



# Deterioration of hydrogen-bonded superprotonic conductors belonging to $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4\text{--H}_2\text{O}$ salt system: a single-crystal neutron diffraction investigation

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**Abstract.** Single-crystal neutron diffraction investigation on  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  superprotonic crystals, belonging to  $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4\text{--H}_2\text{O}$  salt system, is under taken to elucidate the precise hydrogen atom positions in these crystals. The investigation revealed that these crystals are very sensitive to the ambient conditions and can undergo deterioration due to fluctuation in air moisture content.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals are more stable as compared to  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ . Crystal structure of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  is obtained both before and after deterioration, it is found that the asymmetric O–HO hydrogen bond between the  $\text{PO}_4$  and  $\text{SO}_4$  ions of this crystal becomes stronger after deterioration. This led to the shrinkage of the unit cell, and most likely prevented further deterioration. Diabatic state model for hydrogen bonds is used to obtain the energy contour for the O–H...O hydrogen bond of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal. The influence of this change in the hydrogen bonding on the proton conduction ability of the crystal is discussed.

**Keywords.** Hydrogen bonding; neutron diffraction; proton conductors.

## 1. Introduction

Superprotonic crystals with general formula  $M_m\text{H}_n(\text{AO}_4)_{(m+n)/2}\cdot y\text{H}_2\text{O}$  ( $M = \text{K, Rb, Cs, NH}_4$ ;  $\text{AO}_4 = \text{SO}_4, \text{SeO}_4, \text{HPO}_4, \text{HAsO}_4$ ) constitute an important class of crystals that exhibit interesting physicochemical properties like the proton conduction [1,2]. An important feature of  $M_m\text{H}_n(\text{AO}_4)_{(m+n)/2}\cdot y\text{H}_2\text{O}$  crystals is a dynamically disordered sublattice of hydrogen atoms, where the number of structurally equivalent positions of hydrogen atoms forming hydrogen bonds exceeds the number of hydrogen atoms in the unit cell. These properties make these crystals an important component of the electrochemical devices like the fuel cells, which provide the direct conversion of chemical energy into electrical energy [3–5].

Proton conduction is a characteristic property of crystals with delocalized hydrogen bonds, the process of proton diffusion consists of two stages: (i) proton transfer between the two minima of hydrogen bond separated by the energy barrier  $E_{\text{intra}}$  ( $\text{O–H}\cdots\text{O} \rightarrow \text{O}\cdots\text{H–O}$ ); (ii) breaking of hydrogen bond  $\text{O}\cdots\text{H–O}$  and the subsequent reorientation of its short shoulder O–H, this step is thermally activated and is characterized by the energy  $E_{\text{inter}}$ . Review article by

Baranov [1] on crystals with dynamically disordered networks of H bonds describes the criterion required for a crystal to have high proton conductivity. As a first approximation, the energy of proton migration is determined by the value of a higher potential barrier  $E_{\text{intra}}$  or  $E_{\text{inter}}$ , both of which depend on the inherent nature of the O–H...O bonds like the O...O distance, <OHO angle, etc. Hence, the knowledge about the exact location of H atom in these crystals is of paramount importance in order to understand the proton conductivity of these crystals. Single crystal neutron diffraction is one of the most powerful techniques available to obtain the exact information about the hydrogen bonding in crystals.

Crystals belonging to the  $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4\text{--H}_2\text{O}$  salt system [6] have been extensively investigated in order to find new superprotonic conductors with a highly stable superprotonic phase, like in  $\text{CsHSO}_4$  compound, and high proton conductivity like in  $\text{CsH}_2\text{PO}_4$  [1].  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  [6] and  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  [7] are promising crystals belonging to this system. This article discusses the results of single-crystal neutron diffraction investigation on  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  undertaken with an intention to get

