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Analysis of Phase Transition Pathways in $X_3H(SO_4)_2$ (X = Rb, NH_4, K, Na): Variable Temperature Single-Crystal X-ray Diffraction Studies[#]

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Evaluation of phase transitions in a series of hydrogen sulfates ($Rb_3H(SO_4)_2$, $(NH_4)_3H(SO_4)_2$, K_3 $H(SO_4)_2$, and $Na_3H(SO_4)_2$) based on the single-crystal structure analysis has revealed the exact nature of such transitions and has sorted out the various ambiguities involved in earlier literature. $Rb_3H(SO_4)_2$ at 293 K is *C*2/*c*. It is isostructural to its ammonium analogue, $(NH_4)_3H(SO_4)_2$, at room temperature. However, the variable temperature single-crystal diffraction studies indicate that the phase transition mechanism is different. When cooled to 100 K, the structure of $Rb_3H(SO_4)_2$ remains *C*2/*c*. When heated to 350 K, it transforms to *C*2/*m* (with double the volume at room temperature), which changes to *C*2/*c* (with 4 times the volume at room temperature) at 425 K. The high-temperature (420 K) structural phase transition in $(NH_4)_3H(SO_4)_2$ is shown to be $R\bar{3}m$. The structure of $Na_3H(SO_4)_2$ remains invariant ($P2_1/c$) throughout the range of 100–500 K except for the usual contraction of the unit cell at 100 K and expansion at 500 K. The structural phase transitions with temperature for the compound $K_3H(SO_4)_2$ are very different from those claimed in earlier literature. The hydrogen atom participating in the crucial hydrogen bond joining the two sulfate tetrahedra controls the structural phase transitions at low temperatures in all four compounds. The distortion of the SO_4 tetrahedra and the coordination around the metal atom sites control the phase evolution in the Rb compound, while the Na and K analogues show no phase transitions at high temperature, and the NH_4 system transforms to a higher symmetry space group resulting in a disorder of the sulfate moiety.

Introduction

The family of compounds $M_3H(XO_4)_2$, where M = NH_4^+, Na^+, K^+, Rb^+, Cs^+ and where X = S, Se, has been studied extensively. These systems exhibit phase transitions with temperature and pressure and possess ferroelectric and antiferroelectric properties. The number of studies over the years, in particular, relating to the phase transitions is large but misleading due to contradictory results. However, there is no detailed study on the structural phase transitions in these materials with temperature and more so their correlation with properties. Recently, triammonium hydrogen bisulfate, $(NH_4)_3H(SO_4)_2$, has received special attention because of the series of phase transitions exhibited with lowering of the temperature from 413 to 63 K and is found to depend on the strength and nature of the $O^-{-}H^+{\cdots}O^-$ hydrogen bonding.[1] The study further eliminated the nonexistent phase transitions through careful high-resolution X-ray diffraction results. The mechanism of phase transition has been characterized in terms of hydrogen bond strength coupled with rotation of sulfate ions. It is of interest to note that until this elaborate study was reported, the structure of the compound was assigned to contradicting space group symmetries to the various phases. Dielectric measurements on $(NH_4)_3H(SO_4)_2$ have shown the compound becomes ferroelectric on application of higher pressure[2,3] while the corresponding deuterated compound is ferroelectric even at 1 atm.[4,5] The structure at 413 K has been reported to belong to a rhombohedral system (space group $R\bar{3}$)

$Rb_3H(SO_4)_2$, on the other hand, has been shown to undergo successive phase transitions at 56 and 126 °C displaying discontinuous changes in the dielectric constant.[6] Further, it has been shown that down to the liquid nitrogen temperature

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[#] A part of the work reported here received the best poster prize at the IUCr meeting in Florence, Italy, in August 2005.

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Table 1. Crystallographic Data at Different Temperatures for $Rb_3H(SO_4)_2$

temperature (K)	293	100	350	450
chemical formula	$Rb_3H(SO_4)_2$	$Rb_3H(SO_4)_2$	$Rb_3H(SO_4)_2$	$Rb_3H(SO_4)_2$
formula weight (M_r)	449.5	449.5	449.5	449.5
a (Å)	15.1460(5)	15.0406(8)	20.1490(5)	20.4801(1)
b (Å)	5.8914(2)	5.8566(3)	11.7800(5)	11.8150(6)
c (Å)	10.1590(3)	10.0954(5)	8.1620(5)	16.3870(8)
β (deg)	102.540(6)	102.502(9)	112.838(5)	114.577(7)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$C2/m$	$C2/c$
volume (Å^3)	884.87(5)	868.19(2)	1785.42(4)	3606.00(1)
Z	4	4	8	16
density (g cm^{-3})	3.37	3.44	3.34	3.31
radiation type	X-ray Mo Kα	X-ray Mo Kα	X-ray Mo Kα	X-ray Mo Kα
crystal form, color	block, colorless	block, colorless	block, colorless	block, colorless
crystal size (mm)	0.12 × 0.12 × 0.05	0.12 × 0.12 × 0.05	0.12 × 0.12 × 0.05	0.12 × 0.12 × 0.05
diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector	Bruker SMART CCD area detector	Bruker SMART CCD area detector
data collection method	θ and φ scans	θ and φ scans	θ and φ scans	θ and φ scans
absorption correction	SADABS	SADABS	SADABS	SADABS
T_{min}, T_{max}	0.140, 0.427	0.145, 0.415	0.1500, 0.4250	0.155, 0.434
no. of measured reflections	3006	2989	9895	17400
no. of independent reflections	799	785	2202	3316
no. of observed reflections	738	724	1070	1179
criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.031	0.023	0.055	0.058
$\theta_{min,max}$	2.8, 25.4	2.8, 25.3	2.0, 28.3	2.0, 25.4
$h_{max,min}$	−18, 18	−18, 18	−26, 26	−24, 24
$k_{max,min}$	−7, 7	−7, 7	−15, 15	−14, 14
$l_{max,min}$	−12, 11	−12, 10	−10, 10	−19, 19
refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, w$R(F^2)$	0.027, 0.068	0.025, 0.069	0.082, 0.285	0.122, 0.438
GOF (S)	1.225	1.347	1.226	1.328
no. of reflections	799	785	2202	3316
no. of parameters	65	62	137	253
H-atom treatment	located and refined isotropically	located and refined isotropically	fixed from the geometry	fixed from the geometry
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1834P)^2 + 18.3702P]$, where $P = (F_o^2 + 2F_c^2)/3$			
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.730, −1.074	0.630, −0.628	1.673, −1.502	3.995, −1.096

