouple clamped onto the crystal surface. For ionic conductivity measurements, *a*-cut single crystals of typical thickness 1.5 mm and area  $15 \text{ mm}^2$  were prepared with evaporated gold contacts. For comparison, we also prepared compressed polycrystalline samples. The single crystals were crushed finely and pelletized at  $8 \text{ tons cm}^{-2}$ .

The Raman spectrum was excited with 70 mW of 468.0 nm krypton laser light that had been filtered with an Anaspec 300S prism monochromator. The Stokes Raman light scattered at 90° was analysed in the frequency-shifted range 10–1300  $\text{cm}^{-1}$  with a Spex 14018 double monochromator at a spectral resolution of 3  $\text{cm}^{-1}$ , and detected by a cooled RCA 31034A photomultiplier. In the notation used for the polarization measurements, the orthogonal *X*, *Y* and *Z* laboratory axes refer to the crystallographic *a*, *b* and *c* axes, respectively, of the phase V samples before heat treatment.



**Figure 1.** Temperature dependence of the ionic conductivity of a polycrystalline pellet of  $\text{Na}_2\text{SO}_4$ . Numbers indicate the heating/cooling sequence.

The complex impedances were determined by means of an HP model 4192A LF impedance analyser. The complex impedance measured in the frequency range from 100 Hz to 1 MHz allowed us to obtain the bulk conductivity by means of the usual impedance analysis.

The thermal studies were performed by using a Shimadzu DSC TA-50 differential scanning calorimeter. The sample chamber was purged with purified helium at all times. Measurements were carried out at a heating rate of 1 or 0.1  $^{\circ}\text{C min}^{-1}$  from room temperature to 300  $^{\circ}\text{C}$  for both powdered and single-crystalline samples.

### 3. Results and discussion

#### 3.1. Structural phase transitions of powdered $\text{Na}_2\text{SO}_4(\text{V})$

For comparison purposes, we first present results obtained from powdered samples of  $\text{Na}_2\text{SO}_4$ . Figure 1 shows a typical ionic conductivity plot of a polycrystalline pellet of powdered  $\text{Na}_2\text{SO}_4(\text{V})$  crystal for several heating/cooling cycles. It shows that the phase V transforms eventually to phase I near 242  $^{\circ}\text{C}$  (process 1). In the first cooling (process 2), it can be seen that the transitions I  $\rightarrow$  II  $\rightarrow$  III take place, but the intermediate phase II appears in a narrow temperature region. In the second heating cycle (process 3), there is a III  $\rightarrow$  I transition without any apparent occurrence of intermediate phases. In the second cooling cycle (process 4), phase II appears more clearly, and there is no further hysteresis on subsequent cooling cycles. Notice that, for the discussions hereafter, only the I  $\leftrightarrow$  II transition is known to be reversible [2, 16].

In the first heating process of phase V, the conductivity curve between 230 and 242  $^{\circ}\text{C}$  exhibits a small bump before a fast increase of the conductivity, intimating that there may be some complex transitions in this temperature region. This is seen more clearly in the DSC data of powdered  $\text{Na}_2\text{SO}_4(\text{V})$ , as shown in figure 2. In the first heating cycle, the DSC peak is

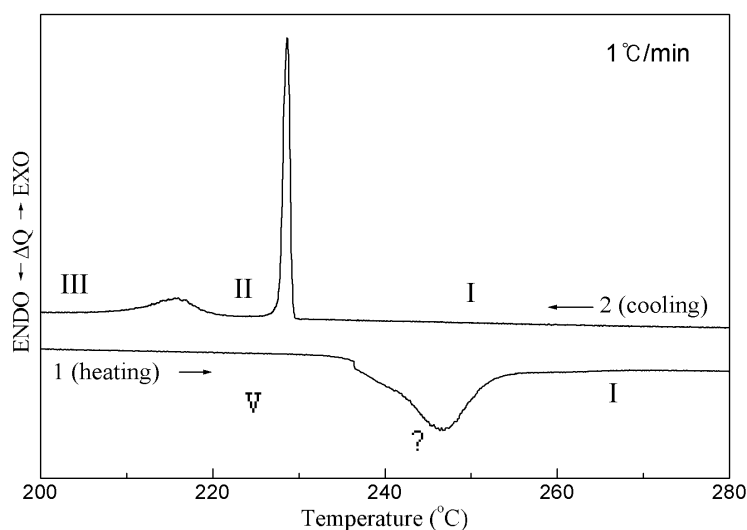
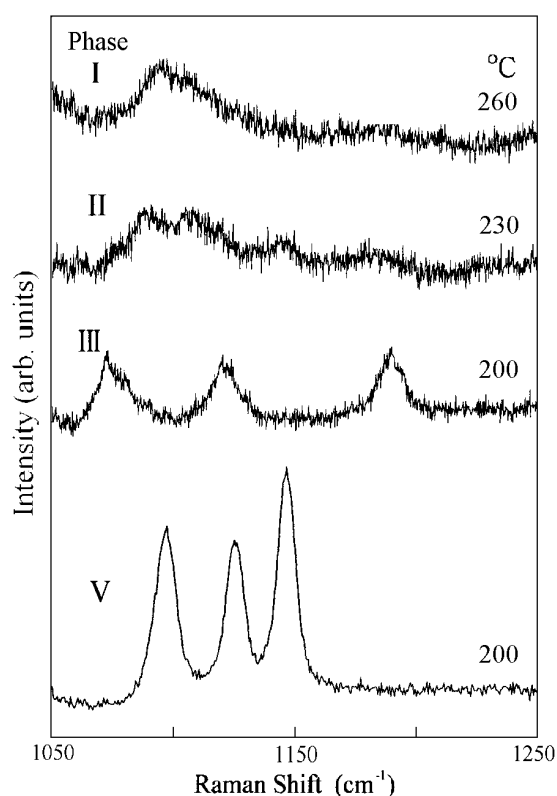