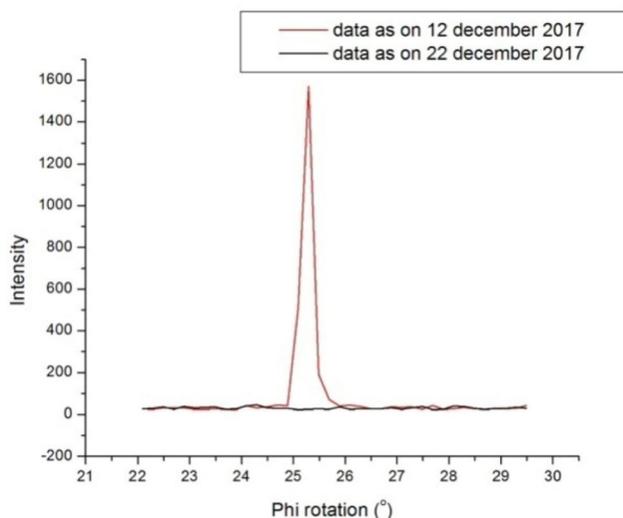
precise information on the hydrogen subsystem of these crystals.

## 2. Crystal growth

$\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals were grown from aqueous solutions by the controlled decrease in temperature of the saturated solution. The crystallization solutions were prepared from  $\text{CsHSO}_4$  and  $\text{CsH}_2\text{PO}_4$  of reagent-grade purity. Details of crystallization procedure have been reported earlier [8].

### 2.1 Structural study on $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$

A large cuboidal crystal of  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  of approximate size  $3 \times 3 \times 3$  mm was mounted on the four circle single-crystal diffractometer with  $\text{BF}_3$  point detector located at Dhruva Reactor at Trombay Mumbai. The crystal was centred and (4 0 0) diffraction peak was located through random peak search. During the room temperature (RT) measurement, the crystal was directly exposed to the atmosphere. When the peak (4 0 0) was scanned after a span of 10 days, the peak intensity had decreased to the background level and the overall background level had increased. Figure 1 shows the phi scans for the (4 0 0) peak taken within the gap of 10 days. This led to the conclusion that the crystal was gradually losing its crystalline nature under the ambient condition with air humidity. Deterioration of  $\text{CsH}_2\text{PO}_4$  crystals at high temperatures has been reported in literature. Since there are similarities in the structures and properties of  $\text{CsH}_2\text{PO}_4$  and  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ , one can assume some analogy of crystal deterioration pathway for the two above-mentioned crystals. The



**Figure 1.** Phi scan of the (4 0 0) peak of  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  crystal, within a span of 10 days.

details of likely deterioration process will be discussed in the later section.

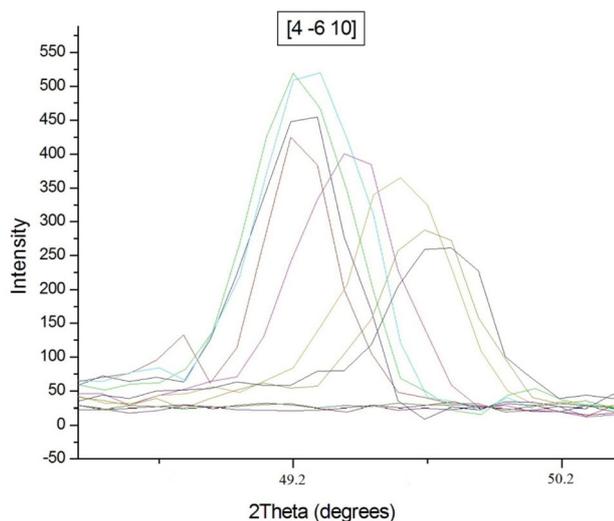
### 2.2 Structural study on $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$

Room temperature single-crystal neutron diffraction investigation on  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  was undertaken. Based on our experience with  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ , this time the sample chosen was shellac coated for protection from moisture, and cuboidal crystal of approximate size  $3 \times 3 \times 3$  mm was mounted on the four circle single-crystal diffractometer with  $\text{BF}_3$  point detector located at Dhruva Reactor at Trombay Mumbai. Complete data up till  $\sin\theta/\lambda = 0.7 \text{ \AA}^{-1}$  was collected, total 401 independent reflections were measured, details of data collection are given in table 1. The integrated neutron counts for Bragg reflections were measured in the symmetrical setting of the diffractometer using  $\theta$ - $2\theta$  coupled step scan mode (0.1 degree step in  $2\theta$ ). The background was scanned for minimum of 1 degree on either side. The standard reflection was measured after every 25 reflections. The variation of the standard reflection intensity was within 3%. Squared observed structure factors were obtained from integrated intensities after incorporating the Lorentz correction using the program DATARED [9]. The structural parameters obtained using X-rays [7] were used as the starting parameters and were subjected to a series of isotropic and anisotropic full-matrix least-square refinement using SHELXL [10]. All the reflections including negative  $F_o^2$  were used for refinement. In the initial stages of refinement, weight ( $w$ ) was taken to be  $1/\sigma(F_o^2)$ , which was derived using counting statistics. It was observed that the  $R(\text{sig})$  for the data set was very high (34%), indicating poor intensity statistics, most likely due to the shellac covering on the crystal, leading to increased background counts. The final  $R$ -factors (table 1) were very high due to poor intensity statistics.