(77 K) there is no discontinuity in the dielectric behavior,[6] and in fact even down to 4.2 K,[7] while the deuterated sample shows dielectric anomalies at 71 K. Several recent NMR studies[8−10] have indicated that there is no structural phase transition down to 4 K. However, the double-minimum potential which localizes the proton at room temperature transforms to a single minimum at 100 K with the H-atom localized at a crystallographic center of symmetry with the distance between O···O reaching a minimum (2.47 Å). The deuterated sample, on the other hand, shows a deuteron self-trapping[11] resulting in a double minimum potential all through the temperature range, and indeed at the $T_c = 82$ K, the space group is seen to transform from $A2/a$ to $A2$ resulting in a noncentrosymmetric space group signaling the origin of a paraelectric to antiferroelectric transition. The room-temperature crystal structure was reported[12] to contain Rb^+ ions occupying two sets of nonequivalent positions. Hence, the coordination around Rb atoms is different and the sulfate ion forms a distorted tetrahedra, since the hydrogen atom could not be located unambiguously, though diffuse electron density of 0.15 e Å^{-3} was found to be at (000), which corresponds to the hydrogen atom position in the ammonium analogue structure. Thus, it can be expected that the hydrogen atom at room temperature would be disordered and maybe it could get localized on cooling.

The room-temperature crystal structure of $Na_3H(SO_4)_2$ has been reported[13] to also possess a short O−H···O bond in a different space group $P2_1/c$. The hydrogen atom is localized at the crystallographic center of symmetry at room temperature. There are several reports on a possible high-temperature structural phase transition in this compound,[14,15] the transition temperature being in the range of 525 K. A possible phase transition has been suggested at 178 K, the space group going over to $P1$ (triclinic). The H-atom is still in a single minimum potential in this structure; however, the compound will be ferroelectric at this temperature owing to the space group being noncentrosymmetric.[16]

The hydrogen bond character of $K_3H(SO_4)_2$ was first analyzed to represent a split hydrogen atom feature in the space group ($A2/a$ or $C2/c$)[17] based on room-temperature X-ray diffraction data. With the examination of the domain structure and ferroelastic behavior in this compound, it was

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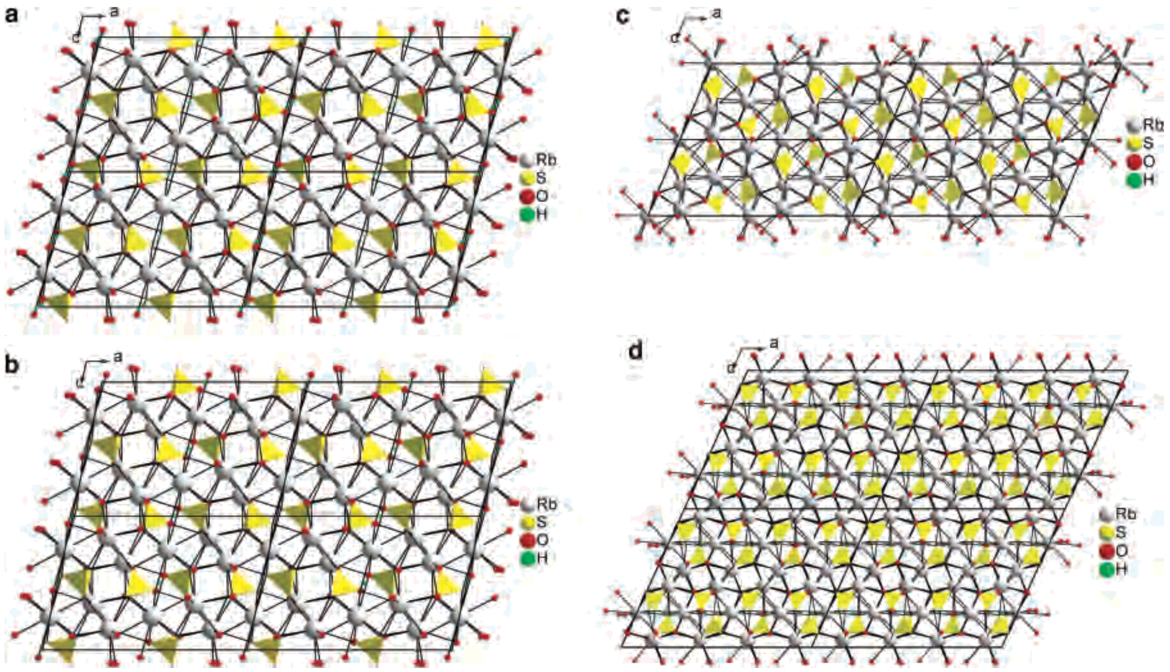

Figure 1. (a) Packing diagram of $Rb_3H(SO_4)_2$ at 293 K. (b) Packing diagram of $Rb_3H(SO_4)_2$ at 100 K. (c) Packing diagram of $Rb_3H(SO_4)_2$ at 350 K. (d) Packing diagram of $Rb_3H(SO_4)_2$ at 425 K.

Table 2. Crystallographic Data at Different Temperatures for $(NH_4)_3H(SO_4)_2$

temperature (K)	293	420
chemical formula	$(NH_4)_3H(SO_4)_2$	$(NH_4)_3H(SO_4)_2$
formula weight (M_r)	247.27	247.27
a (Å)	15.4387(2)	5.9061(4)
b (Å)	5.8627(7)	5.9061(4)
c (Å)	10.1603(1)	22.608(3)
β (deg)	101.818(2)	90.00
crystal system	monoclinic	hexagonal
space group	$C2/c$	$R\bar{3}m$
volume (Å^3)	900.14(18)	682.94(12)
Z	4	1
density (g cm^{-3})	1.825	1.804
radiation type	X-ray Mo Kα	X-ray Mo Kα
crystal form, color	block, colorless	block, colorless
crystal size (mm)	0.25 × 0.20 × 0.10	0.25 × 0.20 × 0.10
diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
data collection method	θ and φ scans	θ and φ scans
absorption correction	SADABS	SADABS
T_{min}, T_{max}	0.8608, 0.9130	0.8622, 0.9139
no. of measured reflections	4951	2360
no. of independent reflections	1094	224
no. of observed reflections	1029	208
criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.021	0.018
$\theta_{min,max}$	2.7, 28.6	2.7, 28.5
$h_{max,min}$	−20, 20	−7, 7
$k_{max,min}$	−7, 7	−7, 7
$l_{max,min}$	−13, 13	−29, 29
refinement on $R[F^2>2\sigma(F^2)]$, wR(F^2)	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, wR(F^2)	0.034, 0.103	0.058, 0.166
GOF (S)	1.206	1.202
no. of reflections	1094	224
no. of parameters	89	33
H-atom treatment	fixed from geometry	fixed from geometry
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1834P)^2 + 18.3702P]$, where $P = (F_o^2 + 2F_c^2)/3$	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.404, −0.363	0.452, −0.305

observed that the compound decomposes at about 445 K on heating without going through a structural phase transition.[18] However, superprotonic transitions were reported to occur at 463 and 500 K, and further, the compound was reported to melt at 543 K in an experiment[19] in which the author claims to have carefully annealed the samples at temperatures

