TRANSPORT AND STRUCTURAL PROPERTIES OF (1-x)CsHSO₄-xKH₂PO₄ MIXED COMPOUNDS

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Solid acids

$M_n H_m (AO_4)_p$

$M=$Cs, Rb, K, NH$_4$; $A=$S, Se, P, As

CsHSO$_4$ shows one of the highest proton conductivity among the compounds of the family. However, its conductivity decreases drastically at 141°C because of structural phase transition.
The aim of this work is to investigate transport, thermal and structural properties of (1-x)CsHSO₄-xKH₂PO₄ compounds, substituted in cation and anion sublattice in large range of molar ratio (x=0.05-0.97)

Structure of presentation:

1. Transport, thermal and structural properties of (1-x)CsHSO₄-xKH₂PO₄ compounds with x≤0.5 – region 1
2. Transport, thermal and structural properties of (1-x)CsHSO₄-xKH₂PO₄ compounds with x≥0.5 - region 2
3. Influence of small amounts of CsHSO₄ on conductivity of KH₂PO₄
Structure of CsHSO₄

Phase III: 76°C
P2₁/m monoclinic

Phase II: 141°C
P2₁/c monoclinic

Phase I: I4₁/amd tetragonal

Lattice parameters:
Phase III: a=8.223, b=5.814, c=10.990Å, β=119.4°
Phase II: a=7.729, b=8.092, c=7.668Å, β=110.9°
Phase I: a=5.729, c=14.21Å

σ~2*10⁻² S/cm

Structure of $\text{KH}_2\text{PO}_4$ (KDP)

Phase II
- $I4_2d$
- Tetragonal

190°C

Phase I
- $P2_1/m$
- Monoclinic

Lattice parameters:
- Phase II: $a=7.460$; $c=6.982$ Å
- Phase I: $a=7.590$; $b=6.209$; $c=4.530$ Å $\beta=107.361$

# Phase composition of a (1-x)CsHSO$_4$-xKH$_2$PO$_4$ system

<table>
<thead>
<tr>
<th>$x$</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>CsHSO$_4$</td>
</tr>
<tr>
<td>0.1</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$ + CsHSO$_4$</td>
</tr>
<tr>
<td>0.2</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$</td>
</tr>
<tr>
<td>0.3</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$</td>
</tr>
<tr>
<td>0.4</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$ + CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.5</td>
<td>CsH$_5$(PO$_4$)$_2$ + Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$ + K$_2$(HSO$_4$)(H$_2$PO$_4$)</td>
</tr>
<tr>
<td>0.6</td>
<td>CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.7</td>
<td>CsH$_5$(PO$_4$)$_2$ + KH$_2$PO$_4$</td>
</tr>
<tr>
<td>0.8</td>
<td>KH$_2$PO$_4$ + CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.9</td>
<td>KH$_2$PO$_4$ + CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>1</td>
<td>KH$_2$PO$_4$</td>
</tr>
</tbody>
</table>

- **Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$** (C2/c)
- **CsH$_5$(PO$_4$)$_2$** (P2$_1$/c)
XRD patterns for (1-x)CsHSO₄-xKH₂PO₄ (x≤0,5)

<table>
<thead>
<tr>
<th>x</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,5</td>
<td>CsH₅(PO₄)₂⁺</td>
</tr>
<tr>
<td></td>
<td>Cs₃(HSO₄)₂H₂PO₄⁺</td>
</tr>
<tr>
<td></td>
<td>K₂(HSO₄)(H₂PO₄)</td>
</tr>
<tr>
<td>0,4</td>
<td>Cs₃(HSO₄)₂H₂PO₄</td>
</tr>
<tr>
<td></td>
<td>+CsH₅(PO₄)₂</td>
</tr>
<tr>
<td>0,3</td>
<td>Cs₃(HSO₄)₂H₂PO₄</td>
</tr>
<tr>
<td>0,2</td>
<td>Cs₃(HSO₄)₂H₂PO₄</td>
</tr>
<tr>
<td>0,1</td>
<td>Cs₃(HSO₄)₂H₂PO₄</td>
</tr>
<tr>
<td></td>
<td>+CsHSO₄</td>
</tr>
</tbody>
</table>

XRD patterns for (1-x)CsHSO₄-xKH₂PO₄ (x≤0,5)
Conductivity of \((1-x)\text{CsHSO}_4-x\text{KH}_2\text{PO}_4\) compounds \((x \leq 0.5)\)

- Increase of low-temperature (LT) conductivity for 2-3 orders of magnitude for \(x=0.05-0.5\)

- Phase transition shifts to the LT region for \(~30^\circ C\) for \(x=0.3–0.5\)

- High temperature (HT) conductivity and its \(E_a\) of compounds still similar to \(\text{CsHSO}_4\) \((10^{-2} \text{ S/cm}, T=200^\circ C, E_a\sim0.3\text{eV})\)
Schematic structure of different phases of $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$

