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Phase transition between two anhydrous modifications of $NaHSO_4$ mediated by heat and water

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Abstract

The phase transition between the two anhydrous modifications of $NaHSO_4$ (α and β) was studied using Raman spectroscopy and differential scanning calorimetry. These measurements indicate that β-$NaHSO_4$ is a metastable phase and readily undergoes phase transition to thermodynamically stable α-$NaHSO_4$ with an exothermic enthalpy change of 3.5 kJ/mol. Both thermal (temperatures >434 K) and chemical (exposure to H_2O) pathways were identified for this transition. The transition is irreversible, and α-$NaHSO_4$ is an intermediate phase between β-$NaHSO_4$ and $NaHSO_4 \cdot H_2O$. The possible mechanism of the phase transition is discussed.

Keywords: α-$NaHSO_4$; β-$NaHSO_4$; Phase transition; Raman spectroscopy; Differential scanning calorimetry

1. Introduction

Previous work from this laboratory has established the existence of a phase transition between two anhydrous modifications of $NaHSO_4$, β- and α-, on the surface of NaCl [1]. This previous report was the first observation of this phase transition and opens a new route for the preparation of pure β-$NaHSO_4$. Previous studies of anhydrous $NaHSO_4$ have shown that β-$NaHSO_4$ is difficult to isolate as the pure phase [2–4]. Thus, it has been speculated that β-$NaHSO_4$ may be metastable. Direct experimental evidence for the relationship between the α- and β-phases, and the stimuli required to initiate a phase transition between them, has yet to be determined. This study elucidates two such stimuli, heat and H_2O vapor, and defines the relationship between α-$NaHSO_4$, β-$NaHSO_4$, and $NaHSO_4 \cdot H_2O$.

$NaHSO_4$ is in a family of compounds with the general formula $MHBX4$ ($M =$ Na, K, Rb, Cs, N_2H_5, NH_4; $BX_4 = BeF_4$, SO_4, and SeO_4) [2–15]. Interest in this class of compounds has been driven by the known superionic proton conductivity of certain members, especially $CsHSO_4$ [3–8,10,12]. These compounds contain different two-dimensional hydrogen bonds that allow several crystallographic phases to exist, each having different physical properties. Metastable phases exist for nearly all such compounds, and these phases undergo transitions to more thermodynamically stable phases via multiple routes, mediated and/or catalyzed by H_2O exposure, temperature, and pressure [4–6,8].

α-$NaHSO_4$ is triclinic, space group $P\bar{1}$, with $a = 0.7005$, $b = 0.7125$, $c = 0.6712$ nm [13,14]. The crystal structure (Fig. 1b) contains two distinct HSO_4^- environments. Type A HSO_4^- are doubly hydrogen-bonded dimers that extend across the plane of symmetry. Type B HSO_4^- are singly hydrogen-bonded to Type A dimers. This combination results in a structure consisting of layered infinite HSO_4^- chains that run in the (110) direction in which each Na^+ is coordinated by six HSO_4^-.

In 1978, Sonneveld discovered a second modification of $NaHSO_4$ termed the β-phase [14]. β-$NaHSO_4$ is monoclinic, space group $P2/n$, with $a = 0.8759$, $b = 0.7500$, $c = 0.5147$ Å. The β phase (Fig. 1a) consists of doubly hydrogen-bonded dimers in which each Na^+ is coordinated by eight HSO_4^-. In this crystal structure, the chemical environment of each dimer is equivalent.

