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Thermo-Raman spectroscopic studies on polymorphism in Na_2SO_4

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Abstract. The phase transformations involved in Na_2SO_4 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as starting material) and predried Na_2SO_4 in a dynamic thermal process of heating from 30 to 500 °C and then cooling down to 30 °C, with a heating/cooling rate of 2 °C min^{-1} in two consecutive thermal cycles, were monitored at 1 °C intervals by thermo-Raman spectroscopy (TRS). The transformations were characterized on the basis of the disappearance of the bands, appearance of new bands, splitting in the internal modes, change in the spectral profile, intensity (area) changes in the internal modes, full width at half maximum (FWHM) of the totally symmetric stretching mode and even the variations observed in the background during the thermal process. This thermo-Raman investigation provided some evidence for the existence of an intermediate phase between phase V and phase I and also for the changes observed in the phase I structure at higher temperatures, in addition to the dynamic transformations between the well known phase V, phase I, phase II and phase III. The intensity study on the ν_3 mode of SO_4^{2-} clearly demonstrated the thermal hysteresis involved among the phases during the heating and cooling process. The differences observed in the polymorphisms of Na_2SO_4 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as starting material) and predried Na_2SO_4 were also discussed.

1. Introduction

Sodium sulfate (Na_2SO_4) exhibits a rich variety of structural phase transformations as the temperature is varied in the range between room temperature and 300 °C [1]. Crystals of anhydrous Na_2SO_4 are usually in phase V at ambient temperature. On heating, Na_2SO_4 transforms to phase I above 250 °C and, upon cooling, phase I transforms to phase II then phase III. On reheating, Na_2SO_4 in phase III transforms directly to phase I. There is still some controversy over the existence of an intermediate phase between phase V and phase I [2]. A brief summary of various experimental studies performed on different phases of this material was reported recently by Rasmussen *et al* [2]. The experiments included thermal hysteresis of Na_2SO_4 by DTA (differential thermal analysis) [3], phase transformations by DSC (differential scanning calorimetry) and electrical conductivity studies [4], phase transformations by DSC and Raman techniques [1], and the phase transformations by x-ray diffraction studies [2, 5–7]. In spite of the extensive experimental studies on the polymorphism of Na_2SO_4 , there are still several inconsistencies regarding the number of transformations, sequence of transformations, transformation temperatures and the reversibility of certain transformations.

The early study by Kracek *et al* on the polymorphism of Na_2SO_4 by thermal analysis postulated that Na_2SO_4 is capable of existing in five distinct modifications, designated as phase V, phase IV, phase I, phase II and phase III in a thermal cycle [8]. Detailed structural

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analyses have only been reported for phase V [5], phase III [6] and phase I [7] of anhydrous Na_2SO_4 . Recently, Rasmussen *et al* reported the crystal structure of phase II using powder x-ray diffraction data [2]. Choi *et al* carried out extensive research work on the polymorphism of Na_2SO_4 by measuring ionic conductivity [9] and Raman scattering measurements [10–12]. They identified phase V, phase I, phase II and phase III. Several inconsistencies were found in the literature about the existence and nature of an intermediate phase between phase V and phase I. Choi *et al* reported that occasionally phase V first transforms to phase II then to phase I instead of the direct phase V to phase I transformation [12]. Some authors thought that the intermediate phase was phase III [9]. Most of the thermal data on the phase transformations of Na_2SO_4 suggested that the intermediate phase was phase IV [1, 3, 8]. Some of the reports also discussed the possibility of multiple transformations between phase V and phase I [1, 13]. However, the presence of an intermediate phase between phase V and phase I is yet to be thoroughly established. The thermal hysteresis exhibited by Na_2SO_4 during the dynamical thermal process was investigated earlier by DTA [3]. Brodale and Giaque reported that in dry state, Na_2SO_4 displayed a marked hysteresis [14].

The transformation of Na_2SO_4 from low temperature orthorhombic phase III to a high temperature hexagonal phase I accompanied an increase in volume of 4% and an increase in conductivity by 10 times [15]. The conductivity of Na_2SO_4 was explained using the percolation-type ion transport mechanism, based on the direct correlation between structural change and conductivity increase [16]. The limitation of Na_2SO_4 as a solid state electrolyte because of its low conductivity and the appearance of microcracks due to the volume change during the phase transformations was removed with a suitable dopant for stabilizing the phase I structure at room temperature [17, 18]. Although the earlier investigations on Na_2SO_4 indicated a complex relationship between the structure and conductivity of the system, the phase transformations of Na_2SO_4 , particularly the phase I structure, require further investigation of its application.

Raman scattering techniques were used earlier to probe the polymorphic phase transformation involved in Na_2SO_4 , both in single crystal [10–12, 19] and polycrystalline samples [1, 20]. Raman spectra, measured as a function of temperature using thermo-Raman spectroscopy (TRS) in a dynamical thermal process, can provide valuable information for the *in situ* investigation of the composition and phase transformations in solid samples because of the availability of these data on a time scale of seconds and a temperature scale of 1°C . The combination of TRS with thermogravimetric analysis (TGA) [21–27] and DSC [28] simultaneously provides thermodynamical and vibrational spectroscopic data and have been used to successfully investigate the composition and phase transformations in solid state. Although the thermodynamical and vibrational data were available for phase V, phase I, phase II and phase III of anhydrous Na_2SO_4 , dynamical thermo-Raman studies on these systems may provide some more insight.

The objectives of the present work were as follows:

- The polymorphism in Na_2SO_4 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as starting material) and predried Na_2SO_4 in two consecutive heating/cooling thermal cycles was investigated dynamically by thermo-Raman studies.
- The possibility of the existence of an intermediate phase between phase V and phase I was investigated. Then, the number of intermediate phases (single or multiple), the nature of the phases and the temperature ranges in which each phase existed during the dynamical thermal process were also explored.
- The nature of phase I at higher and lower temperatures was investigated during the dynamical thermal process. The possibility of a difference in the nature of phase I formed

from phase V (during the heating process of the first cycle) compared with that of phase I formed from phase III (during the heating process of the second cycle) was also studied.

- Thermal hysteresis, involved among the phases during the thermal cycles, was investigated using the intensity of the ν_3 mode of SO_4^{2-} .

2. Experimental

The analytical grade $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ used in this investigation was from Showa Chemicals. The crystals were crushed into powder for the experimental study. The crushed powder, dried at 110°C for 4 days, was also studied for comparison and hereafter is referred to as predried Na_2SO_4 . A Seiko I DSC-200 differential scanning calorimeter was used to record the thermal behaviour. The DSC thermograms were recorded under N_2 atmosphere in a thermal process of heating from 30 to 500°C and then cooling down to 30°C with a heating/cooling rate of 5°C min^{-1} for two consecutive thermal cycles without disturbing the sample in between. The DTA thermogram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was recorded under identical experimental conditions as for DSC using a Seiko I DTA-200 differential thermal analyser. These experimental conditions were maintained for measuring the TG thermogram, with a heating rate of 2°C min^{-1} and using a Perkin Elmer TGA 6 thermogravimetric analyser.

Since the occurrence of phase transformation, transformation temperature and transformation width depend heavily on the sample geometry, heating/cooling rate, stress effects, thermal history and impurity concentration, the thermo-Raman spectra were recorded from the sample placed in an alumina crucible of TGA. In this case, both the thermogram of TG and Raman spectra could be measured simultaneously. Raman scattering was excited with an argon ion laser (Spectra Physics) operating at 514.5 nm with a power of 50 mW . The plasma lines were removed by a filter. The laser light was focused onto the sample through a glass window. The scattered radiation was collected at right angles, analysed by a 0.5 m spectrophotometer (Spex) and detected by a CCD camera (Princeton Instruments, 1024×1024 pixels). Spectra were taken continuously with suitable exposure time in order that each spectrum covered 1°C in a thermal process of heating from 30 to 500°C and then cooling down to 30°C , with a heating/cooling rate of 2°C min^{-1} in two consecutive thermal cycles. The positions of the spectral bands were calibrated using argon spectral lines. The resolution was about 3 cm^{-1} .

3. Results and discussion

3.1. DSC/DTA/TGA

In the present study, TG thermogram and thermo-Raman scattering measurements were made simultaneously in order to record the Raman spectra continuously at the same conditions as those used for DTA and DSC. DSC thermograms of both $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the predried Na_2SO_4 measured during the heating and cooling process of the first and second thermal cycles are shown in figures 1 and 2. The DTA thermograms measured at a heating rate of 5°C min^{-1} and the TG thermograms of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ measured along with the Raman measurements at a heating rate of 2°C min^{-1} are shown in figure 3(a) and 3(b), respectively.