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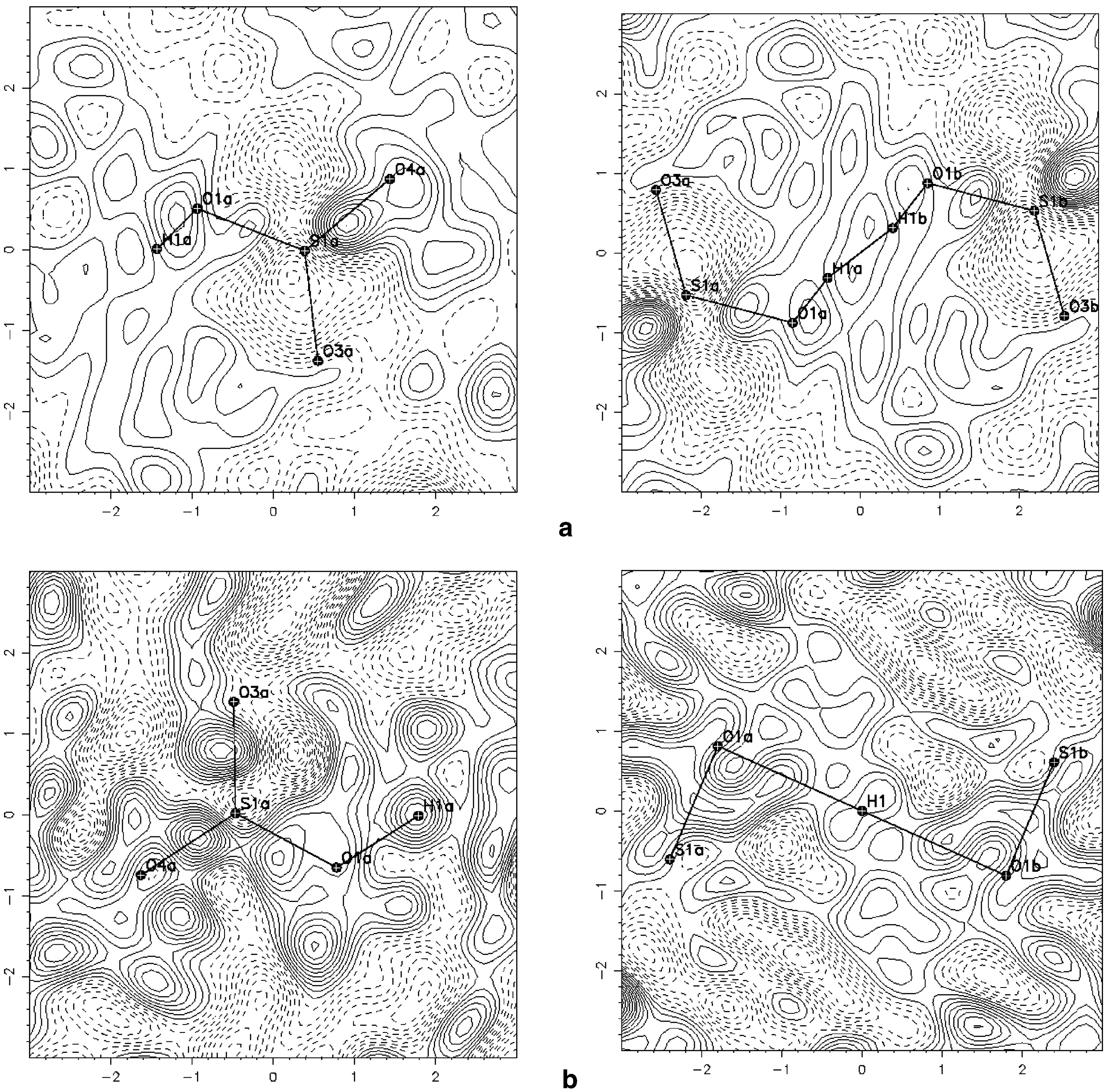

Figure 2. Difference Fourier maps of $Rb_3H(SO_4)_2$ at (a) 293 K and (b)100 K.

(528 K) below the melting point. The compound was subjected to careful optical observation followed by DSC/DTA experiments,[20] which suggest that even though there is no phase transition at high temperatures, the weight loss is primarily due to partial dehydration on the surface of the single crystals of $K_3H(SO_4)_2$. A recent study[21,22] on single crystals grown by the slow evaporation method shows the presence of a phase transition at a T_c of 480 K.

We have investigated the structural phase transitions systematically in $Rb_3H(SO_4)_2$ (100, 293, 350, and 425 K), $(NH_4)_3H(SO_4)_2$ (293 and 420 K), $K_3H(SO_4)_2$ (100 and 293 K, compound decomposes at high-temperature phase at 450 K), and $Na_3H(SO_4)_2$ (100, 293, and 500 K), respectively, with temperature to gain insights into the possible phase transition mechanisms and also to remove several contradictions found in the structure−properties of these compounds. It is imperative that in order to establish the nature of phase transitions, highly reliable data sets are of extreme importance, which appears to have been an enigma in earlier studies.

Experimental Section

Single crystals of all four compounds were grown by slow evaporation from solution containing equimolar quantities of the corresponding salt and H_2SO_4. Single-crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer, and it is to be noted that the data sets were obtained on the same crystal for each compound. An Oxford Cryostream attachment was used to generate variable temperatures. The X-ray generator was operated at 50 kV and 40 mA using Mo Kα radiation. For all