Figure 2. DSC traces of powdered  $\text{Na}_2\text{SO}_4$ , measured with heating/cooling rate of  $1\text{ }^\circ\text{C min}^{-1}$ .

broad and appears to be the sum of a few thermal peaks, indicating that there may be multiple structural transitions in this temperature region. Many authors have reported that the V–I transition is quite sluggish and incomplete. They also reported that there are intermediate phases (II–IV) between phases V and I, although diverging in their phase assignments and the transition sequence [1, 7–17]. In addition, some authors reported that  $\text{Na}_2\text{SO}_4$  may contain many nuclei of phase V even when it is held at temperatures in which phase I is stable [7, 16]. In the first cooling cycle, however, the transitions  $\text{I} \rightarrow \text{II} \rightarrow \text{III}$  are clearly seen.

For more precise assignments of the intermediate phases, we measured Raman spectra for powdered pellets of  $\text{Na}_2\text{SO}_4$  and followed the spectral changes related to structural transitions. A full account of the polarized Raman spectra of phases I, II, III and V of  $\text{Na}_2\text{SO}_4$  and mode assignments has already been given [18–20]. The presence of an intermediate phase IV between phases V and I was never firmly established and has been negated in several previous studies [2, 8, 13, 15]. Raman measurements confirm that phase IV does not exist.

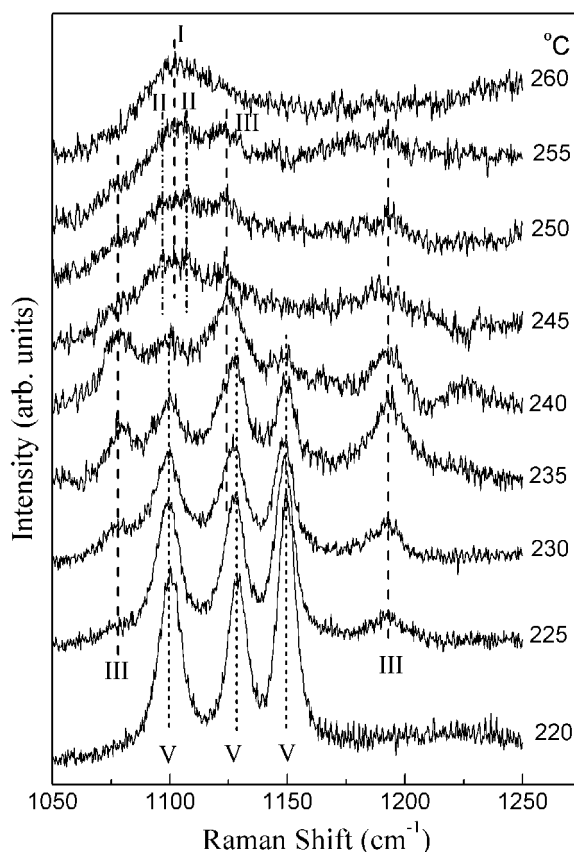
The lattice vibrational modes of the four different phases are most easily distinguished in (ZX) polarized spectra. However, the lattice phonon modes below  $300\text{ cm}^{-1}$  are broad and, therefore, they are not appropriate to analyse the mixed phases that may appear near  $240\text{ }^\circ\text{C}$ . The  $450\text{--}1250\text{ cm}^{-1}$  region of the Raman spectrum exhibits lines due to the  $\text{SO}_4$  group internal vibrations. The internal modes are in well-separated groups of lines consistent with vibrations derived from the free  $\text{SO}_4^{2-}$  tetrahedral ion (point group  $T_d$ ); i.e., a totally symmetric  $\nu_1(\text{A}_1)$ , a doubly degenerate  $\nu_2(\text{E})$ , and two triply degenerate  $\nu_3(\text{F}_2)$  and  $\nu_4(\text{F}_2)$  modes. The internal modes of the sulfate complex are somewhat modified in the  $\text{Na}_2\text{SO}_4$  crystal environment. Among the four different species of  $\nu_i$  vibrations, the antisymmetric  $\nu_3$  band appears in the widest frequency region from  $1050$  to  $1250\text{ cm}^{-1}$ . Hence we chose the spectrum of  $\nu_3$  vibrations to compare and identify each phase occurring in the phase transition progression. For the  $\nu_3$  internal vibrations, the room-temperature phase V and the other metastable room-temperature phase III have three well-separated Raman lines;  $1101.3$ ,  $1131.4$  and  $1152.1\text{ cm}^{-1}$  for phase V at  $20\text{ }^\circ\text{C}$ , and  $1076.2$ ,  $1130.9$  and  $1198.9\text{ cm}^{-1}$  for phase III at  $20\text{ }^\circ\text{C}$ . In the intermediate phase II at  $232\text{ }^\circ\text{C}$ , there appear five  $\nu_3$  peaks at  $1090$ ,  $1108$ ,  $1116$ ,  $1145$  and  $1178\text{ cm}^{-1}$ . In the high-temperature phase I, there appear two broad  $\nu_3$  bands at  $1100$  and  $1170\text{ cm}^{-1}$ . Unpolarized