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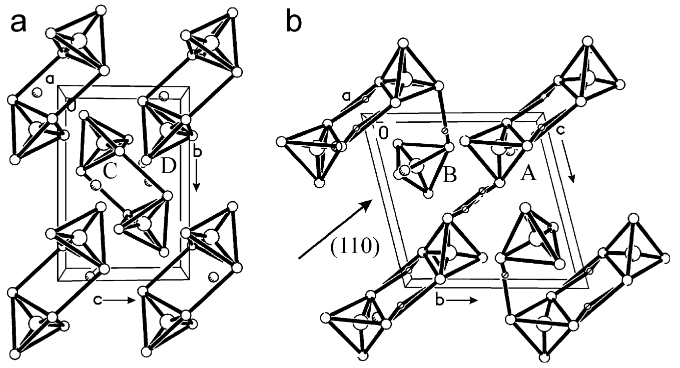

Fig. 1. (a) Crystallographic projection onto b–c plane of β-$NaHSO_4$; ○ = Na^+ ions, ◯ = S atoms, ◯═O atoms; C and D denote equivalent HSO_4^- dimers; (b) crystallographic projection onto b–c plane of α-$NaHSO_4$; ○ = Na^+ ions, ◯ = S atoms, ◯═O atoms.

Raman spectroscopy is used here to monitor the phase transition from β-$NaHSO_4$ to α-$NaHSO_4$ mediated by exposure to temperature and H_2O vapor. The thermodynamic relationship between the two phases is determined with differential scanning calorimetry. These results reported here represent the first such studies on this phase transition and the first Raman spectroscopy of distinct α- and β-phases of $NaHSO_4$ in bulk.

2. Experimental

2.1. Materials

NaCl (>99.999%) and $NaHSO_4 \cdot H_2O$ (99%) were obtained from Aldrich. NaCl was recrystallized prior to use and $NaHSO_4 \cdot H_2O$ was used as received. H_2SO_4 (96 wt%) was obtained from Aldrich and stored in a desiccator after opening. H_2O (18 MΩ, <10 ppb total organic carbon) was obtained from a Millipore-Q UV system.

α-$NaHSO_4$ was obtained through dehydration of $NaHSO_4 \cdot H_2O$ by heating at 420–440 K for 24 h. β-$NaHSO_4$ was prepared by one of two routes. One route followed the procedure published by Sonneveld and Visser [13] that involved heating a 1:1 mixture of H_2SO_4:Na_2SO_4 at 420 K for 24 h. This procedure resulted in a small yield of β-$NaHSO_4$, ~30%, and a large amount of unreacted Na_2SO_4. An alternate preparation developed in this laboratory [1] was therefore used; this approach involves reaction of a 1:1 mixture of H_2SO_4:NaCl at room temperature for 12 h. This procedure results in the complete transformation of all NaCl to β-$NaHSO_4$ [1].

2.2. Instrumentation

Raman spectroscopy was performed using 125 mW of Ar^+ laser (Coherent Innova 90-5) excitation at 514.5 nm. A bandpass filter (Barr Associates) was used to eliminate plasma lines from the beam. A Minolta f/1.2 camera lens was used to collect scattered radiation at 90° with respect to the incident radiation. A Spex 1877 Triplemate spectrometer was used with a 600 g/mm grating in the filter stage and a 1200 g/mm grating in the spectrograph stage. The entrance slit of the spectrograph was set at 0.5 mm, the filter stage slit was set at 7.0 mm, and the spectrograph stage slit was 75 μm for a spectral bandpass of 3 cm^{-1}. A Princeton Instruments RTE-1100-PB thinned, back-illuminated CCD camera of 1100 × 330 pixel format and cooled to ~200 K was used for detection. Spectra were calibrated using Ar^+ plasma lines. Samples were powders contained in 5-mm dia NMR tubes.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC 7 calorimeter with a heating rate of 10 K/min.

3. Results and discussion

The Raman spectrum in Fig. 2a is that of the product produced using the β-$NaHSO_4$ synthesis method of

