Superprotonic conductivity in $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_x$(P,S)O$_4$)

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Abstract

Investigations of the system CsHSO$_4$–CsH$_2$PO$_4$ led to discovery of the new compound, $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_x$(P,S)O$_4$), with a superprotonic phase transition at 125°C. The room temperature structure of $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_x$(P,S)O$_4$) is related to that of $\alpha$-Cs$_3$(HSO$_4$)$_2$(H$_x$PO$_4$) and that of CsSO$_4$·II. It is unique, however, in that P and S occupy the same crystallographic position in the structure, and there is accordingly a variable H content and a partially occupied hydrogen bond. This leads to room temperature conductivity that is significantly higher than either of the two related compounds. The conductivity in the high temperature phase is comparable to that of CsHSO$_4$·I. Furthermore, the transition exhibits a relatively large heat of 30 J g$^{-1}$ and some hysteresis. These are explained by probable disordering between S and P sites upon transition to the superprotonic state.

Keywords: Superprotonic phase transition; Protonic conductivity; Disordered hydrogen bond network

Materials: Cesium; Hydrogen; Sulfate; Phosphate

1. Introduction

Superprotonic phase transitions are known to occur in a number of solid acid sulfates and selenates. These include the prototype compounds CsHSO$_4$ [1] Rb$_2$H(SeO$_4$)$_3$ [2] and Cs$_3$H$_2$(SeO$_4$)$_4$·xH$_2$O [3]. Despite the large number of studies conducted on MHXO$_4$, M$_3$H(XO$_4$)$_2$ and M$_4$H$_3$(XO$_4$)$_4$ compounds (where M = alkali metal or ammonium group, and X = S, Se), no general model describing which materials will undergo a superprotonic phase transition seems to exist. This is in stark contrast to the situation with ferroelectric transitions, in which the presence of locally disordered hydrogen bonds at room temperature is recognized as a structural feature that often leads to ferroelectric behavior at low temperatures [4].

We have recently proposed a model that identifies the presence of oxygen atoms with different hydrogen-bond environments (at room temperature) as a key prerequisite for superprotonic behavior at elevated temperatures [5]. In this model, entropic considerations, that favor chemically equivalent bonds, drive a transition to a disordered state, and it is precisely this disorder that leads to superprotonic conductivity.

In order to test and refine this model and to quantify the influence of chemical and structural features of hydrogen-bonded solids, such as the presence of disordered hydrogen bonds, the dimensionality of the hydrogen-bonded network, the pres-
ence of proton 'intersitials' and/or 'vacancies', and the chemical nature of the XO₄ anion on superprotonic behavior, we have undertaken a study of the CsHSO₄–CsH₂PO₄ system. This particular system has been selected because (1) CsHSO₄ is a well-characterized material with a superprotonic transition at 141°C [1]; (2) the chemical similarity between S and P and the structural similarity between CsHSO₄ and CsH₂PO₄ (at room temperature [6,7]) suggests that any compound within this system, including the end-members, should exist over a significant composition range, and hence the proton content should be subject to control via control of the stoichiometry; and (3) the fact that CsHSO₄ and CsH₂PO₄ are, despite their similarities, not isostructural precludes complete solid solubility and suggests that new intermediate compounds should exist. In this case, control of the H: XO₄ ratio provides control of the overall hydrogen-bonding scheme.

2. Experimental

Aqueous solutions of Cs₂CO₃, H₂SO₄ and H₃PO₄ were prepared such that the Cs to total XO₄ ratio was 1:1, while the SO₄:PO₄ ratio was varied from 0 to 1 in increments of 0.1 (in some cases, increments of 0.05 were examined). Crystals were grown from each solution by slow evaporation of H₂O at room temperature.

The structures of crystals so obtained were determined by single crystal X-ray techniques. Hydrogen-bonded oxygen atoms were identified on the basis of bond length considerations, rather than from a refinement of proton positions from X-ray data. Bonding considerations were also utilized to distinguish between S and P sites.

Chemical analysis was performed by energy dispersive spectroscopy (EDS). Characteristic peak intensities were measured with a JEOL Superprobe 733 and converted into mass per cent using the Tracor Northern analytical software. The following materials were used as standards: CsHSO₄, CsH₂PO₄ and α-Cs₃(HSO₄)₂(H₃(P,S)O₄).