$\alpha$-Cs$_3$(HSO$_4$)$_2$(H$_2$PO$_4$)

P2$_1$/n

a=19.54(6) Å
b=7.87(98) Å
c=9.18(54) Å
β=100.53(4)°

$T_{SPT}$=137°C

$\beta$-Cs$_3$(HSO$_4$)$_2$(H$_2$-x(P$_{1-x}$S$_x$)O$_4$), (x~0.5)

C2/c

a=20.04(1) Å
b=7.854(5) Å
c=8.954(5) Å
β=100.11(2)°

$T_{SPT}$=125°C

Lattice parameters for Cs$_{0.67}$K$_{0.33}$(HSO$_4$)$_{0.67}$(H$_2$PO$_4$)$_{0.33}$ (C2/c)

a=19.799(9) Å, b=7.826(6) Å, c=9.035(2) Å, β=100.3(88)°, Z= 4

Conductivity and structural properties of $Cs_{0.67}K_{0.33}(HSO_4)_{0.67}(H_2PO_4)_{0.33}$

C2/c

a=19.7999(7) Å, b=7.8266(3) Å, c=9.0352(5) Å

$\beta =100.388(14)^\circ$, Z= 4;

The conductivity of $Cs_{0.67}K_{0.33}(HSO_4)_{0.67}(H_2PO_4)_{0.33}$ exceeds conductivity of $\beta$-$Cs_3(HSO_4)_2(H_2-x(P_{1-x}S_x)O_4)$ in low-temperature region due to greater degree of structural disordering.

XRD patterns for (1-x)CsHSO₄-xKH₂PO₄ (x≥0.5)

<table>
<thead>
<tr>
<th>X</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>KH₂PO₄+CsH₅(PO₄)₂</td>
</tr>
<tr>
<td>0.8</td>
<td>KH₂PO₄+CsH₅(PO₄)₂</td>
</tr>
<tr>
<td>0.7</td>
<td>CsH₅(PO₄)₂+KH₂PO₄</td>
</tr>
<tr>
<td>0.6</td>
<td>CsH₅(PO₄)₂</td>
</tr>
<tr>
<td>0.5</td>
<td>CsH₅(PO₄)₂+Cs₃(HSO₄)₂(H₂PO₄)+K₂(HSO₄)(H₂PO₄)</td>
</tr>
</tbody>
</table>

Δ - KH₂PO₄  
* - Cs₃(HSO₄)₂(H₂PO₄)
Structure of CsH$_5$(PO$_4$)$_2$

CsH$_5$(PO$_4$)$_2$ has a layered structure with strong three-dimensional hydrogen-bond network, that restrains H-transfer process. The conductivity of the compound is rather low (10$^{-8}$–10$^{-4}$ S/cm at 90–145 °C) with a high apparent activation energy (E$_a$ =1.6–2.0 eV).

P2$_1$/c
a=10.879 Å  
b=7.768 Å  
c=9.526 Å  
β=96.60°

$T_{\text{melting}}$=152 °C

G.V. Lavrova, E.B.Burgina, A.A.Matvienko, V.G.Ponomareva
Solid State Ionics 177 (2006), 1117-1122
The temperature dependence of conductivity for (1-x)CsHSO\(_4\)-xKH\(_2\)PO\(_4\) (x>0.5)

- The conductivity and activation energy for the samples with x = 0.6–0.9 are close to the ones for CsH\(_5\)(PO\(_4\))\(_2\) (E\(_a\)~1eV,)

- Conductivity dependencies for x = 0.7–0.9 are similar and values slightly depend on KH\(_2\)PO\(_4\) content

- Insignificant increase of activation energy for these compounds can be induced by K\(^+\) or small amounts of KH\(_2\)PO\(_4\) phase along with CsH\(_5\)(PO\(_4\))\(_2\)

G.V. Lavrova, E.B. Burgina, A.A. Matvienko, V.G. Ponomareva
IR spectroscopy ($x>0.5$)

graph showing absorbance vs. wavenumber for different compositions of CsH$_5$(PO$_4$)$_2$ with $x=0.6, 0.7, 0.8, 0.9, 1$

- Hydrogen bonds
- SO$_4$ and PO$_4$ tetrahedrons
Thermal behavior

CsH$_5$(PO$_4$)$_2$
- $T_{ph.tr.} \sim 130^\circ C$
- $T_{melt} \sim 152^\circ C$

Cs$_3$(HSO$_4$)$_2$(H$_2$PO$_4$) (C2/c)
- $T_{ph.tr.} \sim 125^\circ C$
- $T_{melt} \sim 210^\circ C$
Conductivity isotherm and phase composition of \((1-x)\text{CsHSO}_4-x\text{KH}_2\text{PO}_4\) system
Influence of small CsHSO$_4$ amounts ($x \leq 0.07$) on conductivity of KDP