The endotherms observed in the DSC (figure 1(a)) and DTA (figure 3(a)) thermograms of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ below 110°C corresponded to the dehydration process. The TG thermogram in figure 3(b) also showed the major steps involved in the dehydration process. For the predried Na_2SO_4 , the absence of weight loss in TG and endotherm in DSC in that corresponding

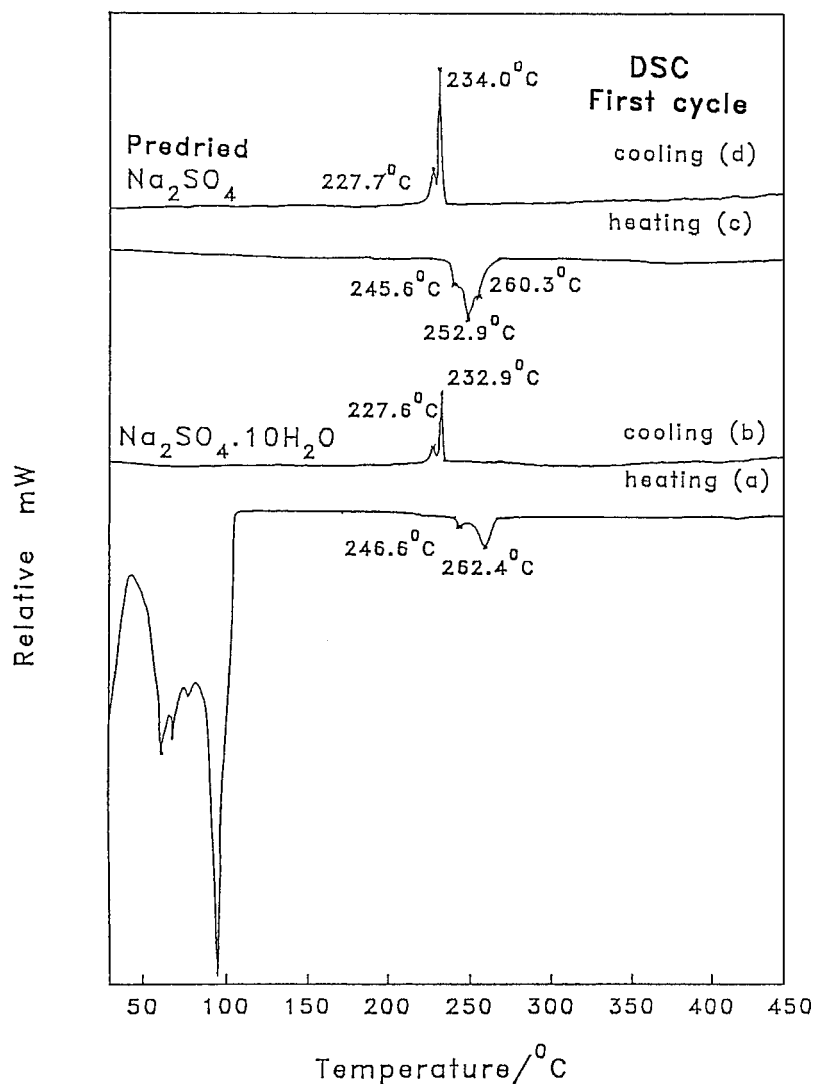


Figure 1. DSC thermograms of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ((a) and (b)) and predried Na_2SO_4 ((c) and (d)) measured with a 5°C min^{-1} heating/cooling rate in the first thermal cycle.

temperature interval indicated that it should be anhydrous Na_2SO_4 . The dehydration of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is discussed in detail with the thermal and thermo-Raman data elsewhere.

Continued heating after the dehydration process produced a small DSC endotherm at 246.6°C and a broad endotherm at 262.4°C for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, as shown in figure 1(a). In the DTA thermogram, shown in figure 3(a), a very small endotherm was observed at 245.6°C in addition to a broad endotherm at 256.1°C . The DSC thermogram of predried Na_2SO_4 in figure 1(c) showed a large endotherm at 252.9°C with two small shoulders at around 245.6 and 260.3°C . In addition to the above distinct signals, the DSC thermogram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (figure 1(a)) also showed broad but extremely weak signals from 200 to 240°C and from 375 to 500°C . Similarly, the DSC thermogram of the predried Na_2SO_4 (figure 1(c)) also showed extremely weak and broad signals from 195 to 240°C and from 375 to 500°C .

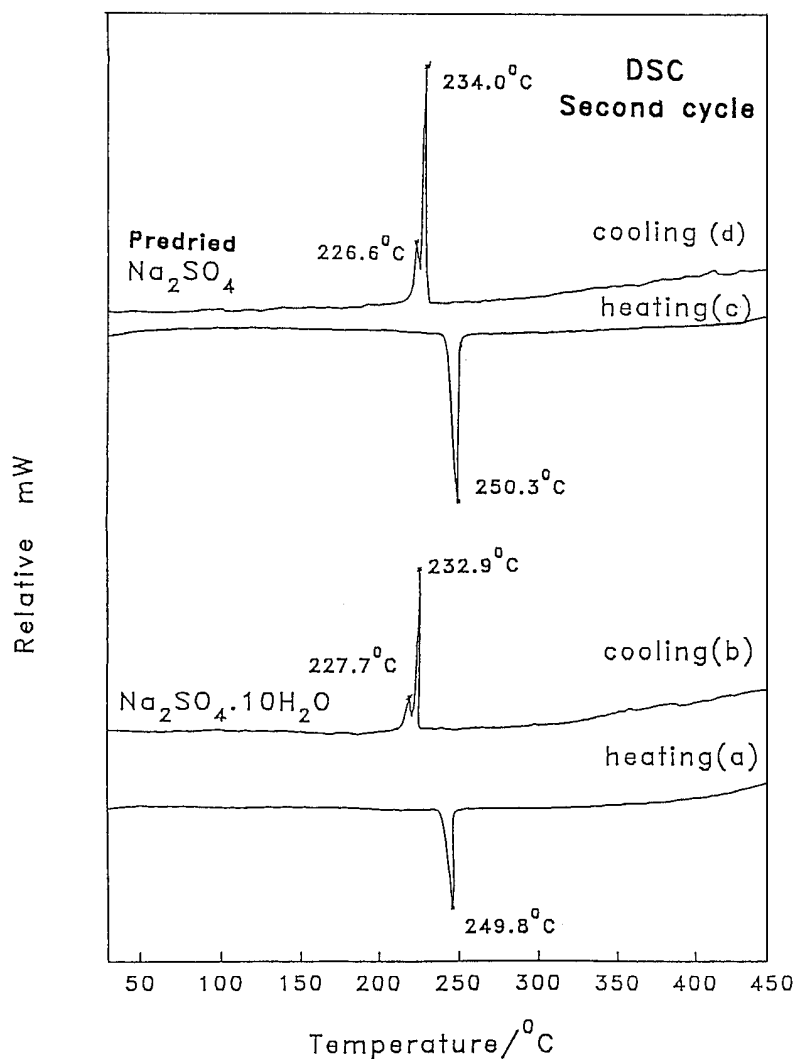


Figure 2. DSC thermograms of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ((a) and (b)) and predried Na_2SO_4 ((c) and (d)) measured with 5°C min^{-1} heating/cooling rate in the second thermal cycle.

The DSC thermograms of both $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (figure 1(b)) and predried Na_2SO_4 (figure 1(d)), measured during the cooling process of the first cycle, clearly showed that the thermogram returned to the baseline below 370°C . On further cooling, a large exotherm was observed at 232.9°C and a small exotherm at 227.6°C for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (figure 1(b)) and similarly, two exotherms were observed at 234.0 and 227.7°C for predried Na_2SO_4 (figure 1(d)). On reheating, besides the deviation from the background above 370°C , only a single large endotherm was observed at 249.8°C for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and at 250.3°C for predried Na_2SO_4 , as shown in figures 2(a) and (c), respectively. On cooling, the thermograms of both samples moved away from the baseline in the initial period and returned to the baseline after 375°C . On further cooling, two distinct exotherms were clearly observed at 232.9 and 227.6°C for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (figure 2(b)) and at 234.0 and 227.7°C for predried Na_2SO_4 (figure 2(d)).

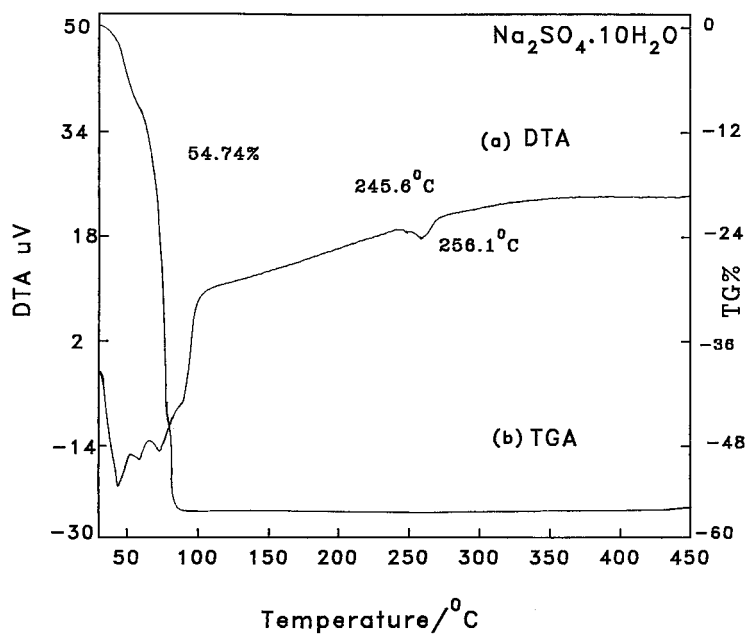


Figure 3. (a) DTA thermogram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ measured with a 5°C min^{-1} heating rate in the first cycle. (b) TG thermogram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ measured *in situ* along with the thermo-Raman measurements during the heating process of the first thermal cycle.

The TG thermogram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (figure 3(b)) did not show any weight loss after 110°C , which indicated that the dehydration process was over and hence the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ sample after dehydration is referred to hereafter simply as Na_2SO_4 . The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ dried for 4 days at 150°C is referred to as predried Na_2SO_4 for the sake of distinction.

3.2. TRS

The free sulfate ion (SO_4^{2-}) belongs to high symmetry point group T_d and gives rise to four fundamental vibrations, designated as ν_1 (A_1), ν_2 (E_2), ν_3 (F_2) and ν_4 (F_2) at 981 , 451 , 1104 and 613 cm^{-1} , respectively [29]. In the crystalline states, the degeneracies may be removed due to the lowering of the symmetry. Ananthanarayanan *et al* discussed the influence of the nature of the cations and crystal structures on the SO_4^{2-} frequencies [30]. The optical and spectroscopic properties of SO_4^{2-} in various crystalline environments have also been discussed by Wu *et al* [31].