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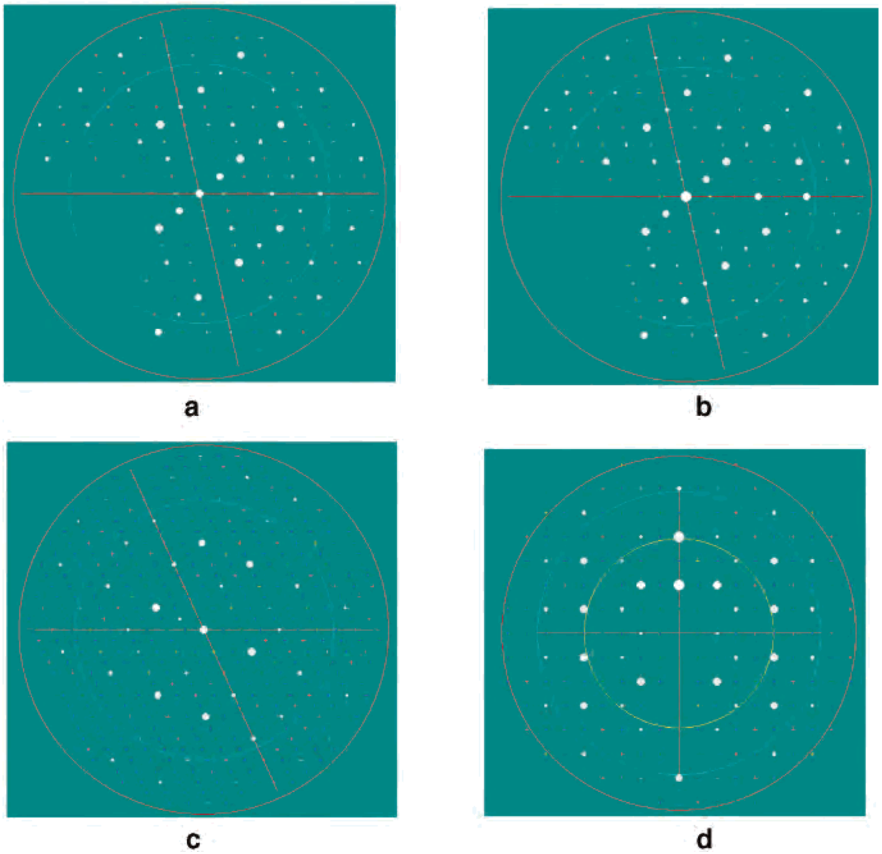

Figure 3. Reciprocal lattice images for $Rb_3H(SO_4)_2$ at (a) 293 K, (b) 100 K, (c) 350 K, and (d) 425 K.

the measurements, 606 frames per set were collected using SMART[23] with four different settings of φ (0°, 90°, 180°, and 270°), with the ω-scan at $-0.3°$ intervals, with a counting time of 15 s, with keeping the sample to detector distance at 6.062 cm, and with the 2θ value fixed at $-28°$. The data were reduced by SAINT-PLUS,[23] an empirical absorption correction was applied using the package SADABS,[24] and XPREP[23] was used to determine the space group. The structures were solved and refined using the SHELXL-97[25] program present in the WinGX[26] suite. The weighted R-factor wR and goodness of fit S are based on F^2, and conventional R-factors are based on F. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors and is not relevant to the choice of reflections for refinements. The hydrogen atom position for $Rb_3H(SO_4)_2$ was located at the center of symmetry with a maximum residual density of 0.14 e/Å^3 but well spread out in the region suggesting a high thermal parameter at 100 K. The hydrogen atoms are clearly located at two sites (0.5 occupancy each) for the data set at 293 K (maximum electron density at each site is 0.035 e/Å^3). Subsequent refinements included the hydrogen atoms as fixed at the positions located by the difference Fourier maps. For higher temperatures, the hydrogen atom positions could not be located. It is of interest to note that at all three temperatures of data collection on $Na_3H(SO_4)_2$ the H-atom could be located uniquely (0.63 e/Å^3 at 100 K; 0.62 e/Å^3 at 293 K; 0.96 e/Å^3 at 500 K). The refinements suggest that the location of the H-atom in all cases is correct and the corresponding thermal parameter are reasonable.

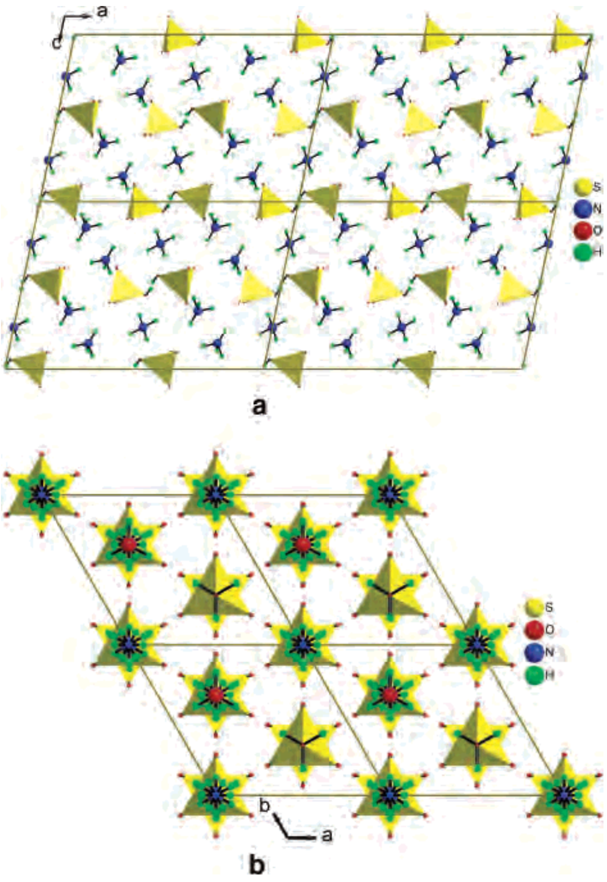

Figure 4. Packing diagram of the $(NH_4)_3H(SO_4)_2$ at (a) 293 K and (b) 420 K.

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Table 3. Crystallographic Data at Different Temperatures for $K_3H(SO_4)_2$

temperature (K)	293	100
chemical formula	$K_3H(SO_4)_2$.	$K_3H(SO_4)_2$
formula weight (M_r)	310.45	310.45
a (Å)	14.7033(16)	14.5676(17)
b (Å)	5.6841(6)	5.6506(7)
c (Å)	9.7756(11)	9.7094(11)
β (deg)	102.981(2)	103.011(2)
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2/c$
volume (Å^3)	796.12(15)	778.72(16)
Z	4	4
density (g cm^{-3})	2.590	2.648
radiation type	X-ray Mo Kα	X-ray Mo Kα
crystal form, color	block, colorless	block, colorless
crystal size (mm)	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20
diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
data collection method	θ and φ scans	θ and φ scans
absorption correction	SADABS	SADABS
T_{min}, T_{max}	0.5890, 0.6380	0.7661, 0.8346
no. of measured reflections	4320	4141
no. independent reflections	965	940
no. observed reflections	921	911
criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.020	0.023
$\theta_{min,max}$	2.8, 28.6	2.9, 28.7
$h_{max,min}$	−19, 18	−18, 19
$k_{max,min}$	−7, 7	−7, 7
$l_{max,min}$	−12, 13	−12, 12
refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, wR(F^2)	0.025, 0.063	0.025, 0.064
GOF (S)	1.212	1.184
no. of reflections	965	940
no. of parameters	62	62
H-atom treatment	located and refined isotropically	located and refined isotropically
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1834P)^2 + 18.3702P]$, where, $P = (F_o^2 + 2F_c^2)/3$	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.335, −0.395	0.495, −0.498