Another  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal of similar size but without shellac coating was mounted on the single-crystal neutron diffractometer and diffraction data were collected. Details of data collected are given in table 1. A marked improvement in the peak to background intensity ratio was observed in the absence of shellac coating on the crystal.  $R(\text{sig})$  for this data set was 21%, this value is high, indicating that this was inherently a weakly diffracting crystal mainly due to the presence large number of hydrogen atoms, which have a large incoherent scattering for neutrons. The cell constant ( $a = b = c = 4.5353(7) \text{ \AA}$ ) was refined by least-square technique from optimized  $2\theta$  angles of 50 reflections using REFINE [11] program, the reflections were so chosen to represent the randomly distributed reciprocal space. As the data collection proceeded, it was observed after  $\sin\theta/\lambda = 0.649 \text{ \AA}^{-1}$ , there was substantial change in the position and intensity of standard reflection (4 -6 10) (figure 2). This indicated a change in the unit cell of

**Table 1.** Data collection and refinement details.

	Before deterioration	After deterioration	With shellac covered
Chemical formula	$\text{Cs}_{0.50}\text{HO}_{2.33}\text{P}_{0.33}\text{S}_{0.25}$	$\text{Cs}_{0.50}\text{HO}_{2.33}\text{P}_{0.33}\text{S}_{0.25}$	$\text{Cs}_{0.50}\text{HO}_{2.33}\text{P}_{0.33}\text{S}_{0.25}$
Mr	123.12	123.12	123.12
Crystal system, space group	Cubic, $I-43d$	Cubic, $I-43d$	Cubic, $I-43d$
Temperature (K)	300	300	300
Cell parameter (Å)	14.5353 (7)	14.3315 (5)	14.5400(1)
$V$ (Å <sup>3</sup> )	3070.9 (4)	2943.6 (3)	3073.92(6)
Z	4	4	4
Radiation type, $\lambda$ (Å)	Neutron, 0.995	Neutron, 0.995	Neutron, 0.995
$\mu$ (mm <sup>-1</sup> )	0.06	0.07	0.06
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	329, 329, 158	319, 319, 93	401, 401, 112
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.649	0.649	0.700
Refinement $R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.087, 0.308, 1.23	0.180, 0.635, 1.04	0.204, 0.596, 1.02
No. of reflections	329	319	401
No. of parameters	42	42	42
$\Delta\rho_{\min}$ , $\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	-1.01, 1.12	-0.93, 0.74	-1.15, 1.18

**Figure 2.**  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal. Change in the position and the intensity of the standard reflection (4 –6 10).

the crystal due to some kind of deterioration, hence the orientation matrix and cell parameter of the crystal were redetermined. It was observed that the cell parameter had changed to  $a = b = c = 14.3315(5)$  Å. Once no further change in the cell parameter was observed, we recollected the complete data up to  $\sin\theta/\lambda = 0.649$  Å<sup>-1</sup> for the same crystal, details of data collected are given in table 1. In order to ensure that no further deteriorations takes place during data collection, the peak position as well as peak intensity of the standard reflection were monitored every day. Since no significant change either in peak position or peak intensity of the standard reflection was observed, it was concluded that no further deterioration took place while rerecording the data. Figure 3 gives a comparison between

few strong diffraction peaks of the crystal before and after the deterioration. It was found the FWHM for diffraction peak increased after deterioration indicating decrease/change in crystallinity, since sharpness of the diffraction peak is the measure of crystal disorder.

