Inorganic Chemistry

Understanding the Mechanism of Ferroelectric Phase Transition in RbHSO₄: A Previous High-Pressure Raman Investigation

Diptikanta Swain,^{*,†} Venkata Srinu Bhadram,[†] Gopal K. Pradhan, and Chandrabhas Narayana*



ACCESS

III Metrics & More

ABSTRACT: High-pressure dielectric and diffraction studies on rubidium hydrogen sulfate (RbHSO₄) observed ferroelectric phase transition below 1 GPa pressure. We have performed high-pressure Raman spectroscopy studies on RbHSO₄ up to a maximum pressure of 5.15 GPa and at ambient temperature to understand the microscopic origin and mechanism of ferroelectric transition. On the basis of the pressure dependence of Raman mode frequencies and their full-width at half-maxima, we observed a transition around a pressure of 0.3 GPa, similar to the ferroelectric transition discovered in dielectric measurements, followed by another transition around 2.4 GPa. These phase transitions are evident from the appearance/disappearance of Raman-active modes and the change in the slope of frequencies with pressures.



Article Recommendations

From the pressure dependence of the S–O and S–OH frequencies, we deduce that HSO_4^- ion ordering results in ferroelectric phase transition around 0.3 GPa. Further, the transition around 2.4 GPa pressure is associated with significant changes in the stretching and bending vibrational frequencies and indicates a structural phase transition with possible lowering of the crystal symmetry. Interestingly, no significant changes are observed in the Raman spectrum around 1 GPa, at which a phase transition was noticed in earlier X-ray and dielectric studies.

■ INTRODUCTION

RbHSO₄, a O-H…O hydrogen-bonded sulfate compound, belongs to the family $AHSO_4$ (A = Cs, NH_4 , Rb, K, and Na), which exhibit various exciting material properties like ferroelectricity and superprotonic conduction as a function of the pressure and temperature, resulting in structural phase transitions.¹⁻²⁵ Moreover, these compounds are considered to be the model hydrogen-bonded materials to understand many physical properties exhibited by polyanionic materials. The ferroelectric property in RbHSO₄ with temperature is established in full detail from diffraction, spectroscopy, and piezoresponse force microscopy techniques, and the mechanism of transition is found to be order-disorder in nature.^{4,6,8–12} However, the pressure-induced ferroelectric phase transition in RbHSO₄, although studied by using diffraction and dielectric measurements, is not yet completely understood. The differing results acquired from dielectric and structural analyses with pressure suggest that there are a few inconsistencies in modeling the pathways of phase transition.¹⁻⁴ For example, the pressure effect on the Curie temperature suggested that the collective motion of protons in the hydrogen bonds is not responsible for the ferroelectric process in RbHSO₄.² In another report on single-crystal X-ray diffraction studies of RbHSO4 at high pressure, it was proposed that a first-order structural phase transition occurs around ~ 1

GPa.³ In the latest paper by Binns et al., RbHSO₄ displays a paraelectric-to-ferroelectric phase transition under pressure before converting to a third high-pressure phase around 1.1 GPa.⁴ Therefore, a detailed understanding of the dynamics of these phase-transition pathways assumes significance for elucidating the structure–property relationships in RbHSO₄ and a related class of materials.

It may be noted that the room temperature crystal structure of RbHSO₄ is monoclinic, space group $P2_1/c$ with Z = 8.⁹ The asymmetric unit of the crystal has two crystallographically independent RbHSO₄ units, out of which one unit is disordered in the HSO₄⁻ moiety.⁹ The structure depicts extended O–H…O hydrogen bonds among HSO₄⁻ ions. Further, from earlier dielectric studies at normal pressure, it was established that RbHSO₄ depicts a paraelectric-toferroelectric phase transition at $T_c = 258$ K.⁸ According to Pepinsky and Vedam, a large anomaly in the dielectric constant

Received: November 13, 2019



is observed for this transition and is second-order in nature.⁸ Below $T_c = 258$ K, the structure remains monoclinic with space group Pc, keeping Z = 8 intact.^{10,11} Hence, RbHSO₄ is a uniaxial ferroelectric at low temperature belonging to Aizuspecies symmetry 2/mFm.⁶ The asymmetric unit of the crystal in the ferroelectric phase contains four crystallographically independent RbHSO₄ units in which all are ordered and the hydrogen-bonding patterns remain similar to that in the paraelectric phase. Furthermore, low-temperature Raman spectroscopy studies on the compound revealed the transition to be of the order–disorder type, where the room temperature disordered paraelectric phase is going into an ordered ferroelectric phase after the transition temperature.¹²