Recently, Rasmussen *et al* refined the crystal structure of phase V, phase I and phase III and they also reported the crystal structure of phase II using powder diffraction data [2]. Na_2SO_4 in phase V has an orthorhombic structure with the space group D_{2h}^{24} ($Fddd$) and contains eight formula units per crystallographic unit cell [5]. Factor group analysis for this structure predicted 18 SO_4^{2-} internal modes and only nine of them were Raman active. The crystal structure of Na_2SO_4 in phase I was determined by Naruse *et al* [7]. It has a hexagonal arrangement with space group D_{6h}^4 ($P6_3/mmc$) and contains two formula units per crystallographic unit cell. Because of the presence of disorder in this crystal system, the correlation method fails for this phase. Rasmussen *et al* predicted that phase II has an orthorhombic arrangement and the space group could be either $Pbn2_1$ or $Pbnm$ [2]. Na_2SO_4 in phase III also has an

orthorhombic arrangement, but its space group belongs to $Cmcm (D_{2h}^{17})$ with four formula units per crystallographic unit cell [6]. Out of 18 predicted SO_4^{2-} internal modes, only 9 modes were Raman active in that phase.

3.2.1. Typical spectra. Typical Raman spectra of Na_2SO_4 , observed in the present work during the heating and cooling process in two consecutive thermal cycles, are shown in figures 4–6. Table 1 lists the positions of the observed Raman bands in the internal mode region of SO_4^{2-} and the assignments. Spectra measured at 30, 110, 235, 290 and 480 °C during the heating process of the first cycle shown in figure 4 represent the characteristic spectra of (a) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ before dehydration, (b) phase V, (c) the possible intermediate phase between phase V and phase I, (d) phase I and (e) phase I at high temperature of Na_2SO_4 . Spectra measured at 495, 245, 227 and 215 °C during the cooling process of the first cycle, as shown in figure 5 represent the characteristic spectra of (a) phase I at high temperature, (b) phase I, (c) phase II and (d) phase III.

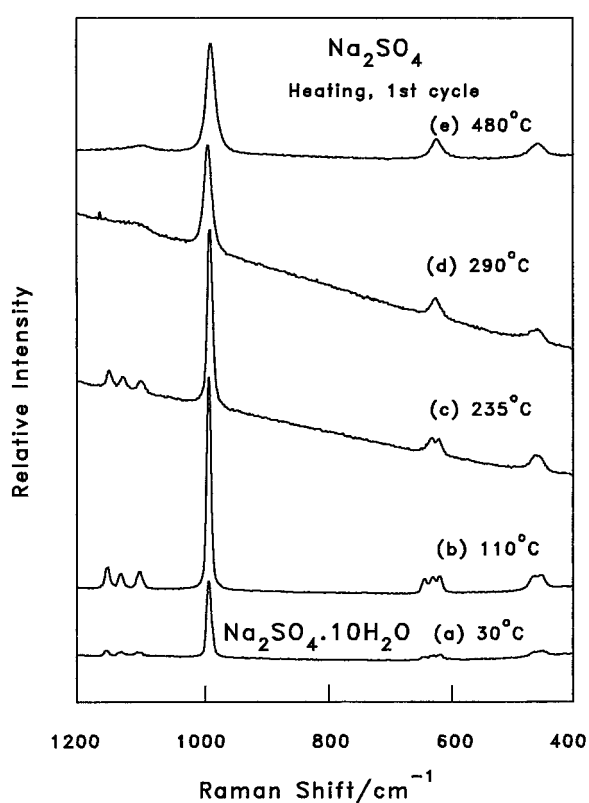


Figure 4. Typical Raman spectra of (a) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ before dehydration and (b) phase V; (c) possible intermediate phase between phase V and phase I, (d) phase I and (e) phase I at high temperature of Na_2SO_4 observed during the heating process of the first thermal cycle.

The Raman spectra of Na_2SO_4 measured at 110 °C during the heating process of the first cycle for phase V (figure 4(b)) showed all nine modes: one for ν_1 , two for ν_2 and three for both ν_3 and ν_4 , as predicted by the factor group analysis. The ν_3 and ν_4 modes are better resolved compared to the ν_2 mode. The Raman spectra observed at 235 °C, as shown in figure 4(c), might be due to the possible intermediate phase between phase V and phase I. The triplet nature

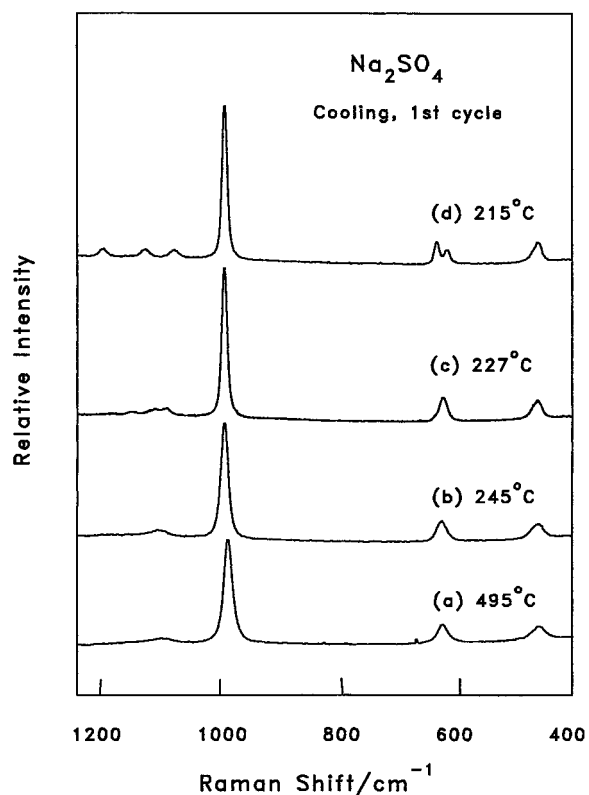


Figure 5. Typical Raman spectra of Na_2SO_4 : (a) phase I at high temperature, (b) phase I, (c) phase II and (d) phase III observed during the cooling process of the first thermal cycle.

Table 1. Band positions of Na_2SO_4 (cm^{-1}).

Phase	Mode			
	ν_1	ν_2	ν_3	ν_4
Phase V ^a	993	453, 467	1100, 1129, 1150	623, 633, 647
Intermediate phase ^b	991	460	1100, 1129, 1150	623, 633, 646
Phase I ^c	994	460	1100	627
Phase I ^d	989	460	1100	627
Phase II ^e	994	460	1088, 1107, 1147, 1179	627
Phase III ^f	994	460	1077, 1124, 1192	619, 637
Phase III ^g	997	460	1077, 1131, 1200	617, 639

^a Phase V measured after the dehydration at 130 °C.

^b Possible intermediate phase between phase V and phase I measured at 235 °C.

^c Phase I measured at 290 °C during the heating process of the first cycle.

^d Phase I measured at 480 °C during the heating process of the first cycle.

^e Phase II measured at 227 °C during the cooling process of the first cycle.

^f Phase III measured at 215 °C during the cooling process of the first cycle.

^g Phase III measured at 30 °C during the heating process of the second cycle.

of the ν_4 mode of phase V was replaced by distinct bands at 633 and 623 cm^{-1} and a shoulder at around 646 cm^{-1} in that intermediate phase. The Raman spectrum of phase I, observed at

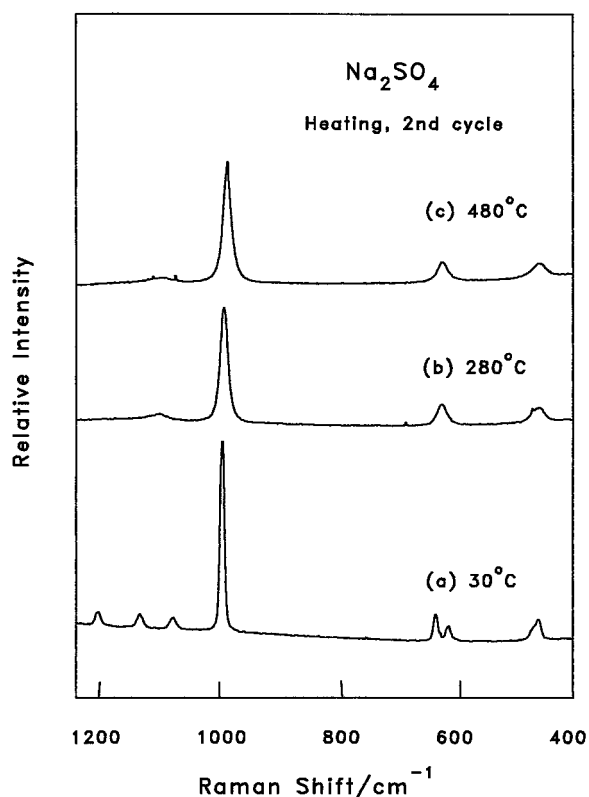


Figure 6. Typical Raman spectra of Na_2SO_4 : (a) phase III, (b) phase I, and (c) phase I at high temperature, observed during the heating process of the second thermal cycle.

290 °C (figure 4(d)), indicated only four vibrational bands similar to the free SO_4^{2-} . The usual site or factor group analysis was not possible for this phase because of the disorder nature. Due to the orientational disorder of SO_4^{2-} in that phase, the modes observed in the Raman spectra were broadened. The spectrum measured at 480 °C (figure 4(e)) indicated a considerable shift in the band position of the ν_1 mode, in addition to the considerable broadening of all four internal modes compared to the phase I spectrum measured at 290 °C. This is referred to as phase I at high temperature. Its structure could be similar to the structure of phase I, since the spectra were similar.

The spectra measured at 495 and 245 °C during the cooling process of the first cycle, as shown in figures 5(a) and (b), were the same as those measured during the heating process. The Raman spectrum of phase II, as shown in figure 5(c), showed major variations in the ν_3 mode. The Raman spectra measured in phase III, presented in figure 5(d), showed a broad band for the ν_1 mode, a triplet for the ν_3 mode and a doublet for the ν_4 mode. The spectra of the sample measured in this work did not show all the nine active modes for phase III as predicted by factor group analysis, but the polarized Raman measurements made on the single crystal by Choi *et al* showed complete agreement with the results of the factor group analysis [11].

Figure 6 represents the characteristic spectra of (a) phase III, (b) phase I and (c) phase I at high temperature, detected during the heating process of the second cycle. The characteristic spectra observed during the cooling processes of the second thermal cycle were very similar to those observed in the first cycle.