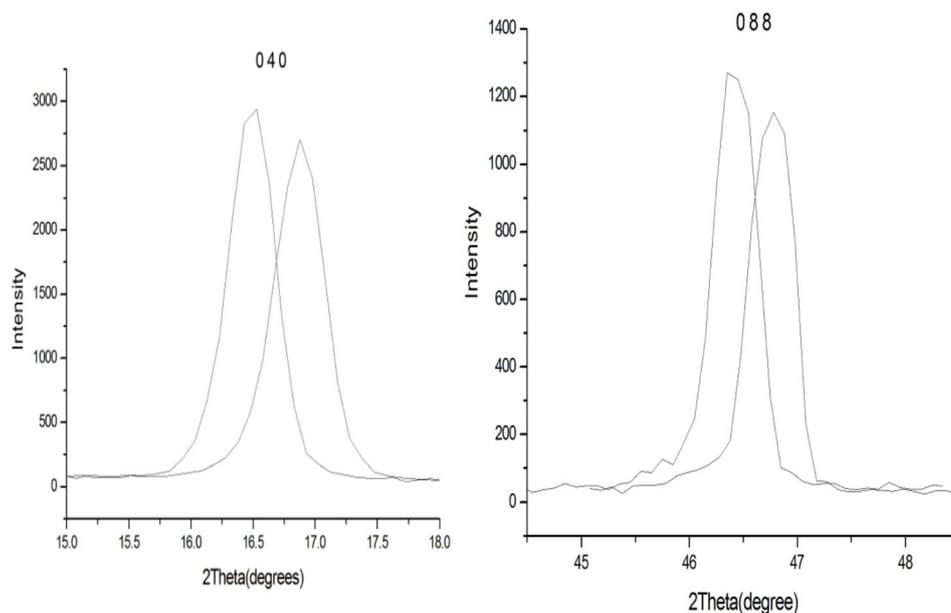
Table 2 shows a comparison between the bond lengths of the  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal before and after the deterioration. It is observed that the Cs–O bond lengths decrease on deterioration, indicating a strengthening of these co-ordinate interactions. An increase in O–H covalent bond length on deterioration indicates that the hydrogen bonds are strengthened after deterioration. Table 3 gives a comparison between the hydrogen bonds of the crystal before and after the deterioration.

### 3. Discussion

In order to understand the deterioration of  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  crystals, one can take clue from the thermal decomposition of  $\text{CsH}_2\text{PO}_4$ , as the two crystals have structural similarities. A systematic study of the thermal decomposition of alkali metal dihydrogen phosphates [12] reported that these undergo complex stepwise dehydration with temperature. The thermal dehydration for  $\text{CsH}_2\text{PO}_4$  occurs at about 500 K, pathway [13] is reported to be as follows:



The transformation from  $\text{H}_2\text{PO}_4$  to  $\text{H}_2\text{P}_2\text{O}_7$  requires removal of  $\text{H}_2\text{O}$  from a pair of hydrogen bonded  $\text{H}_2\text{PO}_4^{1-}$  anions; this step depends directly on the presence of such hydrogen-bonded anionic pairs and also on the strength of the hydrogen bond between the anions [14]. It is found that



**Figure 3.** Comparison between strong diffraction peaks of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  before and after deterioration.

**Table 2.** Comparisons between the bond lengths of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  before and after deterioration.

	Bond lengths			Bond lengths	
	Before deterioration (Å)	After deterioration (Å)		Before deterioration (Å)	After deterioration (Å)
Cs–O3i	3.18 (1)	3.13 (5)	S–O2vii	1.47 (1)	1.45 (3)
Cs–O3ii	3.18 (1)	3.13 (5)	S–O2	1.47 (1)	1.45 (3)
Cs–O1iii	3.23 (1)	3.19 (4)	S–O2xii	1.47 (1)	1.45 (3)
Cs–O1iv	3.23 (1)	3.19 (4)	S–O2ii	1.47 (1)	1.45 (3)
Cs–O1	3.25 (1)	3.17 (3)			
Cs–O1v	3.25 (1)	3.17 (3)			
Cs–O2vi	3.29 (1)	3.27 (4)	O1–Csxi	3.23 (1)	3.19 (4)
Cs–O2vii	3.29 (1)	3.27 (4)	O2–Csxiii	3.29 (1)	3.27 (4)
Cs–O2viii	3.38 (2)	3.32 (5)	O2–Csxiv	3.38 (2)	3.32 (5)
Cs–O2ix	3.38 (2)	3.32 (5)	O3–Csxv	3.18 (1)	3.13 (5)
Cs–Csx	4.481 (2)	4.417 (7)	O3–Csxvi	3.18 (1)	3.13 (5)
Cs–Csiii	4.481 (2)	4.417 (7)	O3–Csxiv	3.18 (1)	3.13 (5)
P–O3	1.48 (3)	1.45 (8)			
P–O1xi	1.52 (1)	1.53 (4)			
P–O1iii	1.52 (1)	1.53 (4)	O1–H	1.05 (3)	1.11 (6)
P–O1	1.52 (1)	1.53 (4)	O2–H	1.50 (2)	1.39 (5)