Results

Structure of $Rb_3H(SO_4)_2$. $Rb_3H(SO_4)_2$ has been studied mainly for the interesting phase transitions even though the exact mechanism of transition has not been understood. Ever since the work of Ichikawa,[27] many attempts have been made to unravel this feature leading to contradicting indicators.[28] The X-ray diffraction data have been collected using the same single crystal at four different temperatures, 293, 100, 350, and 425 K, and the packing at each temperature is given in parts a−d of Figure 1, respectively. The crystal structure remains monoclinic, and the unit cell doubles at 350 K with a change in the space group from $C2/c$ to $C2/m$ (Table 1). The space group reverts to $C2/c$ with further doubling of the unit cell at 425 K suggesting possibilities of a pseudo rhombohedral/hexagonal superlattice.

Structure at 293 K. The structure is similar to the corresponding ammonium analogue, and the observations made in the earlier work[12] hold true. However, it is of interest to note that the hydrogen atom position is identified to be disordered and localized with respect to the respective oxygen atoms. This feature has also been observed in a recent study of the ammonium analogue.[1] The difference electron density map (Figure 2a) in the region clearly shows that the hydrogen atom is split in two positions around the center of symmetry. In the subsequent refinements, the hydrogen atom positions are held fixed at the positions suggested by the difference Fourier map with occupancy fixed at 0.5 for each hydrogen position. Thus, it is very clear that the hydrogen-bonding feature is similar to that of the ammonium analogue.[1] The Rb^+ ions occupy two sets of nonequivalent positions; Rb1 is showing 10 oxygen atom coordinations, whereas Rb2 is showing 9 oxygen atom coordinations. The sulfate tetrahedra are distorted with one of the bond lengths significantly larger than the other three. The bond valence sum (BVS) analysis indicates partial charge transfer on the Rb atoms with the individual values on each Rb atom (Supporting Information Table S2(a)) suggesting the differences in the coordination sphere.

Structure at 100 K. The difference Fourier map suggests strongly the position of the hydrogen atom to be located at the center of symmetry (Figure 2b). The subtle difference does not influence any phase change but appears to stabilize the $O^-{-}H^+\cdots O^-$ hydrogen bonding. There are no other significant changes in the Rb coordination and also in the sulfate tetrahedra. It is noteworthy that the hydrogen atom in the special position displays large anisotropy, even though the residual electron density map shows a highly symmetric distribution. This feature allows for the inference that there is a disorder associated with the hydrogen atom when cooled to 100 K.

Structure at 350 K. Since the structure does not display any phase transitions at low temperature unlike the ammonium analogue, we have investigated the possible phase transition at elevated temperatures. It has been shown by DTA analysis in literature[27] that $Rb_3H(SO_4)_2$ shows two phase transitions at 56 and 126 °C, respectively. Even though

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(27) Ichikawa, M. *J. Phys. Soc. Japan.* **1978**, *45* (1), 355−356.

(28) Gesi, K. *J. Phys. Soc. Jpn.* **1980**, *48* (3), 886−889.

Table 4. Crystallographic Data at Different Temperatures for $Na_3H(SO_4)_2$

temperature (K)	293	100	500
chemical formula	$Na_3H(SO_4)_2$.	$Na_3H(SO_4)_2$	$Na_3H(SO_4)_2$
formula weight (M_r)	262.1	262.1	262.1
a (Å)	8.6436(14)	8.6362(8)	8.6670(17)
b (Å)	9.6408(15)	9.6156(9)	9.6680(19)
c (Å)	9.1386(14)	9.0702(8)	9.2333(19)
β (deg)	108.792(2)	108.746(10)	108.763(3)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
volume (Å^3)	720.9(2)	713.25(11)	732.6(3)
Z	4	4	4
density (g cm^{-3})	2.415	2.441	2.376
radiation type	X-ray Mo Kα	X-ray Mo Kα	X-ray Mo Kα
crystal form, color	block, colorless	block, colorless	block, colorless
crystal size (mm)	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20
diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector	Bruker SMART CCD area detector
data collection method	θ and φ scans	θ and φ scans	θ and φ scans
absorption correction	SADABS	SADABS	SADABS
T_{min}, T_{max}	0.7682, 0.8361	0.7661, 0.8346	0.7712, 0.8384
no. of measured reflections	5309	7050	6965
no. independent reflections	1495	1475	1541
no. observed reflections	1436	1446	1439
criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.024	0.024	0.018
$\theta_{min,max}$	2.5, 27.2	2.5, 27.2	2.5, 27.3
$h_{max,min}$	−11, 11	−10, 10	−10, 10
$k_{max,min}$	−11, 12	−11, 12	−11, 12
$l_{max,min}$	−10, 11	−11, 11	−11, 11
refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, wR(F^2)	0.024, 0.073	0.022, 0.066	0.027, 0.084
GOF (S)	1.176	1.157	1.078
no. of reflections	1495	1475	1541
no. of parameters	126	126	126
H-atom treatment	located and refined isotropically	located and refined isotropically	located and refined isotropically
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1834P)^2 + 18.3702P]$, where $P = (F_o^2 + 2F_c^2)/3$		
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.368, −0.557	0.458, −0.597	0.351, −0.356

the 00l reflections do not appear, there are several highly significant 0*kl*, where l = odd reflections present, giving unequivocal proof for the space group to be $C2/m$. Further, the Rb atoms occupy different site symmetry and hence show different coordination. The hydrogen atom could not be located at a higher temperature; however, it is possible geometrically to identify and fix the hydrogen position on the oxygen, which shows a significant lengthening of the S−O bond. The structural phase transition coincides with the observed dielectric discontinuity shown earlier[27] at 56 °C.

Structure at 425 K. On further heating based on this observation that the dielectric constant displays a small hump at 126 °C,[27] the structure reverts to the space group $C2/c$, but as can be seen from parts a−d of Figure 3, the superlattice reflections are also observed. Indeed we observe a 4-fold increase in the volume of the unit cell. The structure has been solved in this space group $C2/c$ and refined to an R-factor of 12.21%. The rather high R-factor is expected at such high temperatures because of two features: (1) the significant expansion of the unit cell and the other due to the large thermal vibration associated particularly with lighter atoms and (2) the number of $Rb_3H(SO_4)_2$ units is two per asymmetric unit and hence the coordination around Rb shows a different environment.