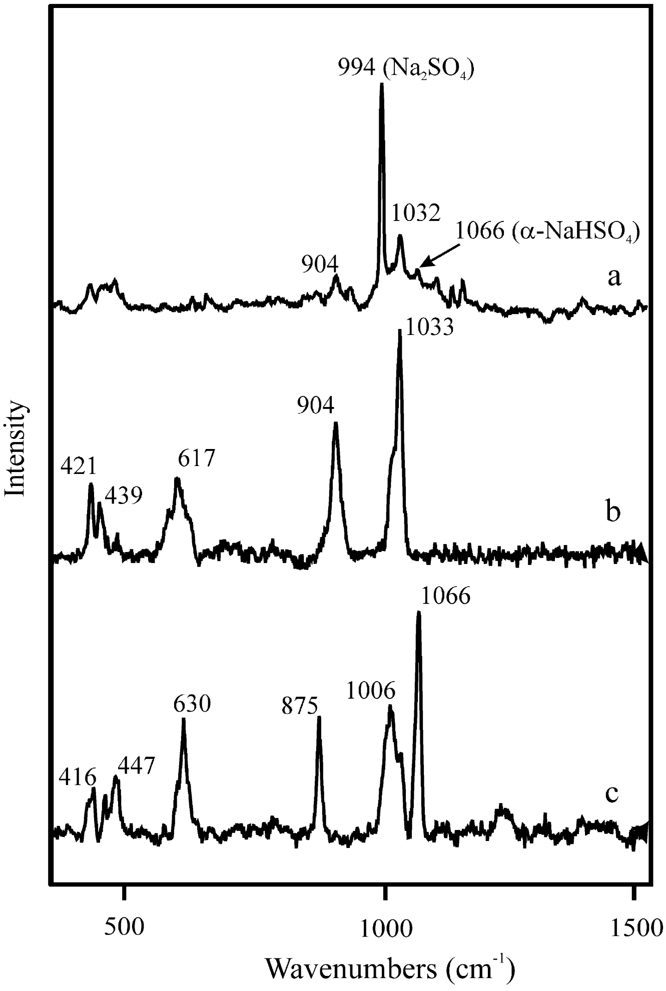

Fig. 2. Raman spectrum of (a) β-$NaHSO_4$ product from heating 1:1 H_2SO_4:Na_2SO_4 at 420 K for 24 h, (b) β-$NaHSO_4$ product from reacting 1:1 H_2SO_4:NaCl at room temperature for 12 h, (c) α-$NaHSO_4$ from heating sample in (b) to 434 K.

Sonneveld and Visser [13] involving the reaction of H_2SO_4 with Na_2SO_4. The most intense peak in this spectrum is the $\nu_s(SO_3)$ of unreacted Na_2SO_4 at 994 cm^{-1}, although low intensity ν_s(S–O–H) and $\nu_s(SO_3)$ peaks of β-$NaHSO_4$ are also observed at 904 and 1032 cm^{-1}, respectively [2,3,10,15–17]. A small peak attributed to the $\nu_s(SO_3)$ of α-$NaHSO_4$ is also observed in this spectrum at 1066 cm^{-1}. Clearly, these synthesis conditions do not result in complete conversion of Na_2SO_4 to β-$NaHSO_4$.

The Raman spectrum of the product resulting from the β-$NaHSO_4$ synthesis method developed in this laboratory is shown in Fig. 2b (peak frequencies and assignments in Table 1.) This spectrum is dominated by the single ν_s(S–O) of β-$NaHSO_4$ at 1033 cm^{-1} with the ν_s(S–O–H) mode observed at 904 cm^{-1}. All peaks in this spectrum are associated with β-$NaHSO_4$ indicating complete conversion of NaCl to β-$NaHSO_4$. The exclusive formation of β-$NaHSO_4$ in this new synthetic approach suggests a specific solid-state reaction pathway that may result from similarities in the crystal structures of NaCl and β-$NaHSO_4$. As in NaCl, the Na^+ in β-$NaHSO_4$ are confined to a single lattice plane (Fig. 1a), and a layer of HSO_4^- reside in a plane offset from the Na^+ plane. Such similarities may facilitate the formation of β-$NaHSO_4$ during anion place exchange. In contrast, the Na^+ in α-$NaHSO_4$ are offset from one another in the unit cell. Thus, a similar place exchange reaction of NaCl to α-$NaHSO_4$ would require substantial lattice rearrangement.