**Figure 3.** Comparison of Raman spectra in the  $\nu_3$  vibrational region of Na<sub>2</sub>SO<sub>4</sub> powder for phases I, II, III and V.

Raman spectra of powdered Na<sub>2</sub>SO<sub>4</sub> are shown, for example, in figure 3; this shows that the four phases are readily distinguished in this frequency region.

The Raman spectra between 1050 and 1250 cm<sup>-1</sup> of the  $\nu_3$  vibrations of powdered pellets of Na<sub>2</sub>SO<sub>4</sub>(V) have been measured on heating, as shown in figure 4. There is some noise in the spectra due to the high background created by elastic light scattering from the powder. First, the spectra reveal that the V → III transition occurs above 220 °C and that phases V and III coexist up to 240 °C, showing that the transition is sluggish. The intensities of phase III peaks start to diminish roughly from 240 °C and persist up to 255 °C. This means that the III → I transition occurs near 240 °C, since any other transition sequences such as III → II are forbidden on heating. However, the overall transition sequence cannot be simplified as V → III → I. On comparing Raman spectra at 235 and 240 °C, one can see that the intensity of the phase V spectrum is considerably diminished, but the intensity of the phase III spectrum is nearly unchanged. This indicates that the phase V nuclei, which are not transformed to phase III until 235 °C, transform to another phase, such as phase I or II, between 235 and 240 °C. On comparing the spectra above 245 °C, it looks like mixed phases of I, II and III exist up to 255 °C. In summary, many particles of phase V in the powdered pellet start to transform to phase III at around 225 °C and then to phase I at around 240 °C in a sluggish manner. Other particles of phase V may be transformed to phase I or II, instead of phase III, at around 235 °C. In this regard, we note that the V → I and V → II transitions are not yet confirmed in the literature. Because of the noise of the spectra and the appearance of mixed phases due to the sluggishness



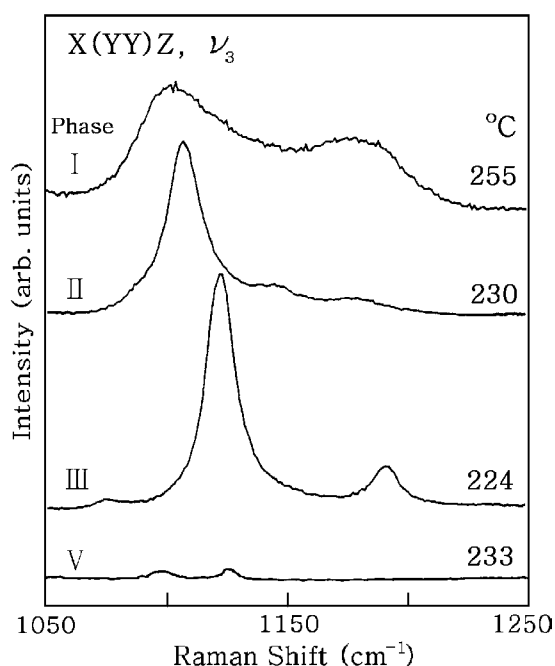
**Figure 4.** Temperature dependence of the Raman spectrum in the  $\nu_3$  vibrational region of  $\text{Na}_2\text{SO}_4$  powder on heating.

of the transitions, the information obtained from powder specimens is not sufficient for precise assignments on the transition sequence.