Gesi and Ozawa have studied the pressure-dependent dielectric constant of RbHSO4 and found a ferroelectric transition around 0.4 GPa and another transition at 0.75 GPa.¹ They assumed that the crystal structure of RbHSO₄ between 0.4 and 0.75 GPa pressure to be monoclinic with space group Pc, which is the same as the structure at the low-temperature ferroelectric phase. However, the dynamics of the ferroelectric transition around 0.4 GPa was not explained by Gesi and Ozawa, while the structure of RbHSO₄ after 0.75 GPa was also not known to them. In another report, Asahi and Hasebe attempted to determine the crystal structure of RbHSO4 at 0.96 GPa and at 295 K from single-crystal X-ray diffraction in a diamond anvil cell (DAC) and found that it is monoclinic, space group $P2_1$ with $Z = 4.^3$ The asymmetric unit of this crystal contains two crystallographically independent ordered RbHSO₄ units, and the hydrogen-bonding aspects remain similar to the paraelectric and ferroelectric phases. Recently, Binns et al. also made an effort to determine the single-crystal structure of RbHSO₄ under pressure in a DAC and found that it undergoes a symmetry-breaking ferroelectric phase transition at 0.4 GPa and the space group transforms from $P2_1/n$ to Pn(monoclinic) with Z = 8 in both cases.⁴ The unit-cell volume is decreased by 1.3% up to 0.4 GPa, while a significant change happened along the *c* axis with a reduction of 0.052 Å, the aaxis decreased by 0.026 Å, the β angle increased by 0.73%, and the b axis remained unchanged.⁴ Interestingly, the ferroelectric structure of RbHSO4 with pressure is isostructural to the ferroelectric phase at low temperature. When the pressure was increased to 1.1 GPa, they observed another structural transition and the space group changed to $P2_1/c$, keeping the monoclinic crystal system intact with Z = 4.

It is well-known that Raman spectroscopy is one of the best techniques for understanding the dynamics of local structural changes during phase transitions. It is also very sensitive to changes in the local structure and environment as well as global symmetry breaking. Thus, the features associated with short/long-range order in the crystal lattice and hydrogen bonding, etc., can be elucidated.^{22,25} Therefore, it is very important to examine the internal vibrations of the molecular units in RbHSO₄ under pressure in order to understand the dynamics of the structural changes associated with the ferroelctric phase transition. In our effort to analyze the pressure-induced phase transitions in RbHSO₄ using Raman spectroscopy, we have observed significant dynamical pathways, leading to an understanding of the changes in the structure associated with the ferroelectric transition. We found significant changes occurring in the vibrational frequencies of HSO₄⁻ ion during the ferroelectric transition at 0.3 GPa that provide insight into the structural changes and dielectric anomalies reported previously. However, we did not find any conclusive evidence for the first-order transition reported earlier around 1 GPa. Interestingly, we found a structural phase transition above 2.4 GPa, which had not been reported previously.