Structure of $(NH_4)_3H(SO_4)_2$: (293 and 420 K). Parts a and b of Figure 4 show the packing features of $(NH_4)_3H(SO_4)_2$ at 293 and 420 K, respectively. The mechanism of phase transitions in triammonium hydrogen disulfate has been analyzed in detail at low temperatures.[1] However, there is one report of the crystal structure at 430 K suggesting a trigonal space group $R\bar{3}$.[29] It is observed that at this temperature there is a ferroelastic to superionic conductor phase transition.[30] On the basis of the observations made on the selenate analogue, the choice of the space group has been made. The transition from the ferroelastic to superionic conduction phase is attributed to the shift and rotation of the SO_4 tetrahedra followed by a shift in the position of the nitrogen atom. Two data sets, one at 293 K to authenticate the existence of triammonium hydrogen disulfate and the other at 420 K to evaluate the structural phase transition, have been collected. Parts a and b Figure 5 and Table 2 show the remarkable changes that appear in the reciprocal lattice as the temperature reaches 420 K. The structure refines in both $R\bar{3}m$ and $R\bar{3}$; however, the statistics favor the centric space group.

Structure of $K_3H(SO_4)_2$: (100 and 293 K). The structure of compound $K_3H(SO_4)_2$ has been solved in the monoclinic space group $C2/c$ (a = 14.7033(2) Å, b = 5.6841(6) Å, c = 9.7756(1) Å, β = 102.981(2) Å) at 293 K and $C2/c$ (a = 14.5676(2) Å, b = 5.6506(7) Å, c = 9.7094(1) Å, β = 103.011(2) Å) at 100 K (Table 3). The structure shows ferroelasticity like the other members of the group at room

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(29) Fukami, T.; Horiuchi, K.; Nakasone, K.; Furukawa, K. *J. Appl. Phys.* **1996**, *35*, 2253−2254.

(30) Fujimoto, M.; Sinha, B. V. *Ferroelectrics* **1983**, *46*, 227.

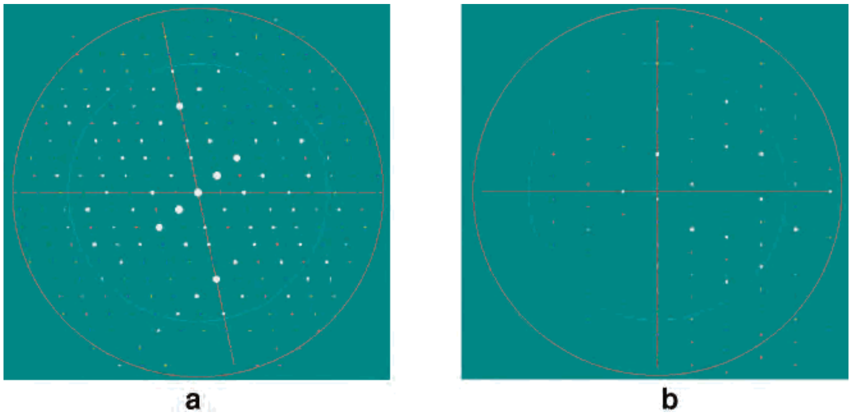

Figure 5. Reciprocal lattice image for $(NH_4)_3H(SO_4)_2$ at (a) 293 K and (b) 420 K.

temperature. Unlike $Rb_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$, the structure does not show any disorder in hydrogen position over the temperature range of 293−100 K though they are isostructural in nature (Figure 6). This effect may be due to the different sizes of the cation atoms. The hydrogen bond length between the two nearest SO_4 groups is 2.515(2) Å at 293 K and is 2.487(2) Å at 80 K. The difference Fourier diagrams show no significant change at both temperatures (parts a and b of Figure 7), and the hydrogen atom is located at the center of symmetry. The structure contains two crystallographically independent K atoms with coordination number of 10 and 9 and with a hydrogen atom at the center of symmetry. Further, in the current study it is observed that the crystal loses its crystallinity around 470 K and subsequently melts at 490 K and does not show any phase transition before decomposition and melting.

Structure of $Na_3H(SO_4)_2$: (100, 293, and 500 K). Three data sets at 100, 293, and 500 K (Table 4) were obtained on the same crystal, and the crystal structure remains invariant with a space group of $P2_1/c$. There are no significant differences in the X-ray diffraction patterns (Figure 8) at these temperatures except that there is an expected contraction of the unit cell parameters at 100 K compared to that at room temperature and an expected expansion of the unit cell at 500 K. The difference Fourier map clearly indicates the position of the hydrogen atom (parts a−c of Figure 9), and it is noteworthy that it does not coincide with the center of symmetry as in the Rb analogue. Further, the thermal features on refinement do not show any significant disorder. The O−H···O hydrogen bonding is normal (O···O = 2.430(2) Å, O−H = 1.136(3) Å, H···O = 1.249(3) Å; 100 K). There are no other significant changes in the Na coordination or in the sulfate tetrahedra.

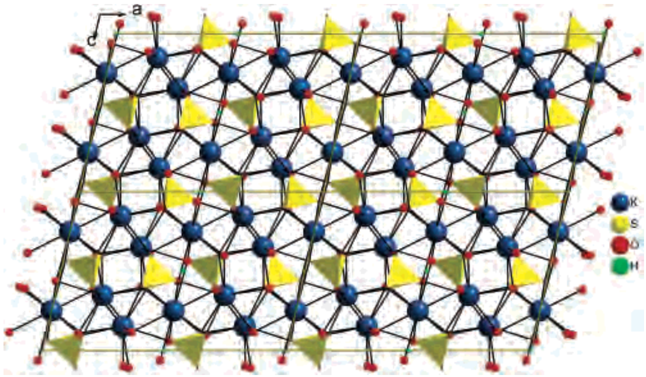

Figure 6. Representative packing diagram of $K_3H(SO_4)_2$ at 100 K.