Sonneveld and Visser qualitatively compared the β- and α-$NaHSO_4$ crystal structures in terms of the relative positions of Na^+ in each [14]. In α-$NaHSO_4$, each Na^+ is coordinated by six HSO_4^- and is comparable to an offset NaCl-like structure. In contrast, in β-$NaHSO_4$, each Na^+ is coordinated by eight HSO_4^- with all Na^+ confined to a single plane as noted above. This comparison suggests that the similarity between the β-$NaHSO_4$ and NaCl crystal structures in terms of Na^+ position is a stronger influence on the formation of β-$NaHSO_4$ in this reaction than the degree of Na^+ coordination.

Table 1
Raman peak frequencies and assignments for anhydrous $NaHSO_4$ modifications

Peak frequency (cm^{-1})		
α-$NaHSO_4$	β-$NaHSO_4$	Assignment[a,b]
416	421	$\delta(SO_3)$
427		
447	439	$\delta(SO_3)$
469		
568	575	$\delta_s(SO_3)$
587	591	
605		$\delta_a(SO_3)$
630	617	
875	904	ν_s(S–O–H)
1006	1033	$\nu_s(SO_3)$
1066		
1250	NO[c]	$\nu_a(SO_3)$

[a] δ = bend; ν = stretch; s = symmetric; a = asymmetric.
[b] From Refs. [2,15–17].
[c] Not observed in these experiments.

3.1. Thermal induction of β-$NaHSO_4$ to α-$NaHSO_4$ phase transition

The effect of heating β-$NaHSO_4$ to 434 K in air results in the Raman spectrum shown in Fig. 2c characteristic of α-$NaHSO_4$ [17]. Heat treatment results in splitting of the $\nu_s(SO_3)$ into two modes at 1006 and 1066 cm^{-1} and the ν_s(S–O–H) mode shifts from 904 to 875 cm^{-1}. This spectrum can also be produced by dehydration of $NaHSO_4 \cdot H_2O$ at 413 K. The $\nu_s(SO_3)$ mode splitting in α-$NaHSO_4$ is the result of two HSO_4^- environments, and is similar to the splitting observed previously in $KHSO_4$ [16,17]. Similar splitting is also observed for the lower frequency bending modes of α-$NaHSO_4$.

The enthalpy change associated with the heat-mediated transition of β-$NaHSO_4$ to α-$NaHSO_4$ has been explored using differential scanning calorimetry. These results are shown in Fig. 3. For α-$NaHSO_4$ (Fig. 3a), a single endothermic event occurs at 453 K due to the melting of α-$NaHSO_4$. For the first heating cycle of $NaHSO_4 \cdot H_2O$ (Fig. 3b), dehydration of $NaHSO_4 \cdot H_2O$ to α-$NaHSO_4$, an endothermic process, occurs at 345 K with a ΔH of 14.5 kJ/mol. This followed by the melting of α-$NaHSO_4$ at 453 K. A second heating cycle of the resulting material (Fig. 3c) is identical to the first heating cycle for α-$NaHSO_4$ with a single endothermic event at 453 K due to melting. Reheating the same sample verifies that dehydration of $NaHSO_4 \cdot H_2O$ results in the formation of α-$NaHSO_4$.

The differential scanning calorimetry behavior for β-$NaHSO_4$ (Fig. 3d) is quite different from that of α-$NaHSO_4$ in that it exhibits a sharp, exothermic transition of $-3.5\,kJ\,mol^{-1}$ at 434 K; this process is assigned to the transformation of β-$NaHSO_4$ to α-$NaHSO_4$. This transition starts with an endothermic rise that is probably due to the onset of β-$NaHSO_4$ melting. This melting appears to trigger the phase transition to α-$NaHSO_4$ that must occur predominantly in the liquid state, since no melting transition for solid α-$NaHSO_4$ is evident in Fig. 3d. In addition, a small but variable magnitude endothermic peak is observed at 425 K that remains unassigned. This may represent release of trapped residual HCl formed in the reaction of H_2SO_4 with NaCl. A second heating cycle of this material (Fig. 3e) is identical to the first heating cycle for α-$NaHSO_4$.