EXPERIMENTAL SECTION

pubs.acs.org/IC

To grow the single crystals, equimolar quantities of aqueous solutions of Rb₂SO₄ and H₂SO₄ were mixed in a stoichiometric ratio of 1:1 and slowly evaporated in an oven at 313 K. Block-shaped transparent crystals were obtained after 2 weeks of crystallization, having a maximum size of 200 μ m. A polarized optical microscope was used to check the quality of the crystals. A Bruker AXS SMART APEX charge-coupled-device (CCD) single-crystal X-ray diffractometer was employed for diffraction data collection at room temperature to verify the correct phase of the crystal used for high-pressure experiments. The X-ray generator of the diffractometer was set at voltage and current values of 50 kV and 35 mA using Mo K α radiation. For all of the measurements, 606 frames/set were collected using SMART in four different settings of φ (0°, 90°, 180°, and 270°) with an ω scan at -0.3° intervals and with a counting time of 5 s. The sample-todetector distance was kept at 6.054 cm, and the 2θ value was fixed at -25°.26 The data were processed using the SAINT-PLUS protocol, where the SADABS package was used for empirical absorption corrections.^{26,27} The space group was determined by XPREP.²⁶ The structure was solved and refined using the SHELX-97 program present in the WinGX suite.^{28,29} The conventional R factor, the weighted R factor (wR), and the goodness of fit S are based on F^2 . For highpressure experiments, we have used a Mao-Bell-type DAC having two low fluorescent diamonds with a culet size of 600 μ m.³ А preindented stainless steel gasket was drilled to have a 300 μ m hole at the center in order to load the RbHSO4 crystal along with NaCl and ruby chip. NaCl is used as the pressure-transmitting medium because it does not react with the sample and has no Raman-active modes overlapping with the sample. In fact, NaCl offers the best quasi-hydrostatic conditions up to 21 GPa compared to widely used pressure-transmitting media such as ethanol/methanol mixtures for the experiments at high pressure.³¹

The pressure applied on the sample was measured by a ruby fluorescence technique.³² A 20× superlong-working-distance microscope objective having a numerical aperture of 0.35 was used to focus the incident light and collect the scattered light in a 180° backscattering geometry. The Raman spectra were recorded by using 532 nm excitation from a diode-pumped frequency-doubled Nd:YAG solid-state laser (model GDLM-5015 L; Photop Suwtech Inc., China). A custom-built Raman spectrometer, equipped with a SPEX TRIAX 550 monochromator and a liquid-nitrogen-cooled CCD (Spectrum One with CCD 3000 controller, ISA Jobin Yovn), was used for data collection. Details about the spectrometer are available in the literature.³³ The laser power at the laser head was ≈ 8 mW, and a typical spectral acquisition time was 4 min, where the pressuredependent Raman data were collected in the frequency range 300-1100 cm⁻¹. The spectral resolution chosen was 2 cm⁻¹, and the profiles were fitted using Lorentzian functions with appropriate background.

RESULTS AND DISCUSSION

The structure of RbHSO₄ determined at 293 K verifies the details of previously published report and belongs to the crystal system monoclinic, space group $P2_1/n$ with Z = 8 (Figure 1).³⁴ The asymmetric unit of the crystal has two crystallographically independent RbHSO₄ units, where all atoms are placed at general crystallographic positions (Wyckoff; 4e). Among two independent RbHSO₄ units, one unit is disordered in a HSO₄⁻ ion, while the other is ordered. The O atoms in the disordered HSO₄⁻ ion show large thermal vibration and are refined with a split-atom model by using the *SHELX-97* refinement protocol.²⁸



Figure 1. Crystal packing of RbHSO₄ at 293 K in the *ab* plane (D = disordered; O = ordered) depicting O–H···O hydrogen bonds. Rb atoms are placed between hydrogen-bonded layers, which form Rb1O₁₀ and Rb2O₉ polyhedra (atoms O5, O6, and O8 are refined with split occupancy; hence, the combined occupancy of atoms A and B is equal to 1).

The sulfate ions have typical tetrahedral geometry, where small deviations from the tetrahedral values of O–S–O angles are observed for the ordered SO_4^{2-} unit; however, it is large for the disordered unit. Strong O–H…O networks among HSO₄⁻ ions form an infinite hydrogen-bond sequence in ordered as well as disordered units along the crystallographic *b* axis by translational symmetry (Figure 1). Rb atoms are located between the layers formed by the O–H…O hydrogen bonds and coordinated to the O atoms from the sulfate ions, forming Rb1O₁₀ and Rb2O₉ distorted polyhedra.