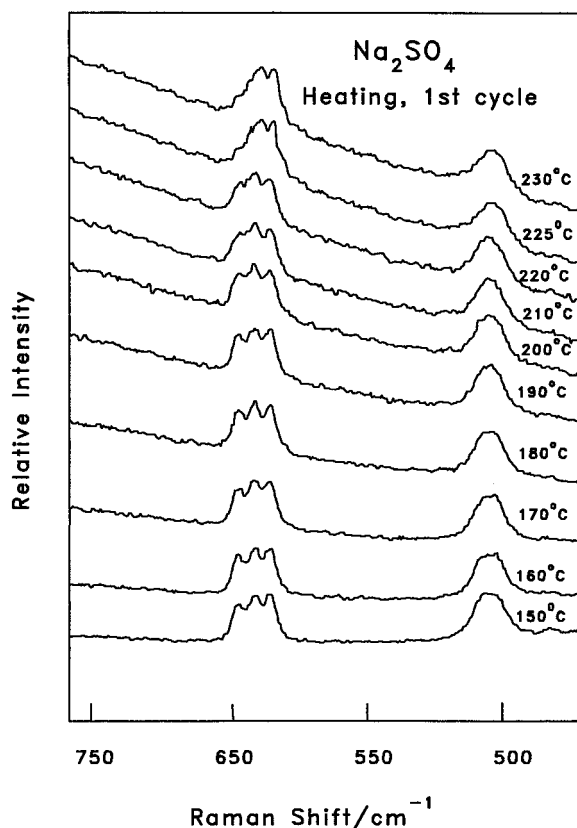


Figure 7. Thermo-Raman spectra of Na_2SO_4 from 150 to 230 °C (transformation from phase V to possible intermediate phase) in the ν_2 and ν_4 region of SO_4^{2-} during the heating process of the first cycle.

3.2.2. Variation in spectra. Although the characteristic spectra of all the phases could be identified, the changes in the spectrum observed by TRS at 1 °C intervals indicate in detail the variation in phase or the structure of the crystal in a dynamical thermal process. The intermediate phase between phase V and phase I has frequently been regarded as phase III or phase IV [1, 3, 8, 9]. The conductivity measurement on a single crystal of Na_2SO_4 by Choi *et al* showed that the conductivity values in that intermediate state were nearly the same as those of phase V and hence they discarded the possibility of the existence of an intermediate phase as phase III [9]. Rasmussen *et al* reported that no crystallographic evidence was observed showing the presence of an intermediate phase between phase V and phase I [2]. Also, they claimed that if such a phase does exist, as indicated by DSC, it must be close to phase V in structure as the heat effect for that transformation is small.

The structure of phase V seems to be stable between -259 and 180 °C [32]. Kracek reported that the presence of traces of water changes the conditions for the stability of phase V [8]. Nord described the crystal structure of phase V in terms of nearly regular SO_4^{2-} tetrahedra with equal S–O distance and distorted NaO_6 octahedra [5]. A comparison of the observed Raman spectra with the nine predicted Raman active internal modes shows good agreement, except with the ν_2 mode. The ν_2 mode appeared as an overlapped doublet at 110 °C in phase V. This might be due to the presence of a small trace of water.

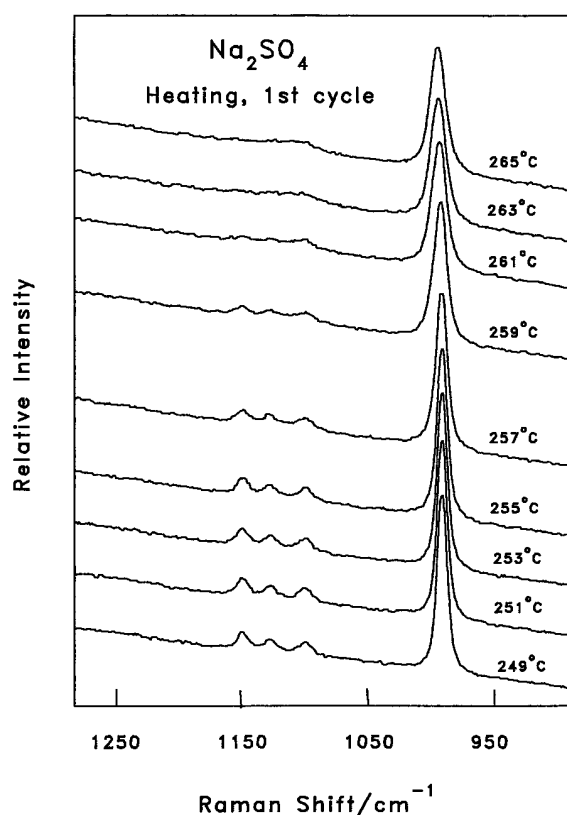


Figure 8. Thermo-Raman spectra of Na_2SO_4 from 249 to 265 °C (transformation from possible intermediate phase to phase I) in the ν_1 and ν_3 region of SO_4^{2-} during the heating process of the first thermal cycle.

The spectral variations in the ν_2 and ν_4 modes observed in the temperature interval from 150 to 240 °C during the heating process of the first cycle are presented in figure 7, which also shows the gradual modification involved in the ν_2 and ν_4 modes. The overlapped doublet nature of the ν_2 mode at 110 °C in phase V became a broad band at 230 °C. The distinct triplet nature of the ν_4 mode was gradually replaced by two distinct bands at 633 and 623 cm^{-1} , along with a shoulder at 646 cm^{-1} , at around 230 °C. The absence of significant spectral variations from 150 to 200 °C revealed that the skeleton structure might be the same as in phase V. The gradual and minor spectral variations observed in the temperature range of 180–225 °C did not rule out the possibility of a pre-transition prior to phase I. However, the minor changes observed in the ν_2 and ν_4 modes suggested that there might be some rearrangements of ions due to the rotation of SO_4^{2-} . From the observed spectral variations alone, it was difficult to decide on either the existence and nature of the intermediate phase or if it was a pre-transition prior to phase I.

The spectral variation observed in the next temperature interval from 249 to 265 °C during the heating process of the first cycle is shown in figure 8. The significant spectral variations observed during this temperature interval were the disappearance of the triplet nature of the ν_3 band and the appearance of a single broad band at around 265 °C. In the meantime, the ν_1 band broadened and shifted from 989 cm^{-1} at 249 °C to 993 cm^{-1} at 265 °C and the ν_4 mode at 640 cm^{-1} gradually broadened and became a singlet (ν_4 mode not shown).

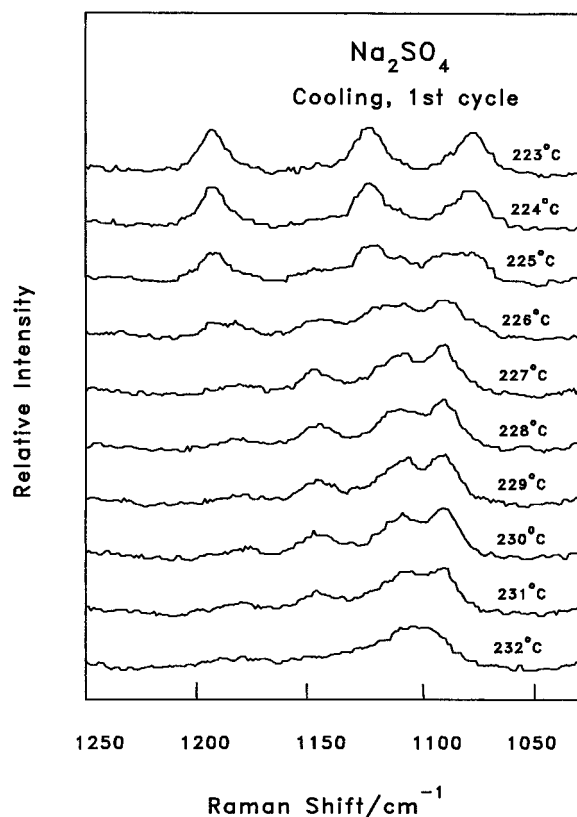


Figure 9. Thermo-Raman spectra of Na_2SO_4 from 232 to 223 °C (transformation from phase I to phase II then to phase III) in the ν_3 region of SO_4^{2-} during the cooling process of the first thermal cycle.

The disappearance of the distinct triplet nature of the ν_4 mode observed at around 225 °C (figure 7) indicated the transformation to an intermediate phase. The clear disappearance of the triplet nature of the ν_3 mode and the major change in the line width (full width at half maximum: FWHM) of the ν_1 mode, which only occurred in the temperature interval from 257 to 265 °C (figure 8), indicated the transformation from that intermediate phase to phase I. The complete spectrum of that intermediate phase is shown in figure 4(c). The observed Raman spectra of phase V and phase I are entirely different and indicated the involvement of a large displacement of cations and anions, along with the rotation of anions during the transformation from phase V to phase I. As compared to other phases, Raman spectra of phase I showed broadened bands due to orientational disorder of SO_4^{2-} . The exact temperatures for these transformations were difficult to ascertain from the observed spectral variations. However, they were estimated to be between 180 and 225 °C for the intermediate phase and between 257 and 265 °C for phase I. Between 225 and 257 °C, the spectra did not show any variation, hence this temperature range was considered as the existence width of the intermediate phase in this dynamical process.