in both  $\text{CsH}_2\text{PO}_4$  [15] as well as  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  [6], there are hydrogen-bonded chains of  $\text{H}_2\text{PO}_4^{1-}$  ions, which can lose water gradually resulting in the formation of chains of linear polyphosphate. The gradual deterioration of  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  when exposed directly to atmosphere, leading to the complete loss of crystallinity, is most probably due to a process similar to that seen in  $\text{CsH}_2\text{PO}_4$  crystals at elevated temperatures, where  $\text{H}_2\text{O}$  molecule is removed from a pair of hydrogen-bonded  $\text{H}_2\text{PO}_4^{1-}$  anions,

resulting in the formation of polyphosphate  $\text{H}_2\text{P}_2\text{O}_7$ . Decomposition commences at much lower temperatures (RT) in  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  as compared to  $\text{CsH}_2\text{PO}_4$  crystals most likely because of weaker hydrogen bonding between  $\text{H}_2\text{PO}_4^{1-}$  anions in  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  ( $\text{O}\cdots\text{O}$  distance 2.477 Å), as compared to that between  $\text{H}_2\text{PO}_4^{1-}$  anions in  $\text{CsH}_2\text{PO}_4$  ( $\text{O}\cdots\text{O}$  distance 2.464 and 2.521 Å). Similar dehydration and decomposition with increasing temperature is described in literature for some other

**Table 3.** Hydrogen-bond geometry.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O1–H...O2				
Before deterioration	1.05 (2)	1.51 (2)	2.56 (2)	180 (2)
After deterioration	1.11 (5)	1.39 (5)	2.50 (5)	178 (5)
O1–H...S				
Before deterioration	1.05 (2)	2.53 (2)	3.48 (1)	149 (1)
After deterioration	1.11 (5)	2.41 (5)	3.42 (3)	149 (3)

superprotonic compounds like  $K_3H(SO_4)_2$  [16]. At ambient temperature, processes occur (or begin) on the surface of the crystal. Since the deterioration is most likely due to loss of molecules like water from the surface of these crystals, one can perform thermogravimetric analysis (TGA) on these samples to estimate the weight loss in the sample.

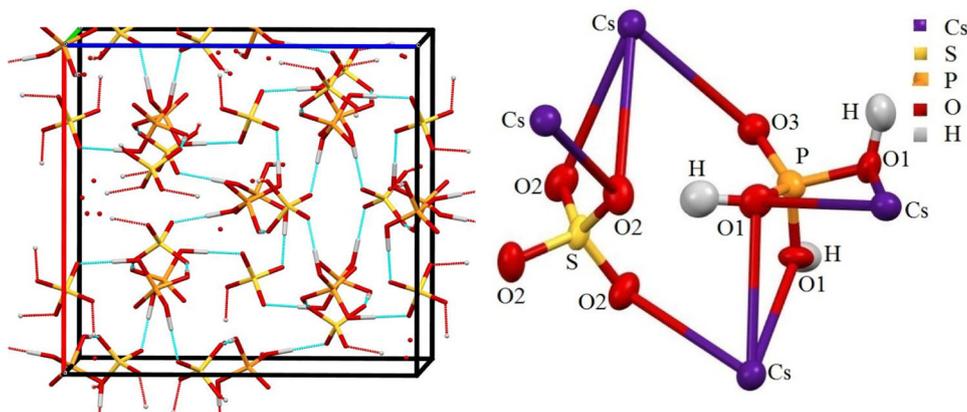
$Cs_6H(HSO_4)_3(H_2PO_4)_4$  is unique among the superprotonic crystals belonging to  $CsHSO_4$ – $CsH_2PO_4$ – $H_2O$  solid solution system, as it is the only crystal that has a cubic structure at room temperature itself. Single-crystal X-ray structure of  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  was reported earlier [7], it was observed that unlike other crystals belonging to this family,  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  crystal has no hydrogen bond between like ions. That is, no hydrogen-bonded  $PO_4$  anionic pairs or hydrogen-bonded  $SO_4$  anionic pairs but instead there is a 3D network of hydrogen bonds between  $PO_4$  and  $SO_4$  ions of this crystal (figure 4a). The structure obtained from neutron diffraction shows that the hydrogen bond between  $PO_4$  and  $SO_4$  ions is asymmetric with H atom lying closer to  $PO_4$  (figure 4b). It is a strong hydrogen bond with significantly elongated O–H covalent bond (table 3), looking at the nearly spherical thermal ellipsoid (figure 4b) of the H atom it can be said that at room temperature there is no disorder of hydrogen atom between the  $PO_4$  and  $SO_4$  ions. This crystal is known to undergo superprotonic structural phase transition at a relatively low temperature of about 390 K.