### 3.2. Structural phase transitions of single-crystal $\text{Na}_2\text{SO}_4(\text{V})$

What actually happens then in the first heating of  $\text{Na}_2\text{SO}_4(\text{V})$ , before the final transition to the high-temperature phase I? For a more precise assignment of the transition sequence on first heating, we then turned to studying single crystals of  $\text{Na}_2\text{SO}_4$  and followed the changes in the Raman spectrum related to structural transitions. In single crystals, the phases I, II and III are most easily distinguished by the  $\nu_3$  vibrations in  $X(\text{YY})Z$  polarization, as shown in figure 5. The  $\nu_3$  vibrations of phase V are very strong in  $(\text{YX})$ ,  $(\text{ZY})$  and  $(\text{ZX})$  polarizations, and the two weak lines appearing in the phase V spectrum of figure 5 are due to polarization leakages of the strong  $\nu_3$  lines in  $(\text{ZY})$  and  $(\text{ZX})$  polarizations.

In the Raman measurements of the first heating cycle of fresh  $\text{Na}_2\text{SO}_4(\text{V})$  single crystals, we have obtained new results regarding the existence and nature of intermediate phases between phases V and I. Surprisingly, a *direct* and *sharp*  $\text{V} \rightarrow \text{I}$  transition is observed at  $242^\circ\text{C}$ , as shown in figure 6. The transition temperature is some  $20^\circ\text{C}$  higher than that of the powdered sample, since the  $\text{V} \rightarrow \text{III}$  transition does not occur. At  $242.5^\circ\text{C}$ , a forbidden  $\nu_3 \text{B}_{1g}$  mode



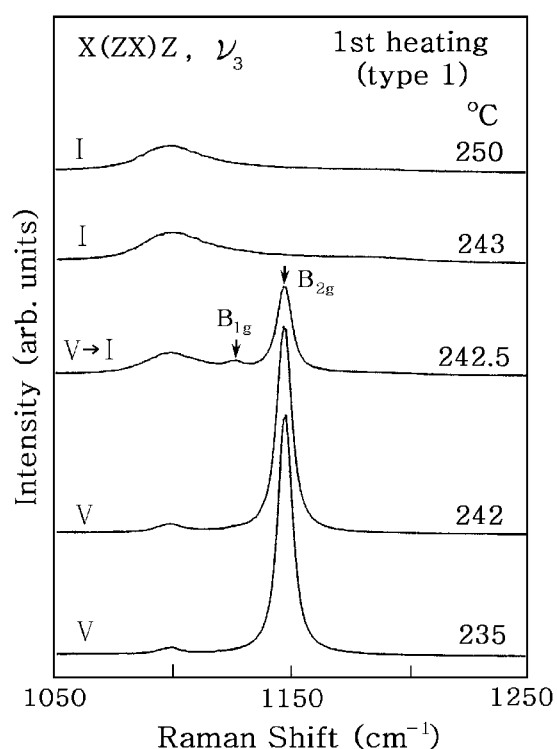
**Figure 5.** Comparison of Raman spectra in  $X(YY)Z$  polarization for the  $\nu_3$  vibrational region of a Na<sub>2</sub>SO<sub>4</sub> single crystal for phases I, II, III and V.

appears in the  $B_{2g}$  spectrum due to symmetry breaking in a middle of the transition. The transition is remarkably sharp, contrary to the much-mentioned sluggishness reported in the previous literature. In a large majority of the samples, the Raman spectrum thus indicated a direct first-order transition between phases V and I at 242 °C without the occurrence of an intermediate phase (type-1 behaviour), but occasionally for some single-crystal samples there occurred multiple transitions having complex intermediate phases between phases V and I (type-2 behaviour).

Figure 7 shows the Raman spectra observed for the type-2 behaviour, in which the structural phase transition occurs at a somewhat lower temperature near 234 °C and phases II and III appear as intermediate phases before the final transition to phase I. As compared with figure 5, the spectrum at 235 and 238 °C is mainly that of phase II with a small overriding phase III peak, and the spectrum above 250 °C corresponds to phase I. The V → II and V → III transitions appear to occur simultaneously at around 234 °C. Then phase II transforms to phase I near 240 °C and the remaining phase III component, which coexists now with phase I, transforms to phase I near 250 °C. The same transition information was obtained in the  $\nu_4$  vibrational region, as shown in figure 8.