In the high temperature region, a continuous shift in the band position of the ν_1 mode towards the lower wavenumber was observed during the heating process of the first cycle. The position of the ν_1 mode at 480 °C was measured as 989 cm^{-1} compared to its position of 994 cm^{-1} at 290 °C. In addition to that, all four internal modes also broadened continuously. Rasmussen *et al* claimed that phase I remains hexagonal up to the melting point [2]. However,

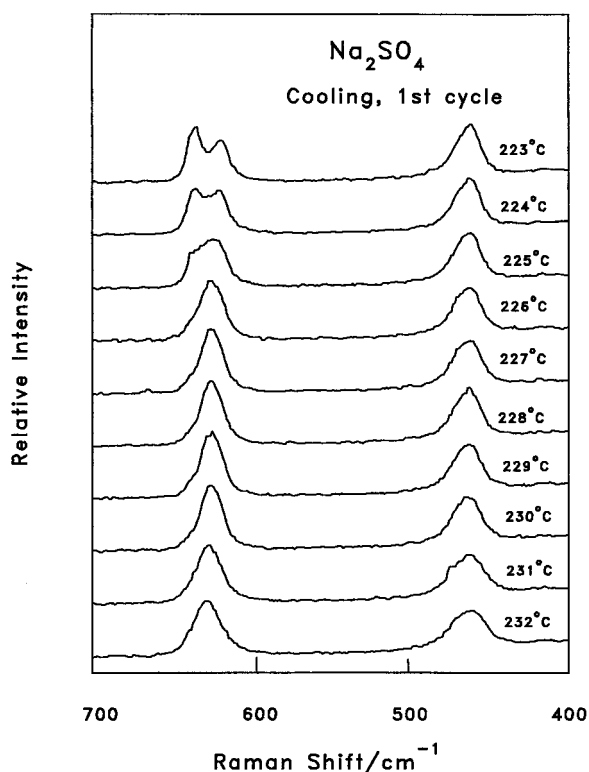


Figure 10. Thermo-Raman spectra of Na_2SO_4 from 232 to 223 °C (transformation from phase I to phase II then to phase III) in the ν_2 and ν_4 region of SO_4^{2-} during the cooling process of the first thermal cycle.

they observed an anisotropic thermal expansion along the a and c axes at high temperatures. This thermal expansion might be the reason for the continuous shift in the position of the ν_1 mode in the high temperature region. During the cooling process of the first cycle, the ν_1 mode continuously shifted its position to a higher wavenumber side, down to 370 °C.

Although several models have been proposed for the structure of high temperature phase I Na_2SO_4 , the arrangement of Na^+ and SO_4^{2-} is the same in all these models, except for the orientation of the SO_4^{2-} groups. According to Naruse *et al*, at high temperatures phase I attains the apex model orientation, where one of the apices of the SO_4^{2-} is pointing statistically up and down the c -axis [7]. However, at lower temperatures, the structure is closer to edge model orientation, which is composed of three superimposed split tetrahedra, each with one edge parallel and one perpendicular to the c -axis [33]. However, in the absence of single crystal polarized Raman dynamic data, it became difficult to judge the adaptability of either edge or apex model orientation.

The spectral variations observed in the ν_3 mode region from 232 to 223 °C during the cooling process of the first cycle are shown in figure 9. The spectrum measured at 232 °C was in phase I. The spectrum measured at 227 °C corresponded to the characteristic spectrum for phase II. The major spectral variation observed in that temperature region was that the band observed at 1101 cm^{-1} in phase I became a doublet at around 1088 cm^{-1} and 1107 cm^{-1} in phase II. In addition, two broad weak bands were also observed at 1147 and 1179 cm^{-1} . The emergence of the additional bands at 1147 and 1179 cm^{-1} and the splitting of the ν_3 modes

in that phase indicated not only the breaking of symmetry for the SO_4^{2-} , but also revealed the structure of phase II with lower symmetry. The observation of entirely new bands at 1147 and 1179 cm^{-1} in phase II compared to the bands in other phases of Na_2SO_4 indicated that the phase II structure is different from other phases and also dismisses the earlier suggestion that phase II is a mixed phase of phase I and phase III [34]. From the observed spectral variations, the phase I to phase II transformation was estimated to occur from 232 to 230 °C. The spectrum measured at 223 °C corresponded to phase III. It showed a clear ν_3 triplet appeared at 1077, 1124 and 1192 cm^{-1} . The significant spectral changes observed during the phase II to phase III transformation were that the doublet observed at around 1088 and 1107 cm^{-1} and the two weak bands observed at 1147 and 1179 cm^{-1} in phase II disappeared in phase III. The transformation was in the temperature range from 227 to 223 °C, within 5 °C. The temperature range of existence of phase II was very short, only within 3 °C (at about 229–227 °C). The spectral variations observed in the ν_2 and ν_4 modes in that temperature interval are presented in figure 10. The major spectral variation observed in the phase I to phase II transformation at 227 °C was that the line width of the ν_2 band was considerably reduced compared to the spectrum measured at 232 °C in phase I. However, the ν_2 and ν_4 modes did not exhibit significant variations in contrast to the marked variations observed in the ν_3 mode in that temperature interval. The phase II to phase III transformation was marked as a clear split in the ν_3 mode, as shown in the spectrum measured at 223 °C in figure 10.

Another interesting observation was found in the ν_3 mode of phase III. The ν_3 mode showed a clear triplet at around 1077, 1124 and 1192 cm^{-1} at 215 °C during the cooling process of the first cycle. On further cooling no major change in the positions of the ν_1 , ν_2 and ν_4 modes was observed. Surprisingly, appreciable and gradual changes in the positions of the two bands (1124 and 1192 cm^{-1}) of the ν_3 modes were observed on further cooling, but not for the third band at 1077 cm^{-1} . The positions of the bands at 1124 and 1192 cm^{-1} shifted to 1131 and 1200 cm^{-1} at 30 °C, respectively. During the heating process of the second cycle these two bands of the ν_3 mode changed their positions gradually towards lower wavenumbers and attained the values of 1124 and 1192 cm^{-1} at around 250 °C. The changes observed in the ν_3 mode during the cooling process of the second thermal cycle were very similar to the first cycle. Davies *et al* [35] previously reported that phase III is metastable and returns to stable phase V in the presence of moisture and also that phase III is very stable in a dry atmosphere. The observations made in the ν_3 mode of phase III during the thermal process in this work might be due to the involvement of some thermal expansion effect.

The spectral change observed in the ν_3 mode region of SO_4^{2-} during the heating process of the second cycle from 251 to 260 °C is presented in figure 11. The major changes observed were the rapid disappearance of the triplet nature of the ν_3 band and the appearance of a single broad band centred around 1100 cm^{-1} . This marked the phase III to phase I transformation and the transformation width was estimated to be from 253 to 260 °C. On the basis of x-ray diffraction and DTA results, Kobayashi *et al* proposed that the phase II to phase III transformation was due to the rotation of SO_4^{2-} in three equivalent directions with the change in lattice constants, but the phase III to phase I transformation was due to the rotation of SO_4^{2-} in one direction, with little change in the lattice constants [34]. They also mentioned that phase II should consist of the domain of phase III, but the observed spectral variation in this work excluded the mixed domain character of phase II.

Similar to the observation in the heating process of the first cycle, a continuous shift in the position of the ν_1 band towards lower wavenumbers and a broadening of all the modes were observed at higher temperatures, from 370 to 500 °C in the heating process of the second cycle. The spectral variations observed during the cooling process of the second cycle were very similar to those observed in the cooling process of the first cycle. The phase I to phase II

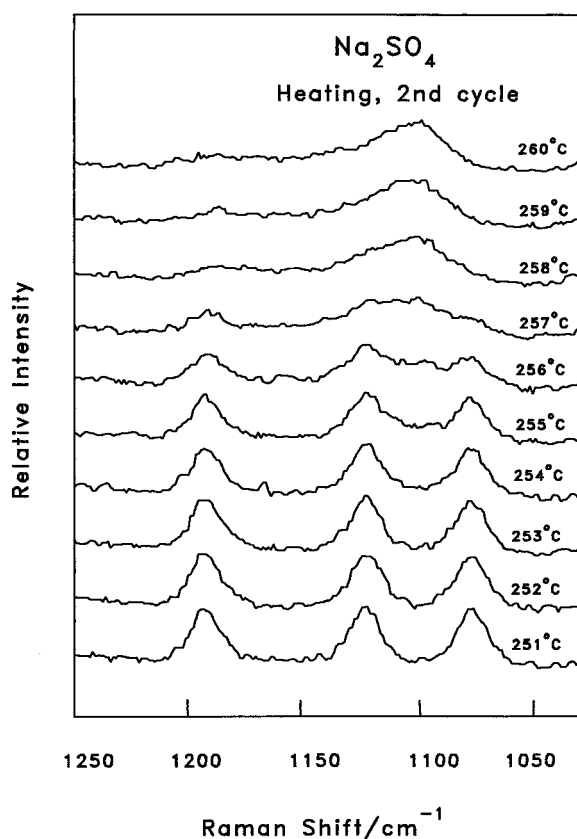


Figure 11. Thermo-Raman spectra of Na_2SO_4 from 251 to 260 °C (transformation from phase III to phase I) in the ν_3 region of SO_4^{2-} during the heating process of the second thermal cycle.

then phase II to phase III transformations were observed from 230 to 227 °C and from 226 to 217 °C, respectively.

3.2.3. Intensity. Raman spectra are not only useful to identify the phase, but also they can show the amount of each species through its band intensity. Hence, in addition to the observation of spectral variation, an investigation on the intensity (area) would be useful to investigate the thermal hysteresis exhibited during the heating and cooling process, in addition to the information on the phase transformations.