- The character of conductivity for $x = 0.93-0.97$ is compared more with KH$_2$PO$_4$

- Conductivity increases for ~2 orders of magnitude for $x = 0.93-0.97$
Reason for increase of proton conductivity

- The same phase of KH$_2$PO$_4$ exist

- $\sigma = N \cdot \mu \cdot eZ$

N – number of mobile particles in the unit of volume
$\mu$ – particle mobility
$eZ$ – ion charge

The substitution produces the vacant crystallographic sites that results in the hydrogen bond weakening. The number of vacant proton crystallographic sites exceeds the number of proton, this facilitates reorientation of the oxyanion tetrahedrons.
Conclusions

• The compounds substituted by cations and anions in the \((1-x)\text{CsHSO}_4-x\text{KH}_2\text{PO}_4\) system \((x=0.05–0.95)\) have been synthesized and their phase composition, transport characteristics and thermal properties have been investigated.

• The addition of \(\text{KH}_2\text{PO}_4\) to \(\text{CsHSO}_4\) \((x=0.05–0.5)\) results in formation of new highly disordered phase with \(\text{Cs}_3(\text{HSO}_4)_2\text{H}_2\text{PO}_4\) \((\text{C2/c})\) structure. \(\text{K}^+\)-containing compounds with \(\text{Cs}_3(\text{HSO}_4)_2\text{H}_2\text{PO}_4\) structure exist at \(x=0.05–0.5\) and are characterized by the lower temperature of superprotonic phase transition. LT conductivity of \((1-x)\text{CsHSO}_4-x\text{KH}_2\text{PO}_4\) mixed compounds \((x=0.05–0.5)\) depends on the composition and exceeds over 2–3 orders of magnitude parent salts.

• Increasing \(x\) up to 0.6–0.9 results in formation of another new phase with \(\text{CsH}_5(\text{PO}_4)_2\) \((\text{P2}_1/\text{c})\) crystalline structure and relatively low thermal stability, low proton conductivity and high activation energy comparable with \(\text{CsH}_5(\text{PO}_4)_2\).

• Small amounts of \(\text{CsHSO}_4\) added lead to the significant increase of proton conductivity of \(\text{KH}_2\text{PO}_4\) \((\text{for} \sim 3\ \text{orders of magnitude})\).
Thank You!
\[ 0.7\text{CsHSO}_4 + 0.3\text{KH}_2\text{PO}_4 = \text{Cs}_{0.7}\text{K}_{0.3}(\text{HSO}_4)_{0.7}(\text{H}_2\text{PO}_4)_{0.3} \]

\[ \text{Cs}_{2.3}\text{K}(\text{HSO}_4)_{2.3}(\text{H}_2\text{PO}_4) \]

\[ \text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4) \]

\[ 0.3\text{CsHSO}_4 + 0.7\text{KH}_2\text{PO}_4 = \text{Cs}_{0.3}\text{K}_{0.7}(\text{HSO}_4)_{0.3}(\text{H}_2\text{PO}_4)_{0.7} \]

The formation of \( \text{CsH}_5(\text{PO}_4)_2 \) can be associated with surface phase containing absorbed water due to hygroscopicity of \( \text{KH}_2\text{PO}_4 \).
K₂(HSO₄)(H₂PO₄)

- $P_2/n$ $a$ (Å) = 7.434
  - $b$ (Å) = 7.341
  - $c$ (Å) = 7.148
  - $\beta$ (Å) = 99.56
  - Vol. = 384.7
  - $Z = 2$

- $T_{\text{melt.}} = 170^\circ C$
  - $T_{\text{decomp.}} = 183^\circ C$
X-ray powder diffraction patterns for (1-x)CsHSO$_4$-xKH$_2$PO$_4$ compounds

<table>
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<td>0.9</td>
<td>KH$_2$PO$_4$+CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.8</td>
<td>KH$_2$PO$_4$+CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.7</td>
<td>CsH$_5$(PO$_4$)$_2$+KH$_2$PO$_4$ (I-42d)</td>
</tr>
<tr>
<td>0.6</td>
<td>CsH$_5$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>0.5</td>
<td>CsH$_5$(PO$_4$)$_2$+Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$</td>
</tr>
<tr>
<td>0.4</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$+CsH$_5$(PO$_4$)$_2$ (P2$_1$/c)</td>
</tr>
<tr>
<td>0.3</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$</td>
</tr>
<tr>
<td>0.2</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$</td>
</tr>
<tr>
<td>0.1</td>
<td>Cs$_3$(HSO$_4$)$_2$H$_2$PO$_4$+CsHSO$_4$(P2$_1$/m)</td>
</tr>
</tbody>
</table>