The observation that O–H...O hydrogen bond between the  $PO_4$  and  $SO_4$  ions is asymmetric is consistent with the pKa equalization rule for strong hydrogen bonds [17], which states that symmetric bonds are possible only when the difference of donor–acceptor acidic constants  $\Delta pK_a$  is zero. For all the other cases, the hydrogen is shifted away from the entity that is more acidic. Since the sulphate ions are more acidic than the phosphates, in a hydrogen bond between the two the hydrogen atom position shifts closer to the phosphate ion. We have used a recently developed Diabatic state model for hydrogen bonds [18, 19] to obtain the energy contour for the O–H...O hydrogen bond of  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  crystal. According to this simple, physically insightful model, the potential energy surfaces are given by the following expression:

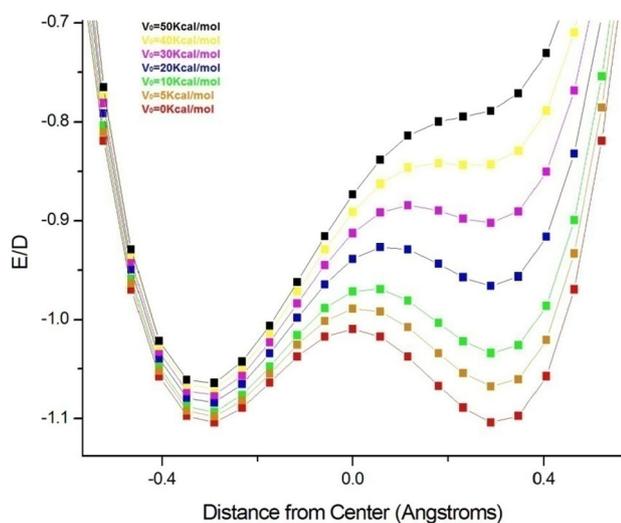
$$\varepsilon \pm (r, R) = \frac{1}{2}[V(r) + V(R-r) + V_0] \pm \frac{1}{2} \left[ (V(r) - V(R-r) - V_0)^2 + 4\Delta(R)^2 \right]^{1/2},$$

here  $R$  represents the O...O distance,  $r$  represents the O–H distance,  $\angle OHO$  is assumed to be  $\approx 180^\circ$ , energies for O–H and H...O bonds are represented by Morse potentials  $V(r)$  and  $V(R-r)$ , respectively. The coupling between the O–H...O and O...H–O diabats is given by  $\Delta(R)$  (detailed expression for  $V(r)$  and  $\Delta(R)$  along with the values of parameters used for calculation are given in Appendix).  $V_0$  here represents the difference between the hydrogen donating powers of donor(X) and acceptor(Y) atoms for a hydrogen bond (X–H...Y). When both donor (X) and acceptor (Y) atoms are identical in all respect  $V_0 = 0$ , the potential energy curve is symmetric and the hydrogen bond is very strong. If X and Y are two different atoms (like: N, F, O, S, etc.), then the hydrogen bond X–H...Y is usually weak and asymmetric,  $V_0$  is expected to have a sizable value for such cases, it was empirically chosen to be  $V_0 = 50 \text{ kcal mol}^{-1}$  for such cases [18]. For the O–H...O hydrogen bond of  $Cs_6H(HSO_4)_3(H_2PO_4)_4$ , both donor as well as acceptor are the same atoms, namely, oxygen atom but as explained earlier they belong to two oxygens with very different acidity. As a result, the O–H...O bond is strong but asymmetric. Hence for this case we expect  $0 < V_0 < 50 \text{ kcal mol}^{-1}$ . Figure 5 shows the energy contours for O–H...O hydrogen bond of  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  with varying  $V_0$  values. For further calculation, we choose  $V_0 = 10 \text{ kcal mol}^{-1}$ . This value gives us a slightly asymmetric strong double well potential with the ground state energy (figure 6) below the second minima, as no hydrogen disorder was observed in the O–H...O bond, we expected the ground state to be the one where H is localized in the deeper well (energy eigenvalues for the double well potentials are calculated using the program FINDIF program [20]).