The intensity change of the ν_3 mode was appreciable during the phase transformations and it was used to demonstrate the thermal hysteresis in addition to the phase transformation, transformation temperature and the transformation width. The change in intensity of the ν_3 mode, observed during the first and second cycles for Na_2SO_4 , is shown in figure 12. During the heating process of the first cycle, the steps involved in the dehydration process were reflected in the temperature interval from 30 to 110 °C. After that, the intensity of this band did not show any major variation up to 200 °C. However, a slight rise in the intensity was observed from 200 to 231 °C. This upward deviation might be due to the transformation to the intermediate phase between phase V and phase I. A sudden drop in intensity was noticed from 250 to 265 °C. This indicated the phase transformation from the intermediate phase to phase I. On further heating,

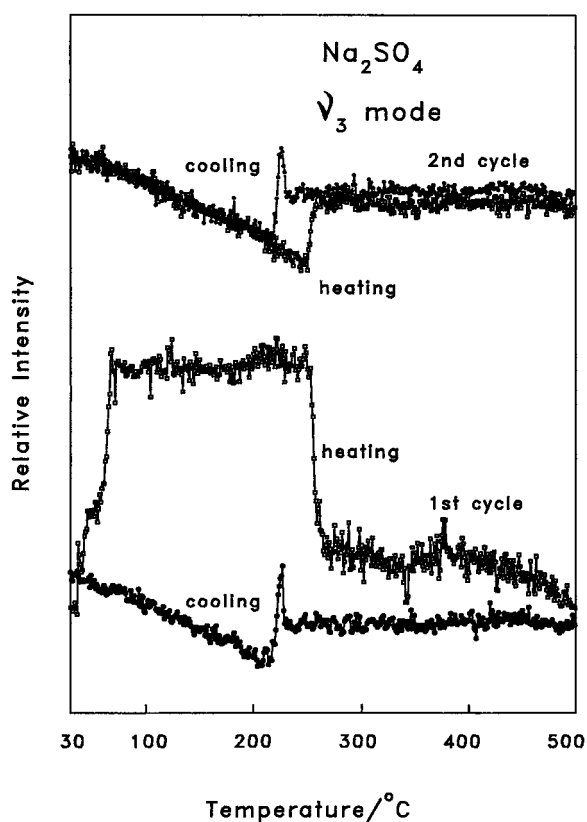


Figure 12. Temperature dependence of the intensity of the ν_3 mode of SO_4^{2-} of Na_2SO_4 in two consecutive thermal cycles.

a slight rise in intensity was observed at around 370 °C. This indicated that slight changes occurred in the phase I structure at higher temperatures.

During the cooling process of the first cycle, the ν_3 band showed a sharp increase in intensity from 229 to 227 °C. This reflected the phase I to phase II transformation and the transformation width was estimated to be from around 229 to 227 °C. After this rapid transformation, a sudden drop in intensity was observed from 226 to 217 °C. This corresponded to the phase II to phase III transformation. The range of existence of phase II was only 1 or 2 °C. After that, the intensity of this band gradually increased until 30 °C.

During the heating process of the second cycle, the intensity of this band showed a rapid increase from 253 to 260 °C. This represented the phase III to phase I transformation and also revealed the sharp transformation nature of phase III to phase I. After that, no appreciable variation was noticed until 500 °C. During the cooling process, a rapid increase in intensity was observed at 230 °C for the phase I to phase II transformation. The phase I to phase II transformation width was measured to be from 230 to 227 °C. A sudden drop in intensity was also observed from 226 to 219 °C for the phase II to phase III transformation, for which the transformation width was from 225 to 219 °C. A continuous increase in intensity was observed after the phase III transformation. The observation of a continuous decrease in the intensity during the heating process and a continuous increase in the cooling process for the ν_3 mode of phase III might be due to the gradual and continuous changes in intensities of the bands at

1124 and 1192 cm^{-1} of the ν_3 mode. The intensity change in the ν_3 mode, shown in figure 12, revealed not only the occurrence of phase transformation, transformation temperatures and transformation widths, but also clearly demonstrated the thermal hysteresis involved in the phase transformations of Na_2SO_4 in the first and second cycles.

3.2.4. FWHM. Figure 13 shows the temperature dependence of the line width (FWHM) of the ν_1 symmetric stretching mode of SO_4^{2-} in two consecutive thermal cycles. The line width was calculated in terms of pixel numbers. A change of one pixel was approximately equivalent to 1.15 cm^{-1} . Hence, the variation in line width in figure 13 is marked in steps of 1.15 cm^{-1} . During the heating process of the first cycle (figure 13(a)), the change in line width of this band in the temperature interval from 30 to 110 °C revealed the dehydration process involved in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Afterwards, a sharp change in the line width was observed at 255 °C, from 10 cm^{-1} at 254 °C to 15 cm^{-1} at around 258 °C. The large increase in the line width at 258 °C indicated the transformation to the disordered phase I. On further heating, the line width of this band broadened to about 16 cm^{-1} at 375 °C and attained a maximum of around 17 cm^{-1} at 500 °C, as shown in figure 13(a). During the cooling process, as shown figure 13(b), the line width of this band decreased gradually during the initial cooling period and showed slight drops at 368 °C and around 229–227 °C. This rapid and large reduction in the line width of this band from 16 cm^{-1} at 230 °C to around 10 cm^{-1} at 227 °C indicated the transformation from the disordered phase I to an ordered phase. During the second cycle, as shown in figures 13(c) and (d), a major change in the line width was observed, which was similar to that of the first cycle.

The relatively large change in the line width of the ν_1 mode during the transformation to and from phase I indicated the presence of orientational disorder of SO_4^{2-} in phase I due to disordered ion–ion interactions. The above results also revealed that there was a large difference in the local symmetry of SO_4^{2-} between phase V and phase I, and also between phase III and phase I. The continuous broadening of this band in the high temperature region might be due to anisotropic thermal expansion along the *a* and *c* axes.

3.2.5. Background variation. The background in Raman scattering experiments causes a real problem because the weak Raman bands may be masked by a strong background. However, recent thermo-Raman scattering studies have revealed that this annoying background might be useful in indicating the phase transformations and the composition changes in a dynamical thermal process [21–27]. The appearance of the background, as well as its behaviour and dependence during the dynamical thermal process, were discussed in earlier papers. The background might increase or decrease dramatically depending upon the character of the newly formed phase. The variation in the background, measured in the region around 1500 cm^{-1} during the heating and cooling process for Na_2SO_4 , is shown figure 14. Similar variations in the background were also noticed in the other regions of the spectra.

The background measured during the heating process of the first cycle (figure 14 (a)) from 30 to 110 °C revealed the nature of the dehydration process clearly. After the dehydration process, no major variation in the background was observed up to 150 °C, but afterwards it started to increase gradually to 180 °C, then the increase was rapid. A slight deviation in the increase was observed with a hump at 225 °C, then it increased further from 255 °C and attained a maximum at 265 °C followed by a decrease. In another run (figure 14 (b)), instead of a slight hump at 225 °C, a clear peak with a maximum at 222 °C was observed. The presence of the hump at 225 °C (figure 14(a)) and a clear peak at 222 °C (figure 14(b)) revealed the possibility of the existence of an intermediate phase between phase V and phase I. The transformation from

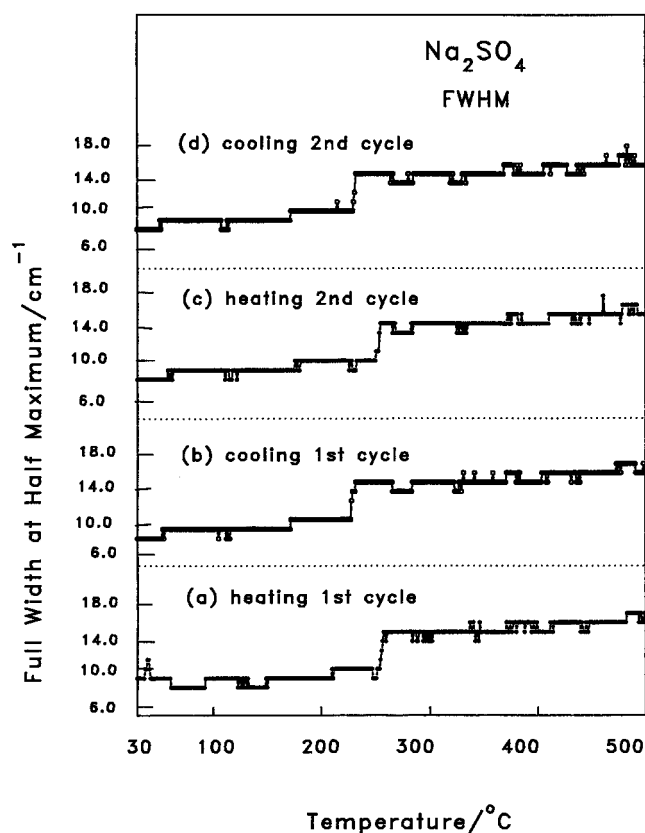


Figure 13. Temperature dependence of the line width of the ν_1 mode of SO_4^{2-} of Na_2SO_4 in two consecutive thermal cycles.

the intermediate phase to phase I was estimated to be from 255 to 265 °C. In this region, the background increased to a maximum, which represented the transformation to phase I. Again, the background decreased up to 344 °C then increased up to 385 °C and afterwards decreased continuously with further heating. The distinct dip at 344 °C in figure 14(a) and that at 348 °C in figure 14(b) revealed an unknown change in the phase I structure at that temperature. The bend at 385 °C revealed the transformation to the phase I structure at high temperature. To add more evidence to this behaviour, a continuous drop in the background from 500 to 460 °C and a sudden rise at around 459–443 °C during the cooling process (figure 14(c)) of the first cycle were observed. A second jump in the background was observed from 230 to 219 °C and this corresponded to the phase I to phase II and phase II to phase III transformations. The background was unable to distinguish these two transformations due to the very narrow transformation widths and close transformation temperatures.