Discussion

Unlike the ammonium analogue, the $Rb_3H(SO_4)_2$ shows phase transitions which are explained based on variation in coordination around the Rb atom, distortion in the sulfate tetrahedra rather than exclusive dependence on hydrogen bonding. It is noteworthy that at room temperature the hydrogen bonding is similar to that of the ammonium analogue. The hydrogen atom in $O^-{-}H^+{\cdots}O^-$ is disordered in two positions (Figure 2a) joining two sulfate tetrahedra, and with lowering of the temperature to 100 K, the split hydrogen positions become localized to one position occupying the center of symmetry between two sulfate ions. This observation is substantiated by recent inelastic neutron scattering experiments,[31] which allow one to trace the dynamics of the movement of proton transfer from the double-minimum low barrier potential at room temperature to the well-defined minimum at 100 K. Infrared and Raman spectra provide further evidence[31] along with the dynamics derived from NMR experiments.[8]

It is of interest to note that structural evidence has been provided for the appearance of dielectric anomalies at higher temperatures for the first time. The dielectric anomaly, which remained unexplained, has now been found to be associated with structural phase transitions. The changing of the space group from $C2/c$ at 293 K to $C2/m$ at 350 K has been carefully followed in terms of the appearance of otherwise systematic absences (Figure 3c). Further, the reappearance of the space group $C2/c$ is evidenced, and the corresponding packing diagrams (parts c and d of Figure 1) clearly bring out the structural differences. The BVS values (Supporting Information Tables S2(a−d))indicate that the sulfur atoms are depleted by a significant reduction in valence charge, which accumulates as excess charge at the rubidium sites thus establishing the nature of the cation disorder.

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(31) Fillaux, F.; Lautié, A.; Tomkinson, J.; Kearley, G. J. *Chem. Phys.* **1991**, *154*, 135−144.

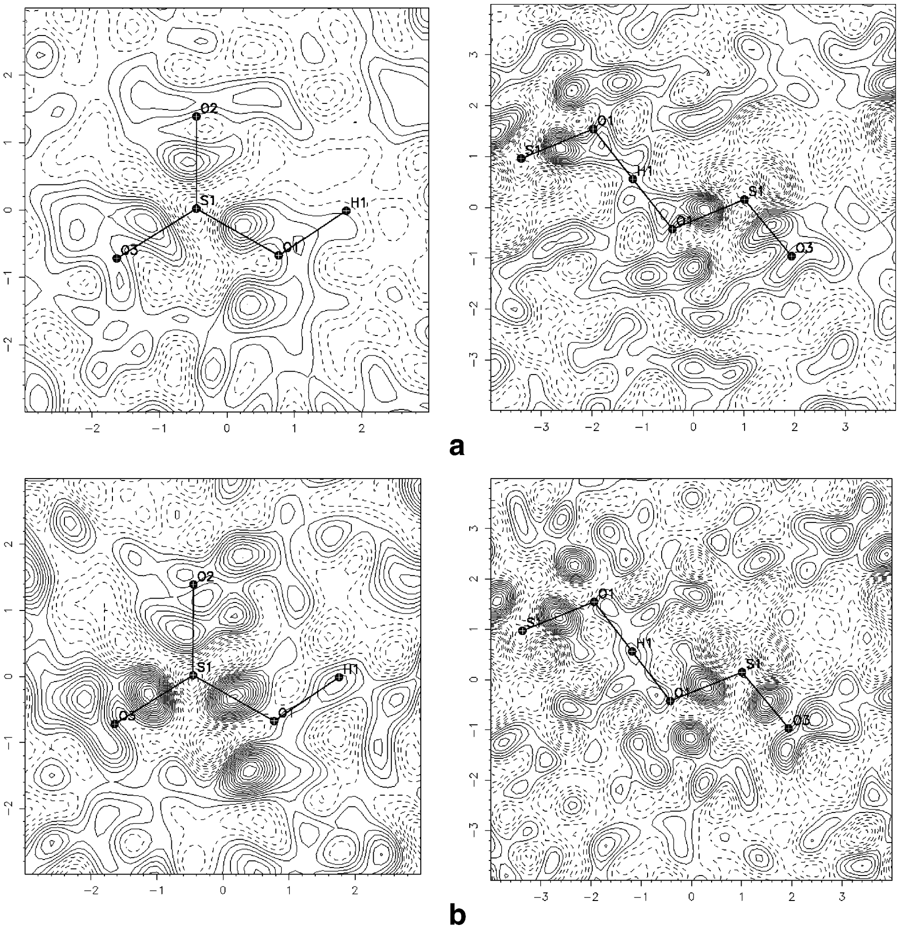

Figure 7. Difference Fourier maps of $K_3H(SO_4)_2$ at (a) 293 K and (b) 100 K showing no disorder in hydrogen position.

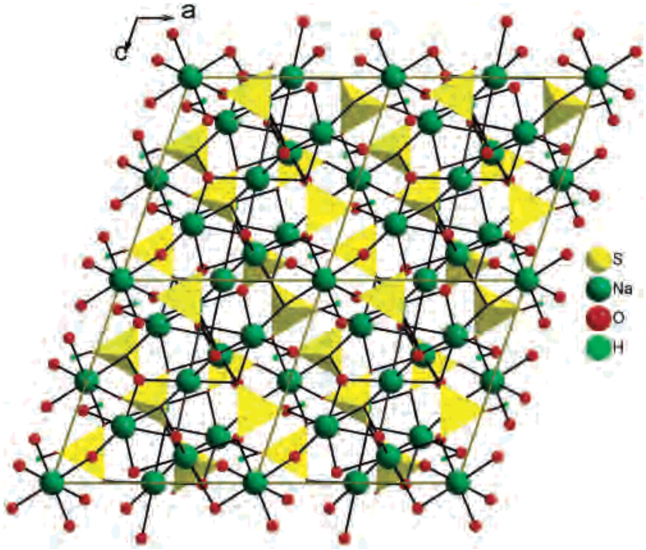

Figure 8. Representative packing diagram of $Na_3H(SO_4)_2$ at 100 K.

The high-temperature form of $(NH_4)_3H(SO_4)_2$ is shown to belong to the space group $R\bar{3}m$. The other possible space groups were also examined, and the refinements clearly suggest this space group. The residuals are significantly lower for $R\bar{3}m$ (Table 2), and in general when tetrahedral units rotate, it is more appropriate to adapt a centrosymmetric space group than a noncentric one since rotation is generally symmetry averaged. Parts a and b of Figure 4 bring out this feature clearly.

$K_3H(SO_4)_2$ (Figure 6) is isostructural to $(NH_4)_3H(SO_4)_2$ and $Rb_3H(SO_4)_2$ but shows no disorder in the hydrogen atom position at the center of symmetry. The absence of any phase transition at high temperatures in these freshly grown single crystals is noteworthy. Several phase transitions have been reported in the range 273−573 K,[19−21] and it may be that the results based on polycrystalline samples could have been contaminated with impurity phases. Indeed, high-temperature work on single crystals with TGA suggests that surface water dehydration might occur and this could be interpreted wrongly as a phase transition.[20] Thus, the observation of a superprotonic transition by NMR studies[21] just before the melting temperature is only an artifact and careful in situ studies on a single crystal verify this observation.