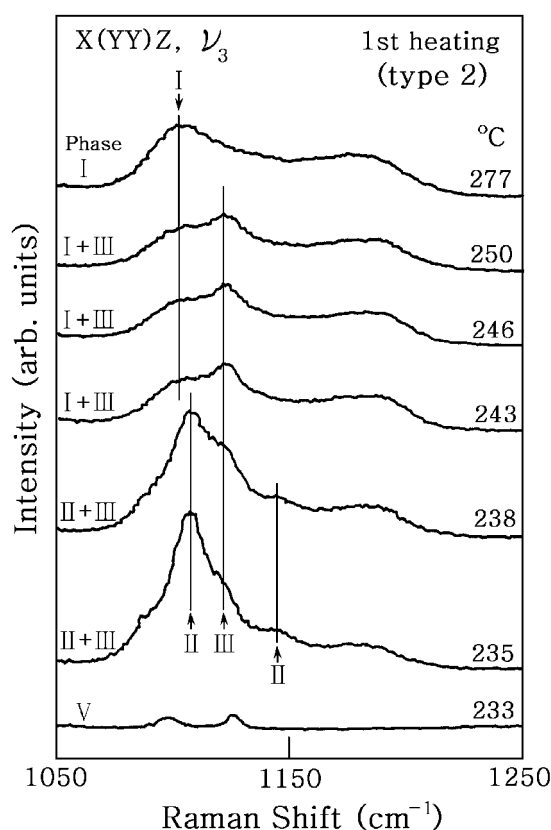
In figures 7 and 8, the assignments of phase information based on the Raman band intensities at each temperature are made by eye. Since each phase is not clearly distinguished by prominent features in the spectra, a more precise analysis requires the use of a peak fitting routine. It is necessary especially to check whether there is a contribution from phase I just after the transition at 235 °C. Thus, we peak fitted the  $\nu_4$  spectral region of figure 8, since this is relatively straightforward as compared with the  $\nu_3$  spectra of figure 7, where the overlapping bands are more heavily damped. In  $X(YY)Z$  symmetry, the  $\nu_4$  vibrations of phase I and III consist of a strong 630 and 635.5 cm<sup>-1</sup> line, respectively [19, 20]. The  $\nu_4$  vibrations of phase II





**Figure 6.** Temperature dependence of the Raman spectrum in  $X(ZX)Z$  polarization for the  $\nu_3$  vibrational region of a  $\text{Na}_2\text{SO}_4$  single crystal on first heating (type-1 behaviour).

in  $X(YY)Z$  symmetry consist of a strong  $626\text{ cm}^{-1}$  line plus a weaker  $620\text{ cm}^{-1}$  line, as shown in figure 9(a), in which each line was fitted using a Lorentzian profile. Hence, the  $\nu_4$  vibrations corresponding to the type-2 transition of figure 8 were fitted with a four-peak structure (two  $\nu_4$  peaks of phase II, one peak of phase III and one peak of phase I). The spectrum at  $235\text{ }^\circ\text{C}$  is well fitted with four Lorentzian peaks, as shown in figure 9(b), with an agreement factor of 0.99975. However, the fitted line at  $632.5\text{ cm}^{-1}$  is somewhat higher in frequency than the  $630\text{ cm}^{-1}$  line corresponding to phase I and is so weak that it is quite reasonable to assume that this peak is an artefact and that phase I does not exist at  $235\text{ }^\circ\text{C}$ . Even if the phase I component really existed, it may not be the expected component transformed directly from phase V, but rather the component just transformed from phase II, since phase II is stable only over a narrow temperature interval of  $1\text{--}2\text{ }^\circ\text{C}$  as shown later in figure 10. If the spectrum is fitted with three Lorentzian peaks, i.e., without the fourth phase I peak, it is equally well fitted with essentially the same accuracy (agreement factor of 0.99972), revealing that the mixed phase does indeed consist of just phases II and III. As the temperature increases, however, the type-2 spectrum of figure 8 has definitely a contribution from phase I, as shown for  $238\text{ }^\circ\text{C}$  in figure 9(c). Here we note that, on heating, transitions such as  $\text{III} \rightarrow \text{II}$  as well as  $\text{II} \rightarrow \text{III}$  are forbidden, but  $\text{II} \rightarrow \text{I}$  and  $\text{III} \rightarrow \text{I}$  transitions are allowed. Since the  $\text{III} \rightarrow \text{I}$  transition is known to occur near  $250\text{ }^\circ\text{C}$ , only the transition  $\text{II} \rightarrow \text{I}$  is allowed on heating in the temperature range of figure 9 ( $235\text{--}243\text{ }^\circ\text{C}$ ). This indicates that the spectral intensity transfer with temperature change is possible only between phases II and I, during a slow  $\text{II} \rightarrow \text{I}$  transition. Hence it is reasonable to suppose that the transitions occur separately in different places in the sample: the spectral