Previous studies of heat-mediated phase transitions in this family of compounds have also resulted in values for phase transition enthalpies [2–10]. For example, endo- and exothermic transitions between anhydrous $CsHSO_4$ phases occur in a similar temperature regime (375–415 K) with typical transition enthalpies of -5.5–$1.1\,kJ\,mol^{-1}$. Thus, the $-3.5\,kJ\,mol^{-1}$ transition observed here for the β-$NaHSO_4$ to α-$NaHSO_4$ phase transition is similar to those measured in related systems.

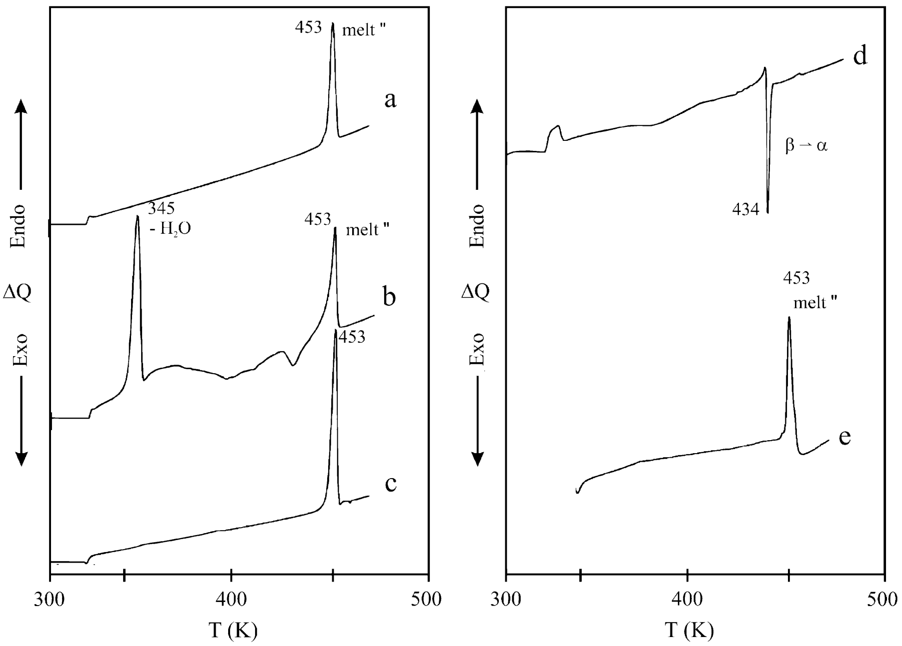

Fig. 3. Differential scanning calorimetry of (a) first heating cycle of α-$NaHSO_4$, (b) first heating cycle of $NaHSO_4 \cdot H_2O$, (c) second heating cycle of material from completion of (b), (d) first heating cycle of β-$NaHSO_4$, (e) second heating cycle of material from completion of (d).

3.2. H_2O induction of β-$NaHSO_4$ to α-$NaHSO_4$ phase transition

In addition to thermal induction of this phase transition, previous studies in this laboratory have demonstrated that it can also be induced by H_2O vapor [1]. The effect of exposing powdered β-$NaHSO_4$ to H_2O vapor was studied as a function of time using Raman spectroscopy (Figs. 4a–c). The spectrum of β-$NaHSO_4$ is shown in Fig. 4a. With exposure of this material to 24 Torr (100% RH) H_2O for increasing time, the three prominent bands of α-$NaHSO_4$ at 875, 1006, and 1066 cm^{-1} increase in intensity at the expense of the bands due to β-$NaHSO_4$. The β-$NaHSO_4$ modes disappear completely after 36 min of H_2O exposure at this partial pressure. The effect of exposing β-$NaHSO_4$ to a lower H_2O partial pressure was also studied and the same transformation to α-$NaHSO_4$ occurs but requires longer time for completion. For example, the Raman spectrum of β-$NaHSO_4$ after (Fig. 4e) exposure to <2.5 Torr ($<10\%$ RH) H_2O vapor for 240 h shows only partial transformation. Not surprisingly, the rate of the H_2O-induced phase transition is related to H_2O partial pressure.