The unpolarized Raman spectra of RbHSO₄ in the frequency range 300-1100 cm⁻¹ collected at room temperature and at normal pressure are shown in Figure 2. The Raman-active modes in RbHSO4 are identified based on the available literature and are consistent with previous reports.^{12,35,36} The internal modes, which are derived from the motions of the HSO₄⁻ ion, are divided into four groups of frequencies, namely, (i) symmetric bending $\nu_2(SO_4)$ (350–480 cm⁻¹), (ii) asymmetric bending ν_4 (SO₄) (540–650 cm⁻¹), (iii) symmetric stretching ν_1 (S–OH) (850–900 cm⁻¹), and (iv) symmetric stretching ν_1 (S–O) (1010–1060 cm⁻¹). These frequencies are derived by considering a HSO4⁻ ion as a distorted tetrahedron with $C_{3\nu}$ symmetry.¹² As mentioned above, the room temperature structure has two crystallographically independent RbHSO₄ units, among which one unit is disordered at the HSO_4^- moiety. This phenomenon is very well noticed by



Figure 2. Raman spectra of $RbHSO_4$ in the frequency range 300–1100 cm⁻¹ at room temperature.

analyzing the symmetric S–O stretching frequencies of the Raman spectra, where we observe three intense Raman peaks centered at 1018, 1041, and 1051 cm⁻¹ at ambient conditions. The frequencies at 1018 and 1041 cm⁻¹ are assigned as the symmetric S–O stretching vibrations of the disordered unit, whereas the mode at 1051 cm⁻¹ is assigned as the S–O stretching vibration of the ordered unit.

Pressure evolutions of the Raman spectra of RbHSO₄ in the pressure range 0–5.15 GPa are presented in Figures 3 and 4. Considerable variations in the spectral features are detected around the transition pressures ($P_{c1} = 0.3$ GPa and $P_{c2} = 2.4$ GPa). Now we discuss the effect of pressure on the vibrational Raman modes and a few selected full-width at half-maxima (fwhm) of the HSO₄⁻ unit to understand the dynamics



Figure 3. (a and c) Pressure evolutions of symmetric S–OH and S– O stretching vibrational frequencies of RbHSO₄ depicting the phase transitions ($P_{c1} = 0.3$ GPa and $P_{c2} = 2.4$ GPa) and (b) fwhm of the particular stretching modes in the pressure range 0.0–5.15 GPa.



Figure 4. (a and b) Pressure evolutions of the SO₄ bending region and mode frequencies of $RbHSO_4$ in the pressure range 0.0–5.15 GPa.

influencing the phase transitions. Very exciting changes are exhibited by the symmetric S–O stretching frequencies around P_{c1} . The mode around 1041 cm⁻¹, which is associated with the disordered S–O bonds, suddenly softens, approaching the 1018 cm⁻¹ mode, while the mode at 1051 cm⁻¹ displays an abrupt increase in frequency (Figure 3c). In the symmetric stretching region of the S–OH mode centered around 876 cm⁻¹, we observe splitting of the mode into two modes, with a new mode appearing around 884 cm⁻¹ at P_{c1} (Figure 3c). The fwhm of the symmetric S–O and S–OH modes around P_{c1} shows anomalous behavior, clearly depicting the phase transition. The fwhm of both modes increase with pressure and decrease steeply after the transition pressure (Figure 3b).

Figure 4 represents the pressure evolutions of the bending modes of SO_4^{2-} in the spectral range 350-650 cm⁻¹. This spectral frequency range comprises six Raman modes centered at 405, 415, 444, 572, 581, and 610 cm⁻¹ at ambient pressure and temperature. Around the transition pressure $P_{c1} = 0.3$ GPa, we observe subtle changes in the mode frequencies in this region unlike the stretching frequencies. When the pressure is increased to 1 GPa, two new modes evolve around 432 and 604 cm^{-1} in the asymmetric and symmetric bending regions of the HSO₄⁻ ion and the intensities of the modes increase with increasing pressure. Interestingly, no significant changes have been detected for all other mode frequencies around 1 GPa. As the pressure is increased further, a second transition is observed around 2.4 GPa (P_{c2}) based on the significant anomalies in the behavior of vibrational frequencies of the stretching and bending modes of HSO₄⁻ ions.