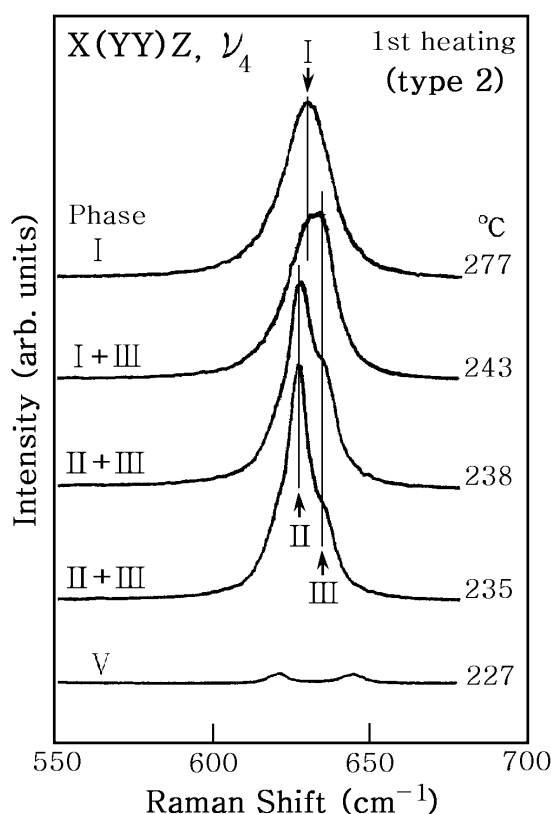


**Figure 7.** Temperature dependence of the Raman spectrum in  $X(YY)Z$  polarization for the  $\nu_3$  vibrational region of a  $\text{Na}_2\text{SO}_4$  single crystal on first heating (type-2 behaviour).

component of phases II and I is concerned with one particular set of regions of the sample and that of phase III is concerned with the other regions. The phase II regions which have just transformed from phase V at 235 °C evidently transform to phase I on heating with a somewhat sluggish manner, as shown in figures 9(c) and (d).

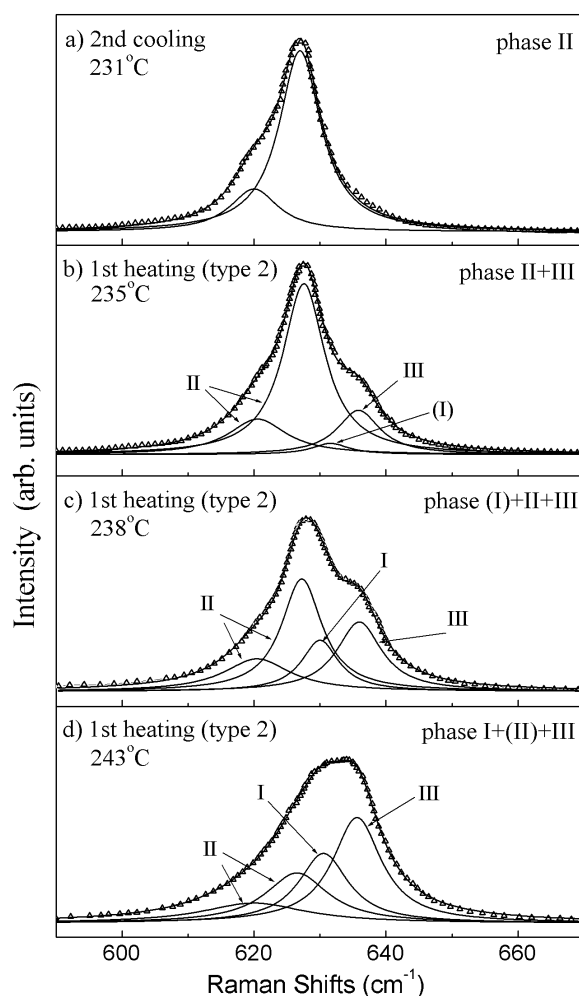
For the spectral component of phase III, which increases in intensity with increasing temperature, it can be assumed that the  $\text{V} \rightarrow \text{III}$  transition occurs very slowly in this temperature range. This kind of sluggishness of the transition in single-crystal  $\text{Na}_2\text{SO}_4$  has been observed before [1, 21], and it is also easily seen in the Raman spectra of the powdered sample in figure 4, in which the spectral intensity transfer between phases V and III is observed to occur for a temperature interval of more than 15 °C. Since the  $\text{II} \rightarrow \text{III}$  and  $\text{I} \rightarrow \text{III}$  transitions are not allowed on heating, we could not assume any other possibility for the sequence of the transitions except for the direct  $\text{V} \rightarrow \text{III}$  transition. Above 250 °C, as expected, the Raman intensity of phase III diminishes corresponding to the occurrence of the  $\text{III} \rightarrow \text{I}$  transition, as shown in figure 7. Thus, to summarize, the single crystal of  $\text{Na}_2\text{SO}_4(\text{V})$  commonly transforms directly to phase I (type-1 transition), but occasionally it transforms to a mixed phase of II and III, in which the  $\text{V} \rightarrow \text{III}$  transition is very sluggish, and then finally transforms piece by piece to phase I (type-2 transition).