3.3. Reversibility of β-$NaHSO_4$ to α-$NaHSO_4$ phase transition

Dehydration experiments at high and low temperature, and with H_2O exposure were conducted on $NaHSO_4 \cdot H_2O$, β-$NaHSO_4$, and α-$NaHSO_4$ to determine the reversibility of the β-$NaHSO_4$ to α-$NaHSO_4$ transition. No experimental conditions that allow direct β-$NaHSO_4$ formation from $NaHSO_4 \cdot H_2O$ or α-$NaHSO_4$ were found. Formation

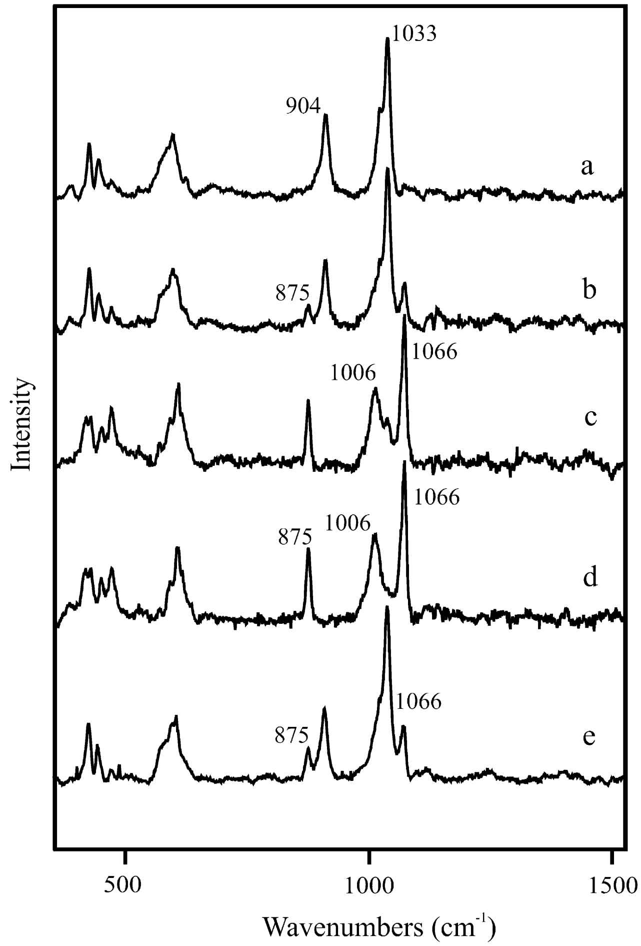

Fig. 4. Solid β-$NaHSO_4$ (a) in dry air, after exposure to 24 Torr (100% RH) H_2O for (b) 16, (c) 24, and (d) 36 min, and (e) after exposure to <2.5 Torr H_2O vapor for 240 h.

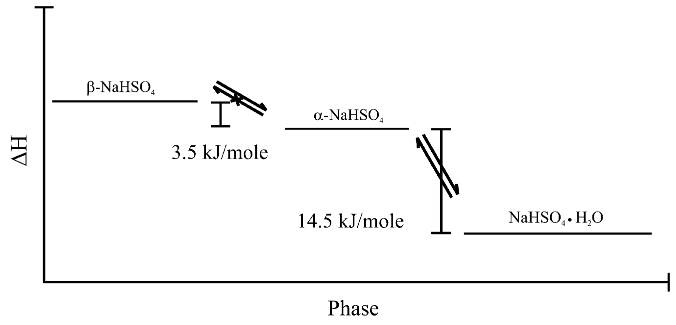

Fig. 5. Proposed thermodynamic relationship between β-$NaHSO_4$, α-$NaHSO_4$, and $NaHSO_4 \cdot H_2O$.

of α-$NaHSO_4$ both from complete dehydration of $NaHSO_4 \cdot H_2O$ and from exposure of β-$NaHSO_4$ to heat or H_2O vapor is possible. However, Raman spectra acquired before and after heating both α- and β-$NaHSO_4$ above their melting points indicate that α-$NaHSO_4$ is the sole product after cooling and solidification of these melts. Thus, it is concluded that the β-$NaHSO_4$ to α-$NaHSO_4$ transition is irreversible under these conditions.