The electrical properties of single crystals of β-Cs₃(HSO₄)₂(H₃(P,S)O₄) were measured by A.C. impedance techniques. For this, an HP 4284A LCR meter was employed. The applied voltage was 100 mV and the frequency range was 20 Hz to 1 MHz. Silver paint served as the electrode material, and samples were examined in both ambient air and flowing, dry argon atmospheres. Data were collected both upon heating and cooling samples; the heating rate was approximately 10°C h⁻¹.

Thermal analytical techniques were employed to further characterize phase transitions. Differential scanning calorimetry (DSC) was performed with a Netzsch DSC 200 in the temperature range -120 to 180°C at a heating rate of 5°C min⁻¹ in a flowing nitrogen atmosphere. Combined differential thermal analysis and thermal gravimetric analysis (DTGA) was carried out utilizing a Netzsch STA 409 cell. Samples were again heated at a rate of 5°C min⁻¹ in flowing nitrogen.

3. Results and discussion

Three intermediary sulfate–phosphate compounds were unambiguously identified in the CsHSO₄–CsH₂PO₄ system. These, as well as the solution compositions from which they were obtained, are listed in Table 1. The compound that is the subject of the present report, β-Cs₃(HSO₄)₂(H₃(P,S)O₄), was grown from solutions containing 15–20 mole% H₂PO₄ (with respect to the total acid content). Chemical analysis (by EDS) of multiple crystals, examined at multiple beam positions, yielded a

<table>
<thead>
<tr>
<th>Solution composition, (H₃PO₄)</th>
<th>Compound(s) obtained</th>
</tr>
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<tbody>
<tr>
<td>0–10</td>
<td>CsHSO₄</td>
</tr>
<tr>
<td>15–20</td>
<td>β-Cs₃(HSO₄)₂(H₃(P,S)O₄)</td>
</tr>
<tr>
<td>30–40</td>
<td>α-Cs₃(HSO₄)₂(H₃PO₄)²+Cs₂SO₄</td>
</tr>
<tr>
<td>50–60</td>
<td>α-Cs₃(HSO₄)₂(H₃PO₄)⁻+Cs₂SO₄</td>
</tr>
<tr>
<td>70–100</td>
<td>CsH₂PO₄</td>
</tr>
</tbody>
</table>

In Refs. [5,8] this compound was referred to simply as Cs₃(HSO₄)₂(H₃PO₄). In the present report it is given the designation α because of its structural and chemical similarities to β-Cs₃(HSO₄)₂(H₃(P,S)O₄).
Cs$_2$(PO$_4$ + SO$_4$) mole ratio of 1.01(2), whereas the SO$_4$:PO$_4$ mole ratio was 4.2(3). The variation in the latter value was significant, ranging from a low of 3.8 to a high of 4.5.

Preliminary X-ray results show that $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_2$(P$_2$SO$_4$) crystallizes in space group C2/c with lattice parameters $a = 20.04(1)$, $b = 7.854(5)$, $c = 8.954(5)$ Å and $\beta = 100.11(2)^\circ$ [11]. Its structure is very similar to that of $\alpha$-Cs$_3$(HSO$_4$)$_2$(H$_2$PO$_4$) (with space group P2$_1$/n and lattice parameters $a = 19.546(3)$, $b = 7.8798(19)$, $c = 9.185(2)$ Å and $\beta = 100.534(14)^\circ$ [8]) and of Cs$_2$HSO$_4$-II [9]. All three structures contain zig-zag chains of XO$_4$ anions and of Cs cations. These chains are arranged in a checkerboard fashion, as shown in Fig. 1, a projection of the structure of $\beta$ along [010]. In Fig. 2 the structures of the $\alpha$ and $\beta$ phases are compared in a projection on the (101) plane.