At first glance of the mode behavior shown in Figures 3c and 4b, we notice large-scale changes in the modes around 3.5 GPa. In fact, this transition starts to appear around 2.4 GPa with changes in the bending mode frequencies. The modes around 572 and 581 cm⁻¹ are upshifted, while the mode at 415 $\rm cm^{-1}$ merged with the one around 405 $\rm cm^{-1}$. It can be noticed from Figure 4b that this particular transition is sluggish and completes around 3.5 GPa. Hence, there would be the possibility of mixed phases between 2.4 and 3.5 GPa pressure, where the ferroelectric and high-pressure phases could coexist. Some of the other salient features of this transition are the appearance of new modes at 476, 567, 848, and 1028 cm^{-1} and disappearance of the modes at 909 and 1011 cm⁻¹. This could be indicative of a first-order transition because in Raman spectroscopy the mode frequency can be considered to be the order parameter. It is of interest to note that the fwhm for the 876 and 1041 cm⁻¹ modes increase beyond 2.4 GPa (Figure 3c). Moreover, the increase in the number of modes could be indicative of the lowering of the lattice symmetry at high pressures beyond $P_{c2} = 2.4$ GPa.

On the basis of our pressure-dependent Raman analysis presented here, we observed three phases of RbHSO₄ evolving with increasing pressure from 0 to 5.15 GPa. Considering the earlier reports, we suggest that below P_{c1} the phase is paraelectric (space group $P2_1/c$), whereas the phase between P_{c1} and P_{c2} is ferroelectric (space group Pc).¹⁻⁴ Beyond P_{c2} , we expect a denser and lower symmetric phase. We predict that the possible crystal system could be triclinic with space group P1 after 2.4 GPa if the transition follows the group-subgroup relationship of symmetry analysis,^{37,38} which can be confirmed by a high-pressure X-ray diffraction experiment. It is also important to note here that there exists a group-subgroup relationship between space groups Pc and P1 according to International Table for Crystallography (volume A).^{37,38} Further, our prediction for the phase above 2.4 GPa is also based on the increased number of modes in the Raman spectrum.

We will now discuss the pressure dependence of the frequencies and fwhm of the Raman modes, exhibiting significant changes in the vicinity of the ferroelectric phase transition at $P_{c1} = 0.3$ GPa and the high-pressure transition at $P_{c2} = 2.4$ GPa. Below P_{c1} , the crystal has a center of inversion (space group $P2_1/c$), hence leading the total polarization of the crystal to zero. It is noteworthy that Gesi and Ozawa demonstrated a ferroelectric transition for RbHSO₄ after P_{c_1} from their pressure-dependent dielectric measurements. Further, it is also important to note that the crystal structure of RbHSO₄ after P_{c1} is determined by Binns et al. from their high-pressure X-ray diffraction measurements, where the space group is found to be noncentrosymmetric $Pn \ (\sim Pc)$.⁴ It is to be noted here that the first transition pressure (P_{c1}) of RbHSO₄ from our Raman experiments matches very well with those of Gesi and Ozawa and Binns et al. On the basis of these facts, we believe that the space group of RbHSO4 in the pressure-induced ferroelectric phase could be Pc. Thus, our results for the first transition pressure (P_{c1}) do not contradict with the earlier report. Above P_{c1} , because of the lowering of the crystal symmetry from $P2_1/c$ to Pc, the structure lost its center of inversion, resulting in nonzero polarization, which has been demonstrated in dielectric measurements with pressure by Gesi and Ozawa.¹ Similar observations were also found for RbHSO₄ and NH₄HSO₄ at low temperatures, where both compounds undergo a paraelectric-to-ferroelectric

CONCLUSIONS

In summary, the pressure-dependent Raman investigation on RbHSO₄ suggests that the dynamics of the HSO₄⁻ ion indeed plays an important role in the ferroelectric transition around 0.3 GPa. The ferroelectric transition around 0.3 GPa is of order-disorder in nature, which introduces ordering in the HSO₄⁻ ion, where significant changes in the symmetric S–O and S-OH stretching frequencies and their corresponding fwhm are observed. The remarkable decrease in the fwhm of some stretching modes around P_{c1} gives clear evidence to the ordering of HSO₄⁻ ions, which leads to the ferroelectric transition. In addition, we observe a new phase transition around 2.4 GPa that is marked by the appearance/ disappearance of Raman modes and associated with large anomalies to the mode frequencies, indicating a structural phase transition, possibly to a lower-symmetry phase. From our Raman-mode analysis, we could not find any conclusive evidence for the previously reported first-order structural phase transition around 1 GPa.