The structural phase transition in $Na_3H(SO_4)_2$ has been studied in detail,[16] and a change in space group symmetry has been reported to occur at 139 K with a definite indication of the start of the transition at 178 K. The hydrogen atoms on the O−H···O hydrogen bond are not located on the center of the bond, and the authors suggest a possible ferroelectric phase (triclinic $P1$) with the dipole moment along the [120] direction. We have found that this observation is incorrect, and careful experiments at several intermediate temperatures ranging from room temperature to 100 K do not indicate

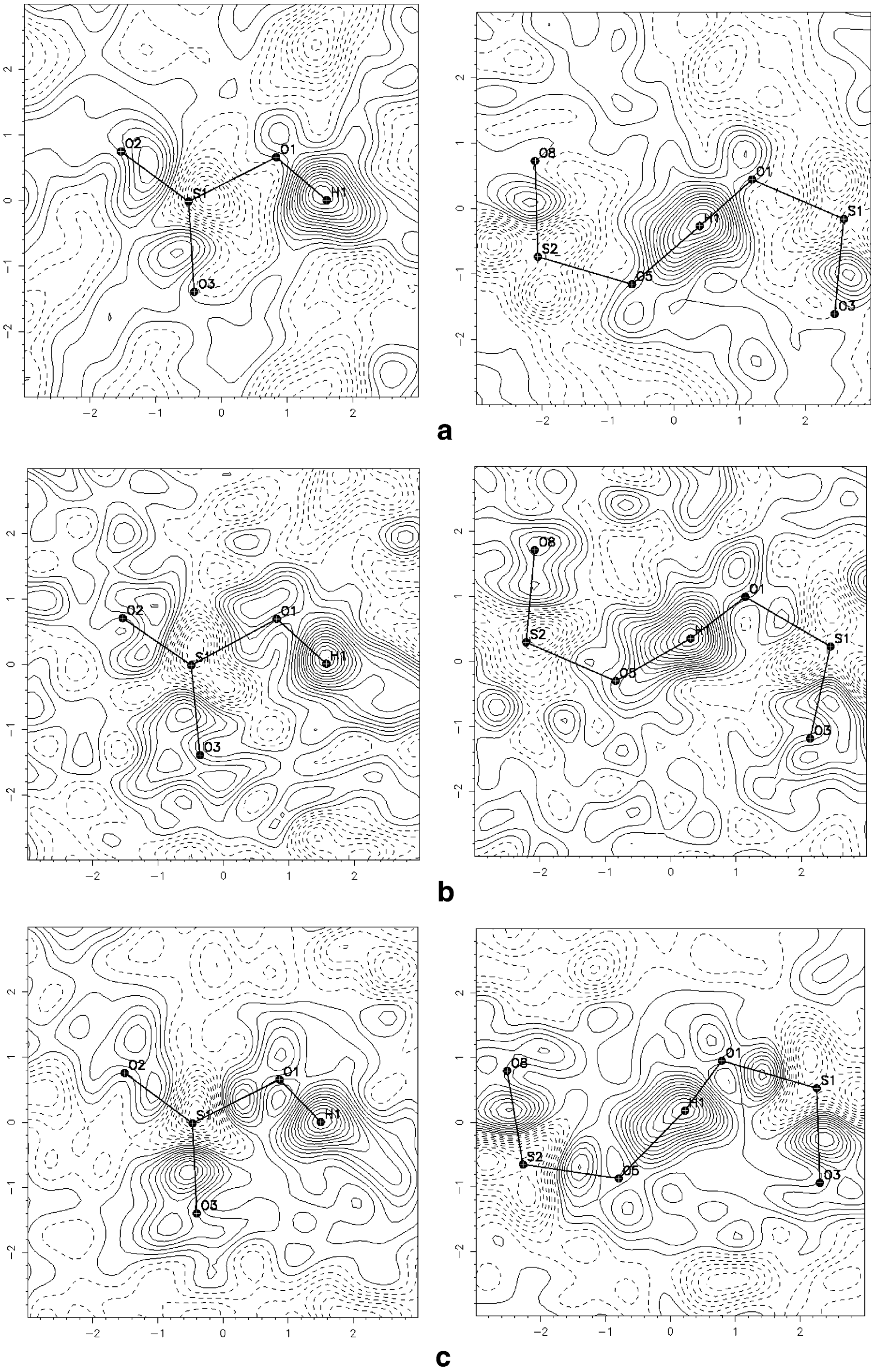

Figure 9. Difference Fourier maps of $Na_3H(SO_4)_2$ at (a) 293 K, (b) 100 K, and (c) 500 K showing no disorder in hydrogen position.

any phase transition. The structural features remain invariant, and the reciprocal lattice points do not indicate any change of symmetry. We have also checked crystals from different batches to ascertain this observation. It is to be noted that the morphology of the crystals used in our experiments are blocks (for example, crystals are 0.30 mm × 0.25 mm × 0.20 mm) while those reported earlier were platelike. It is possible that we have a case of polymorphism in this material, which needs to be investigated further. It is of interest to note that an earlier study[13] reported the O···O distance to be 2.434(4) Å on a needle shaped crystal (0.54 mm × 0.14 mm × 0.10 mm) with an O−H distance of 1.03(6) Å. They suggested a possible twinning is present in the crystal. The only change between the room-temperature structure and the structure at 100 K is at the hydrogen position (O−H = 1.202(2) Å at 293 K changing to 1.136(3) Å at 100 K with no significant change in the O···O distance, 2.432(2) and 2.430(2) Å, respectively). Further, the structure at 500 K has a O···O distance of 2.445(2) Å, and significantly the hydrogen bond angle O−H···O is just off linearity at all three temperatures. The inelastic neutron experiment supports our structural observation indicating that the hydrogen bonds are asymmetric in $Na_3H(SO_4)_2$.

Conclusion

Phase transition characteristics with temperature in $X_3H(SO_4)_2$, where X = Rb, NH_4, K, and Na, have been investigated and correlated with the hydrogen bond features, distortions in sulfate tetrahedra, and changes in X atom coordination via careful X-ray single-crystal diffraction data. The hydrogen positions are confirmed by difference Fourier maps in the intermolecular regions, and the space groups are characterized by reciprocal lattice images. Most of the anomalies observed earlier in properties like dielectric behavior and conductivity characters are now shown to be commensurate with the structural transitions, and the features also correlate with NMR, IR, and INS experiments. It is to be noted that high-quality crystals and high-resolution data sets (with data completion above 98.5%) are prerequisites in any structural phase transition study. Otherwise, contradicting observations in structure−property correlations become persistent.

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Supporting Information Available: Bond-valence sums, interaction geometries, and crystallographic data (in CIF format) for $X_3H(SO_4)_2$, where X = Rb, NH_4, K, and Na. This material is available free of charge via the Internet at http://pubs.acs.org.

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