Despite their similarities, the $\alpha$ and $\beta$ structures are distinct both in terms of the location and quantity of phosphorus and in terms of their hydrogen-bond networks. The compound $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_2$(P$_2$SO$_4$) contains less phosphorus (and accordingly has a lower proton content) than $\alpha$-Cs$_3$(HSO$_4$)$_2$(H$_2$PO$_4$). This lower phosphorus content is reflected in the fact that the site that is completely occupied by P in $\alpha$ has a random distribution of P and S in $\beta$. On the basis of the macroscopic chemical analysis, the average phosphorus occupancy at this site is estimated at $\frac{1}{3}$. With respect to the hydrogen-bond network, all O–H...O bonds observed in $\alpha$ are also found in $\beta$, with the exception of the bond between neighboring SO$_4$ groups along the XO$_4$ chain. In $\alpha$, these SO$_4$ groups are crystallographically distinct and are linked by a single, fully occupied, hydrogen bond. In $\beta$, neighboring SO$_4$ groups are related by a center of symmetry and are hence crystallographically equivalent. The higher symmetry leads to the situation in which placement of a hydrogen bond between one pair of oxygen atoms, O(5) and O(6), linking the two sulfate anions must be accompanied by a second hydrogen bond between a related pair of oxygen atoms, O(5') and O(6'), that links the same two sulfate anions. Fig. 2. This, combined with the long oxygen–oxygen separation of 3.16(1) Å and the lower proton content in $\beta$ relative to $\alpha$, implies that the proton occupancy at the weak O(5)–O(6) hydrogen bond must be much less than one. On the basis of the chemical analysis, it is estimated at $\frac{3}{10}$. It is noteworthy that a similar hydrogen-bonding geometry, in which two SO$_4$ groups are weakly linked by two, partially occupied hydrogen bonds to form a cyclic dimer, has been observed in $\alpha$-NaHSO$_4$ [10].

The mixed site occupancy of S and P gives rise to some flexibility in the composition of $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_2$(P$_2$SO$_4$) and renders this compound unique amongst the three intermediate compounds identified to date in the CsHSO$_4$–CsH$_2$PO$_4$ system. In both $\alpha$ [8] and Cs$_2$S$_x$(HSO$_4$)$_{2y}$(H$_2$PO$_4$)$_z$ [11] P and S reside on crystallographically distinct sites, and no variability in their respective compositions appears possible.

The conductivity of $\beta$-Cs$_3$(HSO$_4$)$_2$(H$_2$(P$_2$SO$_4$), measured in two heating and cooling cycles is shown in Fig. 3. Data for the first cycle were collected in ambient air and those for the second in flowing, dry argon. The choice of atmosphere has apparently little effect on the measured conductivity, as demonstrated by the equivalence of the two sets of data collected on cooling. In Fig. 4, the conductivity of $\beta$ is
compared with that of \( \alpha \) and of CsHSO\(_4\). The DSC data are shown in Fig. 5.

The results shown in Fig. 3 clearly demonstrate that the new compound \( \beta \)-Cs\(_4\)(HSO\(_4\))\(_2\)(H\(_2\)PO\(_4\)) undergoes a superprotonic transition. Upon heating a fresh sample, the transition occurs at 125\(^{\circ}\)C and is accompanied by an increase in conductivity of 2\( \frac{1}{2} \) orders of magnitude. Upon cooling, the reverse transition exhibits some hysteresis, and, furthermore, appears to take place via a two-step process. It is unclear what phase forms upon cooling from the high-temperature, superprotonic phase. Upon reheating, the forward transition also appears to take place via a two-step process. The thermal analysis revealed a transition upon heating at 140\(^{\circ}\)C, with a heat of transition of 30 J g\(^{-1}\). The observation of a slightly higher transition temperature by thermal techniques than obtained from conductivity measurements is likely to be an artifact resulting from the difference in heating rates used in the two types of experiments. A similar effect was observed when investigating \( \alpha \)-Cs\(_4\)(HSO\(_4\))\(_2\)(H\(_2\)PO\(_4\)) [5]. The DTGA data, also collected at a relatively high heating rate, confirmed the presence of a transition at approximately 140\(^{\circ}\)C, and revealed the onset of thermal decomposition at 190\(^{\circ}\)C. The properties associated with the super-
protonic phase transition in the present compound are compared with those of α and CsHSO₄ in Table 2.

From the results presented in Fig. 4 and Table 2, one can draw a number of conclusions. The superprotonic transition in both the mixed compounds takes place at 125°C, a value about 15°C lower than observed in CsHSO₄-I. The driving force for the transition appears then to be greater in the mixed compounds. The entropy of the transition in the mixed compounds is significantly higher than in the end-member sulfate, although neither mixed compound has a conductivity in the superprotonic state that is higher than that of CsHSO₄. This, combined with the significant hysteresis, suggests that P and S disorder accompanies the transition, adding to the entropy without raising the conductivity beyond that observed in CsHSO₄-I. Upon cooling, ordering of these atoms would be expected to be sluggish, resulting in the observed hysteresis. Notice that the heat of transformation and hysteresis are greatest, while the high temperature conductivity is lowest in α, the compound containing the greater fraction of P and for which P and S are completely ordered in the room temperature structure.