AUTHOR INFORMATION

Corresponding Authors

- Diptikanta Swain Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; o orcid.org/0000-0003-4048-5017; Email: diptisscu@gmail.com
- Chandrabhas Narayana Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; o orcid.org/0000-0001-6256-8994; Email: cbhas@jncasr.ac.in

Authors

- Venkata Srinu Bhadram Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, CNRS, Muséum National d'Histoire Naturelle, 75005 Paris, France;
 orcid.org/0000-0002-8872-7903
- Gopal K. Pradhan Department of Physics, School of Applied Sciences, KIIT Deemed to be University, Bhubaneswar, Odisha 751024, India; o orcid.org/0000-0002-1956-7248

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.9b03340

Author Contributions

[†]These authors contributed equally.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Gesi, K.; Ozawa, K. Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric RbHSO₄ and RbDSO₄. *J. Phys. Soc. Jpn.* **1975**, *38*, 459–462.

(2) Gesi, K.; Ozawa, K. Effect of Hydrostatic Pressure on the Ferroelectric Curie Temperature of Rubidium Bisulfate RbHSO₄. J. Phys. Soc. Jpn. **1973**, 35, 1268–1268.

(3) Asahi, T.; Hasebe, K. Crystal Structure of the High Pressure Phase of RbHSO₄. *J. Phys. Soc. Jpn.* **1996**, *65*, 3233–3236.

(4) Binns, J.; McIntyre, G. J.; Parsons, S. Neutron and High-Pressure X-ray Diffraction Study of Hydrogen-Bonded Ferroelectric Rubidium Hydrogen Sulfate. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2016**, *72*, 855–863.

transition and the space group changes from $P2_1/c$ to $Pc.^{12}$ It may be noted that the space groups $P2_1/c$ and $P2_1/n$ have the same space group number (No. 14) in *International Table for Crystallography* (volume A) and should not be confused with two different space groups. It is also the same for the space groups Pc and Pn (No. 7).³⁷

The anomalous behavior of fwhm of the symmetric S-O and S–OH frequencies after P_{c1} signifies that the compound is becoming more ordered with pressure, leading to a lifting of the center of inversion. The significant changes occurring in the fwhm of the symmetric S-OH stretching frequency around P_{c1} suggest its major role in the ferroelectric property of RbHSO₄. Generally, the state of O-H…O hydrogen bonds in a HSO₄⁻ system could be analyzed by studying the symmetric S-O and S-OH vibrational frequencies.¹⁸ The increase of the symmetric S-O and S-OH frequencies with pressure (Figure 3b) suggests a weakening of the O-H…O hydrogen bonds beyond P_{c1} until P_{c2} , which brings ordering in the HSO₄⁻ ion. However, after P_{c2} , there could be the presence of mixed types of hydrogen bonding, where one type of O-H…O hydrogen bond hardens and the other type softens (Figure 3b). This could be due to the presence of more crystallographically independent HSO₄⁻ units in the structure. This can be understood in the following manner. Beyond P_{c2} , as the pressure increases, the interaction between the HSO₄ ions establishes order and the earlier disordered ions are forced to adopt either of the orientations along the chains. The symmetry requirement then would demand the O…O distances to be different for the nonequivalent orientations, giving rise to two different types of hydrogen bonding. In addition, more Raman-active modes in the bending region of the spectra indicate a further reduction in the crystal symmetry.

Further, we add here that the behavior of the S-O and S-OH stretching frequencies around P_{c1} is strikingly similar to that of NH₄HSO₄ across a temperature-induced paraelectricto-ferroelectric transition, as reported earlier.²⁵ In fact, both compounds exhibit the same crystal symmetry in both the paraelectric and ferroelectric phases. In NH4HSO4, the separation between the two S-O stretching modes arising from the disordered units reduces drastically across the ferroelectric phase transition. This behavior was assigned to enhancement of the covalency due to ordering of the HSO₄⁻ units. However, the discontinuity in the corresponding fwhm across the phase transition indicates that the transition is rather abrupt. In the case of RbHSO₄, although the ferroelectric transition is around 0.3 GPa, the ordering process is not abrupt but rather progressive up to at least 2.4 GPa (P_{c2}) , as seen in the continuous decrease in fwhm of the S-O and S-OH modes with an increase in pressure (Figure 3b). In addition, new bending modes emerge at 432 and 604 cm⁻¹ around 1.17 GPa, whose intensities increase with pressure, while the intensities of their neighboring modes at 415 and 610 cm⁻¹ decrease and eventually disappear at P_{c2} . In the absence of any significant changes in the stretching mode region around 1.17 GPa, we could not conclusively assign this behavior to the firstorder structural phase transition observed in earlier studies.^{2,3} We think that the behavior of the bending modes between 1.17 GPa and P_{c2} may indicate the progressive conversion of disordered units into ordered units. A detailed study of external modes in this pressure range might give more insight; however, we could not access this low-frequency region because of limitations in our Raman setup, along with inherent background associated with the DAC and sample environment.