In a previous paper [1], we reported from ionic conductivity measurements on single crystals of  $\text{Na}_2\text{SO}_4$  that multiple transitions occur in the first heating process of  $\text{Na}_2\text{SO}_4(\text{V})$ ,



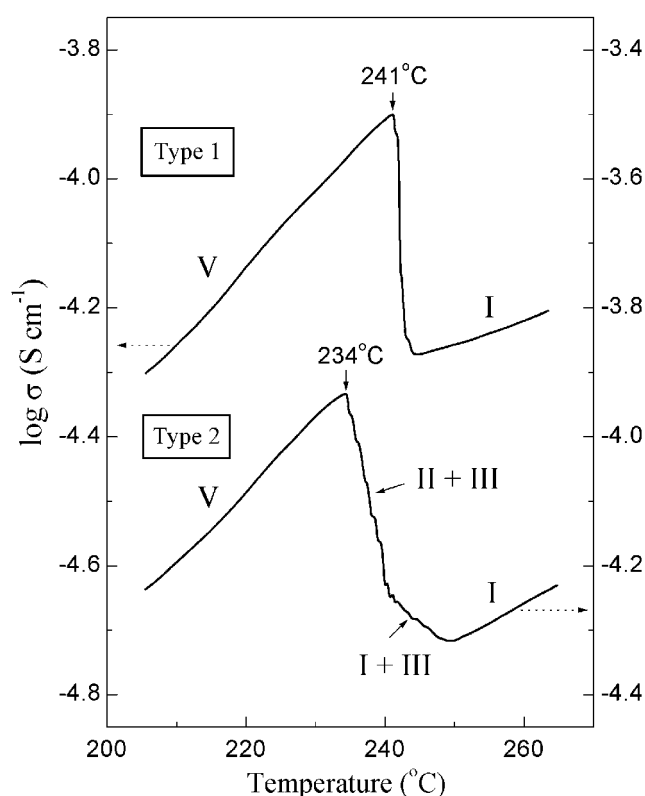
**Figure 8.** Temperature dependence of the Raman spectrum in  $X(YY)Z$  polarization of the  $\nu_4$  vibrational region of a  $\text{Na}_2\text{SO}_4$  single crystal on first heating (type-2 behaviour).

but also that sometimes a sharp transition, which from Raman spectroscopy may now be assigned to a direct V–I transition, can occur under conditions of exceptionally slow heating. The direct transition behaviour we observed at that time was contradictory to the previously reported sluggishness of the transition and, therefore, we could not give a proper assignment for the direct transition. Now, in the conductivity measurements for  $a$ -cut single crystals, we have been able to observe the two types of transitions during the first heating process, as shown in figure 10. Notice that the phase V conductivity of an  $a$ -cut single crystal is more than 100 times larger than that of a polycrystalline powder (see figure 1). This is because of the large anisotropy in the  $\text{Na}^+$  ion conduction in the stable room-temperature phase V [1]. The two types of transitions found in the Raman data are thus now well matched by the conductivity data, and aided by the Raman results definite assignments of the intermediate phases are given in the figure. The type-1 behaviour shown in figure 10 was obtained when the sample was heated with a very slow heating rate of  $0.033\text{ }^\circ\text{C min}^{-1}$ . It distinctly shows that the transition is abrupt and sharp, as opposed to the previously mentioned sluggish transition. The type-2 behaviour, exhibiting multiple transitions, was obtained only with the normal heating rate of  $0.5\text{ }^\circ\text{C min}^{-1}$ . However, the two types of behaviour are not clearly distinguished experimentally in terms of just the heating rate, though the type-1 behaviour is most commonly observed only for a slow heating process. It must also be dependent on various other factors of the sample states such as thickness, area, cracks, voids, and inclusion of water.



**Figure 9.** Peak fittings of (a) a phase II spectrum of the  $\nu_4$  vibrational region with  $X(YY)Z$  symmetry that appears when cooling a  $\text{Na}_2\text{SO}_4$  single crystal, and (b) the type-2 mixed phase spectrum of figure 8 at 235 °C, (c) 238 °C, and (d) 243 °C.