The conductivity of β-Cs₄(HSO₄)₂(H₂(PS)O₄) in the high temperature phase is comparable to that of
CsHSO₄-I, suggesting that the high temperature structures are similar. While the structure of the superprotonic phase of α-Cs₂(H₂O)(H₂PO₄) has yet to be determined, X-ray powder diffraction measurements have shown it to be distinct from CsHSO₄-I [8]. The low temperature conductivity of β-Cs₂(H₂SO₄)₂(H₂PSO₄) is significantly higher than that of either α-Cs₂(H₂SO₄)₂(H₂PO₄) or CsHSO₄, about one order of magnitude greater than that of the former and two orders of magnitude greater than that of the latter. The difference in low temperature properties surely results from the partially occupied hydrogen bond found in β. The end-member sulfate has fully occupied, asymmetric (ordered) bonds in phase III, whereas α has both ordered and locally disordered hydrogen bonds, but no bonds that contain fewer than one proton.

The fact that β-Cs₂(H₂SO₄)₂(H₂PSO₄) undergoes a superprotonic phase transition supports our earlier model [5] that the presence of ‘chemically inequivalent’ oxygen atoms, as would be found whenever H₂XO₄ ≠ 2, drive the superprotonic phase transition. On the other hand, it is evident that the chemistry of phosphorous (and presumably that of arsenic as well) does not prevent superprotonic transitions. Furthermore, the dimensionality of the overall hydrogen-bonded network appears to have little influence on the presence or absence of a transition: CsHSO₄-II has a one-dimensional structure (SO₄ groups linked into chains), α has a three-dimensional structure (XO₄ chains cross-linked at PO₄ sites), β has a weak three-dimensional structure (XO₄ sheets weakly linked at SO₄ groups) and M₄H(XO₄)₂ compounds have a zero-dimensional structure (SO₄ or SeO₄ groups linked to form pairs).

4. Summary

The new compound β-Cs₂(H₂SO₄)₂(H₂PSO₄) is structurally related to α-Cs₂(H₂SO₄)₂(H₂PO₄), a recently reported superprotonic conductor [5,8]. Despite their similarities, the two compounds differ in subtle but significant features. Unlike α-Cs₂(HSO₄)₂(H₂PO₄), the present compound contains an XO₄ site that is randomly occupied by both PO₄ and SO₄ groups, it accommodates a variable H content, and it has a partially occupied hydrogen bond. This last trait leads to a relatively high conductivity at room temperature. The compound undergoes a superprotonic transition at 125°C, at which the conductivity jumps from 2×10⁻⁵ to 6×10⁻³ Ω⁻¹ cm⁻¹. The conductivity in the high temperature phase is comparable to that of CsHSO₄-I. The transition exhibits a relatively large heat of 30 J g⁻¹ and shows some degree of hysteresis. These are explained by probable disordering between S and P sites upon transition to the high temperature phase, which would add to the heat of the transition and slow the reverse transformation, without increasing the conductivity in the high temperature phase beyond that observed in CsHSO₄-I. Moreover, because the molar ratio of PO₄ to SO₄ is not fixed by the crystal structure, it may be possible to precisely tune the electrical properties of β-Cs₂(HSO₄)₂⁻(H₂PSO₄) via control of the stoichiometry.

The presence of a superprotonic transition in β-Cs₂(HSO₄)₂(H₂PSO₄) reveals that the chemistry of phosphorous by no means precludes such transitions. Furthermore, the dimensionality of the hydrogen-bonded network appears to have little bearing on the presence or absence of superprotonic transitions.
On the other hand, the properties of \( \beta\)-Cs\(_4\)(HSO\(_4\))\(_2\)(H\(_4\)(P,S)O\(_4\)) support our earlier model in which the presence of ‘chemically inequivalent’ oxygen atoms (distinguished in terms of their participation in hydrogen bonding) drive the transition into a state of disorder, which results in chemically equivalent oxygen atoms and, simultaneously, superprotonic conductivity.

References