(5) Zachek, I. R.; Shchur, Y.; Levitskii, R. R. Electromechanical and Relaxation Dielectric Properties of RbHSO₄ Crystal. *Phys. B* **2015**, 478, 113–121.

(6) Lilienblum, M.; Hoffmann, Á.; Soergel, E.; Becker, P.; Bohatý, L.; Fiebig, M. Piezoresponse Force Microscopy at Sub-Room Temperatures. *Rev. Sci. Instrum.* **2013**, *84*, 043703.

(7) Sinitsyn, V. V. Pressure Effect on Phase Transitions in $MeHAO_4$ Superprotonic Conductors (A= S, Se and Me= NH_4 , Rb, Cs). J. Mater. Chem. 2010, 20, 6226–6234.

(8) Pepinsky, R.; Vedam, K. Ferroelectric Transition in Rubidium Bisulfate. *Phys. Rev.* **1960**, *117*, 1502.

(9) Itoh, K.; Ohno, H.; Kuragaki, H. Disordered Structure of Ferroelectric Rubidium Hydrogen Sulfate in the Paraelectric Phase. *J. Phys. Soc. Jpn.* **1995**, *64*, 479–484.

(10) Itoh, K.; Moriyoshi, C. Structural Study of Phase Transition in Ferroelectric RbHSO₄. *Ferroelectrics* **2003**, *285*, 91–104.

(11) Nalini, G.; Guru Row, T. N. Phase Transitions in Rubidium Hydrogen Sulfate: Crystal Structures at 293 and 200K. *Phase Transitions* **2003**, *76*, 923–934.

(12) Toupry, N.; Poulet, H.; Le Postollec, M. Raman Study of the Phase Transition in RbHSO₄. J. Raman Spectrosc. **1981**, 11, 81–91.

(13) Haile, S. M.; Boysen, D. A.; Chisholm, C. R.; Merle, R. B. Solid Acids as Fuel Cell Electrolytes. *Nature* **2001**, *410*, 910–913.

(14) Mikhaleva, E. A.; Flerov, I. N.; Bondarev, V. S.; Gorev, M. V.; Vasiliev, A. D.; Davydova, T. N. Phase Transitions and Caloric Effects in Ferroelectric Solid Solutions of Ammonium and Rubidium Hydrosulfates. *Phys. Solid State* **2011**, *53*, 510–517.

(15) Baranov, A. I.; Shuvalov, L. A.; Shchagina, N. M. Superion Conductivity and Phase Transitions in $CsHSO_4$ and $CsHSeO_4$ Crystals. *JETP Lett.* **1982**, *36*, 459–462.

(16) Barron, O.; Su, H.; Linkov, V.; Pollet, B. G.; Pasupathi, S. CsHSO₄ as Proton Conductor for High-Temperature Polymer Electrolyte Membrane Fuel Cells. *J. Appl. Electrochem.* **2014**, *44*, 1037–1045.

(17) Ponyatovskii, E. G.; Rashchupkin, V. I.; Sinitsyn, V. V.; Baranov, A. I.; Schuvalov, L. A.; Shchagina, N. M. P-T Phase Diagram of a Proton Superionic Conductor CsHSO₄. *JETP Lett.* **1985**, *41*, 139–141.

(18) Yamawaki, H.; Fujihisa, H.; Sakashita, M.; Honda, K. Vibrational Spectra of $CsHSO_4$ at High Pressure and High Temperature. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 094111.

(19) Pepinsky, R.; Vedam, K.; Hoshino, S.; Okaya, Y. Ammonium Hydrogen Sulfate: A New Ferroelectric with Low Coercive Field. *Phys. Rev.* **1958**, *111*, 1508.