During the heating process of the second cycle, the background decreased continuously up to 252 °C, but from 253 to 260 °C it showed a sudden drop (figure 14(d)) for the phase III to phase I transformation. Afterwards no major variation in the background was observed except a gradual decrease and a slight bend after 370 °C. During the cooling process, the phase I to phase II and phase II to phase III transformations were marked by a sudden increase in the background from 226 to 217 °C (figure 14(e)). Distinct dips at 344 and 348 °C, a clear bend at 385 °C in the background during the heating process, a continuous drop up to 460 °C, and a

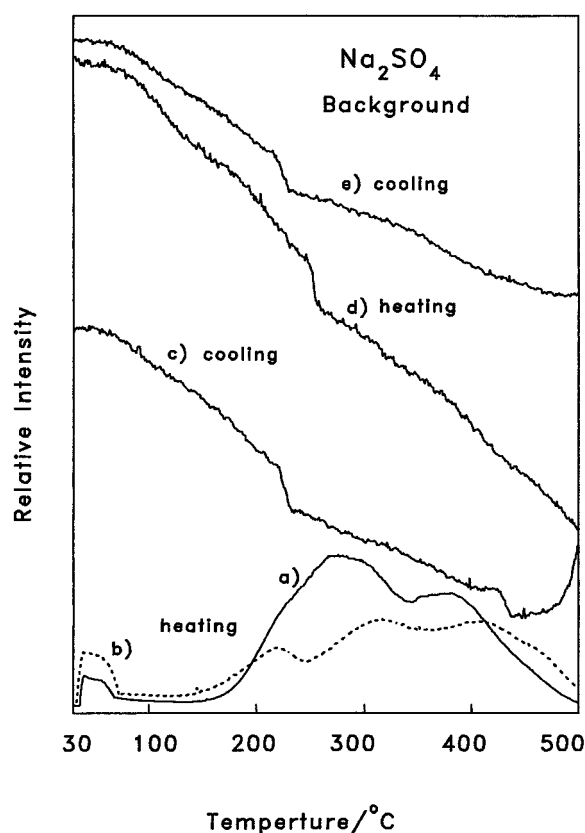


Figure 14. Temperature dependence of the background for Na_2SO_4 : (a) and (b) heating process of the first thermal cycle, (c) cooling process of the first cycle, (d) heating process of the second cycle, and (e) cooling process of the second cycle.

sudden rise at around 459–443 °C were observed during the cooling process in the first cycle for the phase I structure. However, no such clear observations were made in the background in the second cycle which indicated that there might be some slight difference between phase I formed in the first cycle and that in the second cycle. Choi *et al* also observed some differences in the phase I structures formed during the first and the second cycles on the basis of higher conductivity of phase I formed from the phase V structures than that of subsequent cycles [9]. The reason for this might be due to the difference in the orientation of SO_4^{2-} during the phase transformation from phase V to phase I (first cycle) and from phase III to phase I (second cycle). The existence of a small trace of water in Na_2SO_4 might not be the reason for the slight difference observed between the phase I structure formed in the first cycle and that in second cycle, since the background for the predried Na_2SO_4 sample observed in this work was similar to that of the Na_2SO_4 .

Another interesting observation was the similarity of the behaviour of the background with the conductivity results of Choi *et al* [9]. With a single crystal specimen, they observed a gradual increase in the conductivity of phase V until 226 °C, then a slight deviation and followed by a smooth up to 241 °C. On further heating, they observed a sudden drop in conductivity. They also reported that, instead of a shoulder at 226 °C in the temperature dependence of the electrical conductivity plot, sometimes they observed a clear peak at around that temperature.

With a polycrystalline sample, they observed that the corresponding variation at 226 °C was not well resolved and also the transformation widths were broader compared to the single crystal. Their observations were very similar to our observation of the background. During the cooling process of the first cycle, Choi *et al* observed a rapid drop in the conductivity value at 234 °C and another drop at around 229 °C in the single crystal specimen, corresponding to the phase I to phase II and phase II to phase III transformations [9]. In the present background study, the corresponding transformation was observed as a rapid increase in the background from 230 to 219 °C.

3.3. Comparison of DSC/DTA/TGA with TRS

The present thermo-Raman studies on Na₂SO₄ after the dehydration of Na₂SO₄·10H₂O predicted the gradual modification in the phase V structure from 150 to 225 °C, the transformation to the intermediate phase at around 180–225 °C and the transformation from the intermediate phase to phase I at around 255–265 °C. The above observations corresponded to the extremely weak signal from 195 to 225 °C and a broad endotherm observed at 262.4 °C in the DSC thermogram (figure 1(a)). The reason for the observation of a weak DSC endotherm at 246.6 °C and a weak DTA endotherm at 245.6 °C was not clearly visible from the present thermo-Raman studies. A broad and extremely weak DSC endotherm observed during the heating process in the temperature range from 375 to 500 °C (figures 1(a) and 2(a)) corresponded to the continuous broadening of the Raman bands of all the internal modes of SO₄²⁻ in that temperature interval. Similarly, the observation of a broad but weak DSC signal extending from 500 to 370 °C (figures 1(b) and 2(b)) during the cooling process also corresponded to changes observed in the phase I structure in the high temperature region. The phase I to phase II and phase II to phase III transformations in the cooling process of the first cycle were marked as two DSC exotherms at 232.9 and 227.6 °C, as shown in figure 1(b). The thermo-Raman spectra showed two successive phase transformations from phase I to phase II and then to phase III in the temperature ranges from 232 to 228 °C and from 227 to 223 °C, respectively.

During the heating process of the second thermal cycle, the thermo-Raman studies predicted the phase III to phase I transformation at around 253 °C, the corresponding transformation was marked as a sharp DSC endotherm at 249.8 °C as shown in figure 2(a). The thermo-Raman studies predicted the phase I to phase II and phase II to phase III transformations at around 230 and 226 °C during the cooling process of the second thermal cycle; the corresponding transformations were marked as two distinct exotherms at 232.9 and 227.6 °C as shown in figure 2(b). In all, the transformation temperatures observed in these thermo-Raman studies are in good agreement with the DSC measurements. In addition, these studies have identified the phases, the nature of the transformations and also the reason for the broad and extremely weak nature of the DSC signals.

3.4. Polymorphic difference in Na₂SO₄ (Na₂SO₄·10H₂O as starting material) and predried Na₂SO₄

The major difference observed in the DSC thermograms of Na₂SO₄ and predried Na₂SO₄ during the heating process of the first cycle (figures 1(a) and (c)) was the appearance of only two endotherms at 246.6 and 262.4 °C for Na₂SO₄ but three endotherms at 245.6, 252.9 and 260.3 °C for predried Na₂SO₄. The spectral variations observed in the temperature intervals from 165 to 240 °C and from 244 to 262 °C for predried Na₂SO₄ in the ν_2 and ν_4 modes of SO₄²⁻ are shown in figures 15 and 16, respectively, which revealed a two step transformation from phase V to phase I. The ν_2 mode measured at 165 °C showed a clear doublet at 466 and

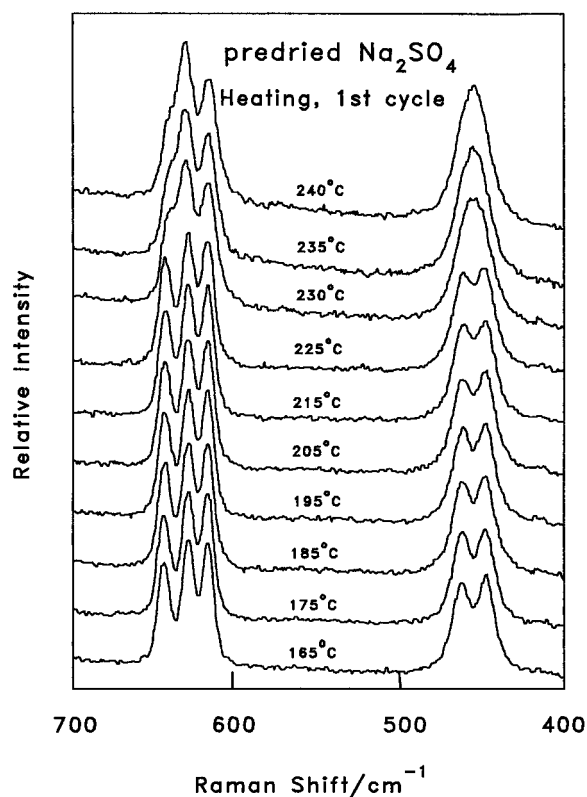


Figure 15. Thermo-Raman spectra of predried Na_2SO_4 from 165 to 240 °C (transformation from phase V to possible intermediate phase) in the ν_2 and ν_4 region of SO_4^{2-} during the heating process of the first thermal cycle.

453 cm^{-1} , as shown in figure 15, in contrast to the overlapped nature of this mode in Na_2SO_4 . The doublet nature of the ν_2 mode gradually disappeared and was replaced by a singlet from 225 to 235 °C. The 647 cm^{-1} band of the ν_4 mode gradually broadened and became a shoulder, along with the other two distinct bands at 633 and 623 cm^{-1} . The shoulder shifted further to 644 cm^{-1} and became weaker and finally vanished at around 246 °C (figure 16). On continuous heating, the ν_4 mode became a singlet and ν_2 broadened from 250 to 260 °C. The spectral variations observed in these temperature intervals for predried Na_2SO_4 (figures 15 and 16) were more distinctive compared to those of Na_2SO_4 (figures 7 and 8). The thermo-Raman spectra did not show any major changes corresponding to the weak DSC endotherms at 245.6 and 252.9 °C (figure 1(c)).

The DSC thermograms presented in figures 1 and 2 did not show any major changes in the behaviour of Na_2SO_4 and predried Na_2SO_4 after the heating process of the first cycle. In general, the DSC exotherms corresponding to the phase II to phase III transformation were relatively enhanced in the second cycle compared to the first cycle. The intensity of the ν_3 mode observed during the first and second thermal cycles for predried Na_2SO_4 is shown in figure 17. The thermal hysteresis involved in the phases of predried Na_2SO_4 was clearly revealed. However, the transformation from phase V to the intermediate phases could not be distinguished, but merged with the transformation from the intermediate phase to phase I to form a smooth curve.