The abrupt change in the unit cell of  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  during the neutron single-crystal data collection appears to be due to surface deterioration, most likely triggered by change in the ambient humidity during experiments. Fact that the crystal retained its crystallinity after initial deterioration indicates towards the possibility of bulk rearrangement of intermolecular interactions, leading to a new stable structure. Our neutron diffraction

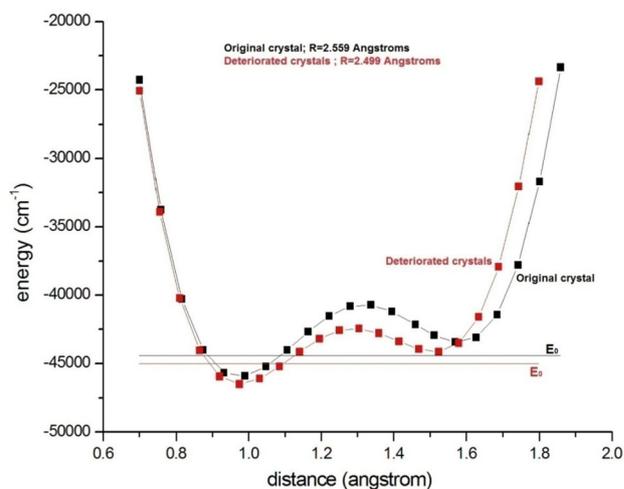


**Figure 4.** (a) Hydrogen bonding in  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$ . (b) Asymmetric unit of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$ .



**Figure 5.** Energy contours for O–H...O hydrogen bond of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  with varying  $V_0$  values.

investigation on  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal after deterioration showed although the overall structure remained the same, co-ordinate bonds between the  $\text{Cs}^+$  ion and surrounding oxygen atoms became stronger and also the hydrogen bond (table 3) between  $\text{PO}_4$  and  $\text{SO}_4$  ions was significantly strengthened. This change in hydrogen bond strength led to the shrinkage of the unit cell and most likely prevented further deterioration. Since there are no hydrogen bonded  $\text{PO}_4$  anionic pairs in  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal, the deterioration pathway for this crystal will be different than that in  $\text{CsH}_2\text{PO}_4$  or  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  crystals discussed earlier. Instead of loss of water, it can be the loss of some other small molecule like the  $\text{H}_3\text{PO}_4$  molecule from the surface that can lead to the initial deterioration observed in these crystals, in order to confirm this one can perform TGA on these crystals. Diabatic state model for hydrogen bonds was once again used to obtain the energy contour for



**Figure 6.** Comparison between the energy contours for O–H...O hydrogen bond of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  before and after deterioration.

the O–H...O hydrogen bond of deteriorated  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal (figure 6).

A comparison between the energy contours for the O–H...O hydrogen bond before and after deterioration indicates that as the O...O distance shrinks, the energy barrier ( $E_{\text{intra}}$ ) between the two minima of the hydrogen bond potential reduces from  $10.6 \text{ kcal mol}^{-1}$  for the original crystal to  $7.3 \text{ kcal mol}^{-1}$  for the deteriorated one. There is an overall strengthening of the hydrogen bond on deterioration as indicated by the decrease in the ground state energy eigenvalue from  $-126.9$  to  $-128.6 \text{ kcal mol}^{-1}$ . The reduction in the potential barrier height ( $E_{\text{intra}}$ ) makes the first step for proton diffusion, namely, proton transfer between the two minima of hydrogen bond easier. However, strengthening the O–H...O hydrogen bonds makes the second step, namely, breaking of hydrogen bond O...H–O more difficult. Hence, the resultant effect of deterioration on proton diffusion will depend on which of these two