Collectively, these results allow construction of an energy relationship between β-$NaHSO_4$, α-$NaHSO_4$, and $NaHSO_4 \cdot H_2O$ as shown in Fig. 5. H_2O is a catalyst in this system and reduces the activation barrier for the phase transition into a regime that is accessible at room temperature. α-$NaHSO_4$ is the thermodynamically stable anhydrous modification and is the intermediate phase between β-$NaHSO_4$ and $NaHSO_4 \cdot H_2O$. However, α-$NaHSO_4$ is spontaneously rehydrated to form $NaHSO_4 \cdot H_2O$.

3.4. *Proposed mechanism for β-$NaHSO_4$ to α-$NaHSO_4$ phase transition*

Insight into the mechanism of the β-$NaHSO_4$ to α-$NaHSO_4$ phase transition can be obtained by considering the crystal structures of these modifications and thermodynamic data obtained in this study. Crystallographic projections of the two $NaHSO_4$ modifications are shown with a view down their *a* axes in Fig. 1. The transformation of β-$NaHSO_4$ is proposed to occur through breaking of the hydrogen bonds of HSO_4^- groups C and D (Fig. 1a) in β-$NaHSO_4$, either thermally or by hydration of Na^+, to allow interior movement of either the C or D HSO_4^- with eventual formation of two new hydrogen bonds (dimeric HSO_4^- A in Fig. 1b) that result in the infinite chain-like structure of α-$NaHSO_4$. Formation of monomeric HSO_4^- B in Fig. 1b in α-$NaHSO_4$ would result from concomitant rotation of either the C HSO_4^- (if the D participates in forming the two hydrogen bonds of the infinite chain) or the D HSO_4^- (if the C participates in forming the two hydrogen bonds of the infinite chain) to form a single hydrogen bond with an infinite chain HSO_4^- of α-$NaHSO_4$.

Na^+ movement is significant between these two modifications, and is hypothesized to be initiated by HSO_4^- movement resulting from hydrogen bond breaking in β-$NaHSO_4$, leading to Na^+ translation into position to form α-$NaHSO_4$.

H_2O vapor may induce this transition through hydration of Na^+ on the β-$NaHSO_4$ surface. This would have the effect of shielding the Na^+ positive charge and decreasing the activation energy required for hydrogen bond breaking and rearrangement. Surface-bound H_2O may also hydrate the second layer of the β-$NaHSO_4$ lattice once hydrogen bonding in the top layer is disrupted. In this way, H_2O could catalyze the phase transition without significant uptake of bulk H_2O.

On the basis of the Raman spectroscopy and differential scanning calorimetry studies presented here, it is proposed that the β- to α-$NaHSO_4$ phase transition is irreversible. However, the small transition enthalpy ($-3.5\,\mathrm{kJ\,mol^{-1}}$) between β- and α-$NaHSO_4$ suggests that this irreversibility is dictated by thermodynamic considerations other than ΔH, such as ΔS for the transformation. Given the relatively small enthalpy for this transformation ($-3.5\,\mathrm{kJ\,mol^{-1}}$), one infers that ΔS must be sufficiently positive to make the process spontaneous. Based on the crystal structures of each phase, one can propose the change in entropy from β- to α-$NaHSO_4$ to be positive on the following basis. The infinite chain HSO_4^- structures of α-$NaHSO_4$ may be more thermodynamically stable than the dimer HSO_4^- structures in β-$NaHSO_4$. However, the addition of a singly hydrogen-bonded HSO_4^- into the α-$NaHSO_4$ structure is proposed to increase the entropy in this structure relative to the doubly hydrogen-bonded HSO_4^- dimers in β-$NaHSO_4$.

4. Conclusions

The phase transition of NaHSO4 from the β- to α-anhydrous modifications is induced by temperature and H_2O vapor exposure. This observation is similar to that for related compounds in this family and appears governed by the presence of hydrogen bonds in their structures. Differential scanning calorimetry results suggest that this phase transition may be dictated by changes in ΔS.

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