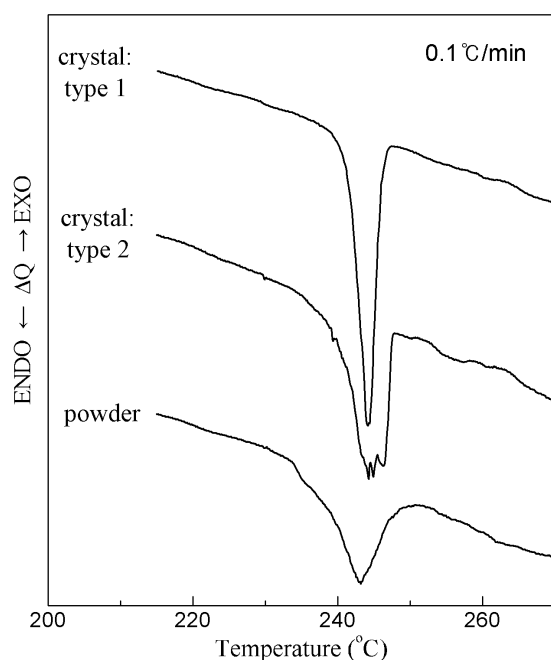
The two types of transition are also seen in DSC measurements of single crystals. Figure 11 shows representative DSC data measured for single crystals of  $\text{Na}_2\text{SO}_4(\text{V})$  with a heating rate of  $0.1\text{ }^\circ\text{C min}^{-1}$ . We found that many crystals exhibit a relatively sharp DSC peak (type 1), but others show a complex nature corresponding to the type-2 sluggish behaviour. The endothermic heat of transition is measured to be  $-29.6\text{ J g}^{-1}$  for the type-1 transition and  $-30.1\text{ J g}^{-1}$  for the type-2 transition. The transition heats are nearly the same, revealing that neither of the transition types is thermally preferable. For comparison, the DSC data of a powdered sample, measured with same heating rate, are also depicted in the figure. The DSC peak of the powdered sample is broad, with an endothermic heat of  $-27.6\text{ J g}^{-1}$ , and can be seen to include both types of transition. The exothermic heats of the  $\text{I} \rightarrow \text{II}$  and  $\text{II} \rightarrow \text{III}$  transitions on cooling single-crystal samples were measured to be  $11.4$  and  $4.6\text{ J g}^{-1}$ , respectively. The endothermic heat of the  $\text{III} \rightarrow \text{I}$  transition on reheating was measured to be  $-16.5\text{ J g}^{-1}$ , which is roughly



**Figure 10.** Temperature dependence of the ionic conductivity of an *a*-cut single crystal of  $\text{Na}_2\text{SO}_4$  on first heating.

40% lower than that of the V–I transition. This indicates that the heat of transition on first heating of a fresh  $\text{Na}_2\text{SO}_4(\text{V})$  crystal is significantly larger than those of any other subsequent transitions. Hence the crystal structures of phases I and V are so different [4, 5] that the structural transition has to involve large displacements of cations and anions together with rotations of the anions. Our results indicate that the order of occurrence of these displacements and concomitant rotations is not unique and, therefore, more than one sequence is possible with little energy difference between them. Thus the sample conditions and heating rate are very sensitive factors.

In summary, we found that the structural transitions  $\text{V} \rightarrow \text{II} \rightarrow \text{I}$ ,  $\text{V} \rightarrow \text{III} \rightarrow \text{I}$  and  $\text{V} \rightarrow \text{I}$  are all possible sequences on heating of fresh  $\text{Na}_2\text{SO}_4(\text{V})$  crystals. In single crystals,  $\text{V} \rightarrow \text{I}$  commonly occurs particularly with a slow heating process, otherwise  $\text{V} \rightarrow \text{II}$  and  $\text{V} \rightarrow \text{III}$  occur simultaneously. In polycrystalline pellets, the above-mentioned transitions are all possible, but especially  $\text{V} \rightarrow \text{III} \rightarrow \text{I}$  transitions are dominant. The  $\text{V} \rightarrow \text{I}$  transition involves such a drastic alteration in crystal structure that the changes may occur via several routes according to experimental conditions as well as sample states. Most of the previous thermal studies of  $\text{Na}_2\text{SO}_4$  were performed on powder or pressed pellet samples and it has been determined that the occurrence of polymorphism is dependent on the method of sample preparation [8, 10, 11, 16], i.e., on particle size, pressure of die, grinding time and water contamination, though these have not been clarified quantitatively. Hence, in the polycrystalline powder, each crystalline particle transforms differently via one of two routes,



**Figure 11.** DSC traces of single crystals and a powder of  $\text{Na}_2\text{SO}_4$  on first heating, measured with a heating rate of  $0.1\text{ °C min}^{-1}$ .

which are the two types of behaviour presented here. Given the complexity of the transitions in  $\text{Na}_2\text{SO}_4$ , other routes may also be possible, but none have been identified in our samples.

#### 4. Conclusions

This first detailed study of Raman spectra obtained from oriented single crystals of  $\text{Na}_2\text{SO}_4$  has revealed new information about its sequence of structural phase transitions. We have found that as-grown single-crystal  $\text{Na}_2\text{SO}_4(\text{V})$  transforms directly to phase I at  $242\text{ °C}$  without the occurrence of an intermediate phase (type 1), but occasionally it transforms to a mixed phase of II and III at  $234\text{ °C}$ , in which case phase III appears in only a small part of the sample, and then phases II and III finally transform bit by bit to phase I (type 2). The DSC and ionic conductivity data for single crystals, which have not been fully understood until now, also proved to exhibit these two types of behaviour. In the polycrystalline powder, each crystalline particle may transform according to one or other of the two types of behaviour discussed here. Hence the experimental data for powdered  $\text{Na}_2\text{SO}_4(\text{V})$  transitions exhibit a much more complex nature. Many controversies in the previously published reports, in which most of the data have been obtained for powdered specimens, regarding the intermediate phases between phases V and I are now seen to be a consequence of the simultaneous occurrence of these two types of transitions in the powdered samples.

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