above-mentioned changes predominates. The literature data [1] showed that for O–H···O hydrogen bonds with O···O distance, approximately 2.65 Å, the two energies  $E_{\text{inter}}$  as well as  $E_{\text{intra}}$  are comparable. For hydrogen bonds with O···O distance less than 2.65 Å, effect of  $E_{\text{inter}}$  is more pronounced, whereas for hydrogen bonds with O···O distance more than 2.65 Å  $E_{\text{intra}}$  is the deciding factor. According to the above-mentioned criterion, for the  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  crystal the effect of strengthening of the hydrogen bonds will have more pronounced effect on proton diffusion and proton conductivity.

#### 4. Conclusion

Single-crystal neutron diffraction investigation on  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals belonging to  $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4\text{--H}_2\text{O}$  solid solution system revealed that these crystals are very sensitive to the ambient conditions and can undergo deterioration due to changes in ambient conditions like air humidity. Our experiments show that under ambient conditions  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals are more stable as compared to  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ . It was seen that  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  lost its crystalline quality over a span of few days, without defenses from air humidity. Crystal deterioration pathway for  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  is expected to be similar to that observed in  $\text{CsH}_2\text{PO}_4$  at elevated temperatures, since both these crystals have chains of hydrogen bonded  $\text{H}_2\text{PO}_4^{1-}$  anions that can lose water gradually resulting in the formation of chains of linear polyphosphates. Deterioration commences at much lower temperatures in  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  as compared to  $\text{CsH}_2\text{PO}_4$  crystals, because of weaker hydrogen bonding between  $\text{H}_2\text{PO}_4^{1-}$  anions in  $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$  as compared to  $\text{CsH}_2\text{PO}_4$ .

The abrupt change in the unit cell of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  during the neutron single-crystal data collection appears to be due to surface deterioration, most likely triggered by change in the ambient humidity during experiments. The crystal retained its crystallinity after initial deterioration, indicating bulk rearrangement of intermolecular interactions. Crystal structure of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  both before and after the deterioration were compared. It was revealed that deteriorated  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal had stronger hydrogen bonding between  $\text{PO}_4$  and  $\text{SO}_4$  anions as compared to original sample, this led to the shrinkage of the unit cell, and most likely prevented further deterioration. The change in the hydrogen bonding is expected to affect the overall proton conductivity of the crystal.

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#### Appendix: Diabatic state model for H-bonding

According to the diabatic model the O–H···O hydrogen bond can be represented by two interacting diabatic states  $|\text{O–H}\cdots\text{O}\rangle$  and  $|\text{O}\cdots\text{H–O}\rangle$ . The effective Hamiltonian describing the two interacting diabatic states has the form

$$H = \begin{pmatrix} V(r) & \Delta(R) \\ \Delta(R) & V(R-r) + V_0 \end{pmatrix}$$

Here  $r$  and  $R$  are the O–H and O–O distances, respectively, and  $r_0$  is the equilibrium free O–H distance of 0.96 Å.  $V_0$  is the vertical off set to take into account the asymmetry of the O–H···O hydrogen bond.  $V(r)$  is Morse potential for O–H bond with a depth ( $D$ ) of 120 kcal mol<sup>-1</sup>, exponential parameter  $a$  of 2.2 Å<sup>-1</sup>, corresponding to O–H stretch harmonic frequency of 3600 cm<sup>-1</sup>.

$$V(r) = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}]$$

The coupling between the diabats  $|\text{O–H}\cdots\text{O}\rangle$  and  $|\text{O}\cdots\text{H–O}\rangle$  is given by  $\Delta(R)$  defined as

$$\Delta(R) = \Delta_1 \exp[-b(R-R_1)]$$

This model has essentially two free parameters  $b$  and  $\Delta_1$ . The parameter values used here are,  $\Delta_1 = 0.4D \approx 2$  eV and  $b = 2.2$  Å<sup>-1</sup>.  $R_1$  is a reference distance that is taken as  $R_1 = 2r_0 + 1/a \approx 2.37$  Å.

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