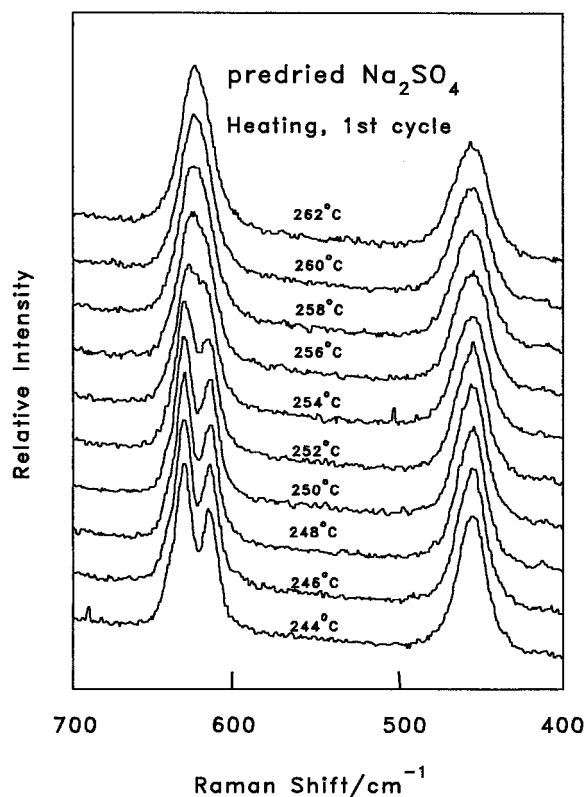


Figure 16. Thermo-Raman spectra of predried Na_2SO_4 from 244 to 262 °C (transformation from phase V to possible intermediate phase) in the ν_2 and ν_4 region of SO_4^{2-} during the heating process of the first thermal cycle.

4. Conclusion

In this work, detailed thermo-Raman studies were carried out on Na_2SO_4 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as starting material) and predried Na_2SO_4 for the phase transformations involved during a dynamical thermal process at a resolution of 1 °C. The characteristic Raman spectra for phase V, phase I, phase II and phase III were identified and the observed modes in each phase agreed well with the reported values [10–12]. In addition to the above well known phases, the characteristic spectra for an intermediate phase between phase V and phase I and the phase I at high temperature were also identified. The spectral variation, intensity and background studies revealed evidence for the existence of an intermediate phase. However, although the exact nature of the intermediate phase was not clearly revealed, the structure of the intermediate phase was thought to be very close to that of phase V. The spectral variations in the ν_2 and ν_4 modes of SO_4^{2-} in that temperature interval suggested that there might be some rearrangements of ions due to the rotation of SO_4^{2-} . After passing through the intermediate phase, Na_2SO_4 transforms to phase I and shows broadened Raman bands due to the orientational disorder of SO_4^{2-} . At higher temperatures, the observation of a continuous shift in the position of the ν_1 mode might be due to the anisotropic thermal expansion in the crystal structure of phase I.

Although the DSC thermograms signalled the possibility of multiple intermediate phases in the heating process, the present thermo-Raman studies did not give strong evidence for

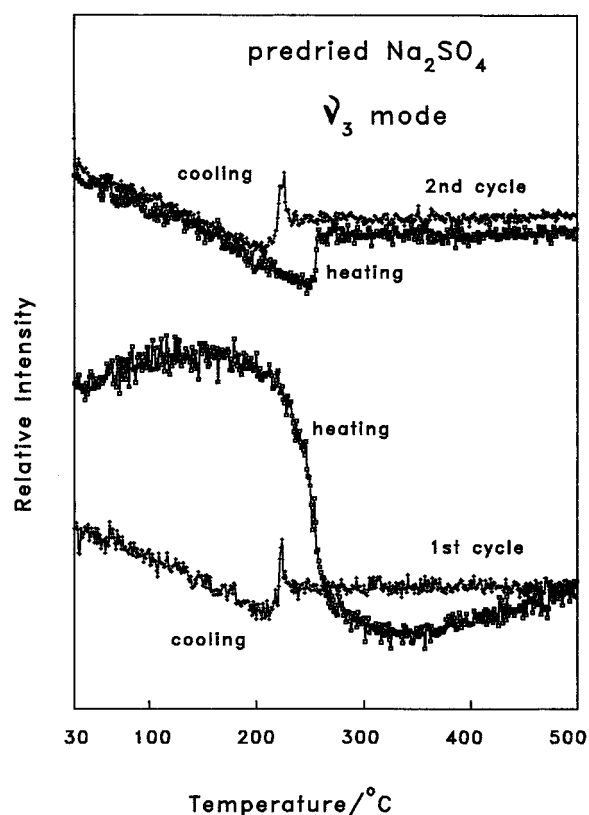


Figure 17. Temperature dependence of the intensity of the ν_3 mode of SO_4^{2-} of predried Na_2SO_4 in two consecutive thermal cycles.

the multiple intermediate phases, even in the case of predried Na_2SO_4 . The transformation temperatures of phase I to phase II then to phase III, given by these thermo-Raman studies, agree well with the DSC and the reported values [1, 10–12]. These two transformations occurred one after another within just a few degrees. The emergence of the additional bands at 1147 and 1179 cm^{-1} and the split in the ν_3 mode in phase II clearly revealed that the phase II structure was different from those of phase I and phase III and it was confirmed again by the sharp intensity changes observed in the ν_3 mode of SO_4^{2-} . The observation of appreciable changes in the positions of the bands at 1124 and 1192 cm^{-1} of the ν_3 mode in phase III with temperature indicated the involvement of some thermal effect. The rapid disappearance of the triplet nature of the ν_3 mode and the appearance of a single broad band centred at around 1100 cm^{-1} in the temperature interval from 253 to $260\text{ }^\circ\text{C}$ during the heating process of the second cycle indicated the sharp nature of the phase III to phase I transformation. The intensity studies on the ν_3 mode of SO_4^{2-} for both Na_2SO_4 and predried Na_2SO_4 clearly demonstrated the thermal hysteresis involved in the phase transformations during the first and second thermal cycles. The rapid and large change in the line width of the ν_1 band in phase I signalled the presence of the orientational disorder of SO_4^{2-} in that phase. The usual annoying background in Raman spectroscopy was used successfully in the present work to detect the occurrence of phase transformations and also the slight difference in the phase I structure formed during the first and second cycles.

In all, these thermo-Raman studies detected the occurrence of phase transformations, transformation temperatures, transformation widths and they also revealed the nature and sequence of the phase transformations involved both in Na₂SO₄ and predried Na₂SO₄ at a resolution of 1 °C. In addition, this provided some evidence for the existence of an intermediate phase between phase V and phase I, the difference in the phase I structure at high temperatures and the difference in the structure of phase I formed during the first cycle compared to that of the second cycle. The thermal hysteresis involved in the phases of Na₂SO₄ and predried Na₂SO₄ during the dynamical thermal process were clearly demonstrated.

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References

- [1] Cody C A, Dicarolo L and Darlington R K 1981 *J. Inorg. Nucl. Chem.* **43** 398
- [2] Rasmussen S E, Jorgensen J E and Lundtoft B 1996 *J. Appl. Cryst.* **29** 42
- [3] Rao K J and Rao C N R 1966 *J. Mater. Sci.* **1** 238
- [4] Murray R M and Seco E A 1978 *Can. J. Chem.* **56** 2616
- [5] Nord A G 1973 *Acta Chem. Scand.* **27** 814
- [6] Mehrotra B N 1981 *Z. Kristallogr.* **155** 159
- [7] Naruse H, Tanaka K, Morikawa H, Marumo F and Mehrotra B N 1987 *Acta Crystallogr. B* **43** 143
- [8] Kracek F C 1929 *J. Phys. C: Solid State Phys.* **33** 1281
- [9] Choi B K and Lockwood D J 1989 *Phys. Rev. B* **40** 4683
- [10] Choi B K and Lockwood D J 1989 *Solid State Commun.* **72** 133
- [11] Choi B K, Labbe H J and Lockwood D J 1990 *Solid State Commun.* **74** 109
- [12] Choi B K and Lockwood D J 1990 *Solid State Commun.* **76** 863
- [13] Saito Y, Kobayashi K and Maruyama T 1982 *Thermochim. Acta* **53** 289
- [14] Brodale G E and Giaque W F 1972 *J. Phys. C: Solid State Phys.* **76** 737
- [15] Murray R M and Secco E A 1978 *Can. J. Chem.* **56** 2616
- [16] Leblanc M D, Gundusharama U M and Secco E A 1986 *Solid State Ion.* **20** 61
- [17] Singhvi A, Gomathy S, Gopalan P and Kulkarni A R 1998 *J. Solid State Chem.* **138** 183
- [18] Gomathy S, Gopalan P and Kulkarni A R 1999 *J. Solid State Chem.* **146** 6
- [19] Montero S 1976 *Spectrochim. Acta A* **32** 843
- [20] Hapanowicz R P and Condrate R A 1996 *Spectrosc. Lett.* **29** 133
- [21] Chang H and Huang P J 1997 *Anal. Chem.* **69** 1485
- [22] Huang P J, Chang H, Yeh C T and Tsai C W 1997 *Thermochim. Acta* **297** 85
- [23] Chang H and Huang P J 1998 *J. Raman Spectrosc.* **29** 97
- [24] Chang H and Huang P J 1998 *J. Chin. Chem. Soc.* **45** 59
- [25] Chang H, Huang P J and Hou S C 1999 *Mater. Chem. Phys.* **58** 12
- [26] Murugan R, Huang P J, Ghule A and Chang H 1999 *Thermochim. Acta* at press
- [27] Murugan R, Ghule A and Chang H 1999 *J. Appl. Phys.* at press
- [28] Harju M E E 1993 *Appl. Spectrosc.* **47** 1926
- [29] Nakamoto K 1986 *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 4th edn (New York: Wiley)
- [30] Ananthanarayanan V 1963 *Indian J. Pure Appl. Phys.* **1** 58
- [31] Wu G J and Frech R 1977 *J. Chem. Phys.* **66** 1352
- [32] Pitzer K S and Coulter L V 1938 *J. Am. Chem. Soc.* **60** 1310
- [33] Eysel W, Hofer H H, Keester K L and Hahn T H 1985 *Acta Crystallogr. B* **41** 5
- [34] Kobayashi K and Saito Y 1982 *Thermochim. Acta* **53** 299
- [35] Davies J E D and Sandford W F 1975 *J. Chem. Soc. Dalton Trans.* **19** 1912