(20) Gesi, K.; Ozawa, K. Pressure-Temperature Phase Diagram of Ferroelectric Ammonium Bisulfate NH4HSO₄. J. Phys. Soc. Jpn. **1977**, 43, 563–569.

(21) Swain, D.; Row, T. N. G. In situ Crystallography of KHSO₄: Probing the Kinetic Pathway For the Evolution of a Pyrolysis Reaction in the Crystalline State. *Inorg. Chem.* **2008**, 47, 8613–8615.

(22) Swain, D.; Bhadram, V. S.; Pradhan, G. K.; Bhat, S. V.; Narayana, C.; Rao, C. N. R. Superionic Phase Transition in KHSO₄: A Temperature-Dependent Raman Investigation. *J. Phys. Chem. A* **2010**, *114*, 10040–10044.

(23) Bagdassarov, N.; Lentz, G. High Pressure Behaviour of KHSO₄
Studied by Electrical Impedance Spectroscopy. *Solid State Commun.*2005, 136, 16–21.

(24) Zangmeister, C. D.; Pemberton, J. E. Phase Transition Between Two Anhydrous Modifications of NaHSO₄ Mediated by Heat and Water. *J. Solid State Chem.* **2007**, *180*, 1826–1831.

(25) Swain, D.; Bhadram, V. S.; Chowdhury, P.; Narayana, C. Raman and X-ray Investigations of Ferroelectric Phase Transition in NH_4HSO_4 . J. Phys. Chem. A **2012**, 116, 223–230.

(26) SMART, SAINT, SADABAS, XPREP, and SHELXTL; Bruker AXS Inc.: Madison, WI, 1998.

(27) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

(28) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

(29) Farrugia, L. J. WinGX Suite for Small-Molecule Single-Crystal Crystallography. J. Appl. Crystallogr. **1999**, 32, 837–838.

(30) Mao, H. K.; Bell, P. M. Yearbook; Carnegie Institute for Science: Washington, DC, 1978; Vol. 77, p 904.

(31) Celeste, A.; Borondics, F.; Capitani, F. Hydrostaticity of Pressure-Transmitting Media for High Pressure Infrared Spectroscopy. *High Pressure Res.* **2019**, *39*, 608–618.

(32) Barnett, J. D.; Block, S.; Piermarini, G. J. An Optical Fluorescence System for Quantitative Pressure Measurement in the Diamond-Anvil Cell. *Rev. Sci. Instrum.* **1973**, *44*, 1–9.

(33) Kumar, G. V.; Narayana, C. Adapting a Fluorescence Microscope to Perform Surface Enhanced Raman Spectroscopy. *Curr. Sci.* **2007**, *93*, 778.

(34) Crystal data: chemical formula RbHSO₄, fw = 182.54 g/mol, monoclinic, space group $P2_1/n$, a = 14.3769(13) Å, b = 4.6186(4) Å, c = 14.4144(13) Å, $\beta = 118.005(1)^\circ$, V = 845.06(13) Å³, Z = 8, $\rho_{cal} = 2.78$ g/cm³, T = 293 K, $\mu = 12.082$, no. of reflns measd = 8975, no. of unique reflns = 2025, no. of obsd reflns = 1817, R = 0.0447, and wR = 0.1094.

(35) Herzberg, G. The Infrared and Raman Spectra of Polyatomic Molecules; Van Nostrand: New York, 1945.

(36) Gargouri, M.; Hassen, R. B.; Mhiri, T.; Daoud, A. Crystal Structure Phase Transitions and a Vibrational Study of Disordered RbH(SO₄)_{0.81}(SeO₄) Solid Solution. *J. Phys.: Condens. Matter* **1998**, *10*, 8235–8245.

(37) Hahn, T. International Tables for Crystallography, Vol. A, Space-Group Symmetry, 5th ed.; Kluwer Academic Publishers, Dordrecht, The Netherlands, 2005.

(38) Aroyo, M. I.; Perez-Mato, J. M.; Orobengoa, D.; Tasci, E. M. R. E.; de la Flor, G.; Kirov, A. Crystallography Online: Bilbao Crystallographic Server. *Bulg. Chem. Commun.* **2011**, *43*, 183–197.