High-temperature phenomena in RbD$_2$PO$_4$ and CsH$_2$PO$_4$
Polymeric transformations or polymorphic phase transitions?

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X-ray analysis has been performed for RbD$_2$PO$_4$ and CsH$_2$PO$_4$ over the temperature range from 288 K to 537 K and 507 K, respectively. The refinement of the crystal structure of RbD$_2$PO$_4$ at 430 K has revealed that the high-temperature paraelectric phase of this crystal is isomorphic with the monoclinic $P2_1/m$ paraelectric phase of CsH$_2$PO$_4$. The X-ray diffraction CCD images obtained for RbD$_2$PO$_4$ have proved that the high-temperature paraelectric phase is stable up to approximately 525 K. At this temperature, polycrystallisation of the single-crystal samples and their subsequent decomposition has been observed. CsH$_2$PO$_4$ undergoes a structural phase transition at 504 K, from the monoclinic paraelectric phase to a cubic superionic phase ($P2_1/m$ transforms to $Pm-3m$ symmetry). The reversibility of the superionic phase transition in the crystals is a strong evidence for a polymorphic character of this solid–solid transition.

Key words: X-ray analysis; crystal structure; phase transition; polymorphic transformation

1. Introduction

In AH$_2$PO$_4$-type crystals (where $a$ = K, Rb, Tl, NH$_4$ or Cs), two kinds of crystal systems can be stably crystallized at room temperature. The crystals of KH$_2$PO$_4$, RbH$_2$PO$_4$, and NH$_4$H$_2$PO$_4$ belong to the tetragonal system [1–3], whereas the crystals of CsH$_2$PO$_4$, TlH$_2$PO$_4$, and RbD$_2$PO$_4$ belong to the monoclinic system [1, 2, 4–8].

The RbD$_2$PO$_4$ crystal exhibits a superlattice structure with the lattice parameters $a = 15.352(2)$ Å, $b = 6.184(1)$ Å, $c = 9.566(2)$ Å, $\beta = 108.8(1)^\circ$ [9], which are doubled along both the $a$ and $c$ axes compared to the dimensions of the unit cell of ferroelectric CsH$_2$PO$_4$ [5]. RbD$_2$PO$_4$ undergoes phase transitions at 317 K and 377 K [4]. The low-temperature phase is antiferroelectric or approximately antiferroelectric (fer-

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rielectric with $2a, b, 2c, Z = 8, P_{21}$ \cite{4}; the intermediate (non-polar, with $a, b, 2c, Z = 4, P_{21}/c, \cite{10}$) and high-temperature ($a, b, c, Z = 2, P_{21}/m \cite{9}$) phases are paraelectric \cite{11}. The crystal structure of the ferrielectric phase was determined at room temperature \cite{9, 12}, the structure of the intermediate phase was determined at 332 K \cite{10}. Suzuki et al. \cite{10} reported that the high-temperature paraelectric phase has the space group $P_{21}/m$ with the basic lattice parameters, but the structure of that phase has not yet been determined.

The CsH$_2$PO$_4$ crystal exhibits ferroelectric properties below 154 K and has $P_{21}$ symmetry \cite{13, 14}. In the paraelectric phase, the crystal has $P_{21}/m$ symmetry \cite{5–8, 13, 14}. The ionic conductivity of CsH$_2$PO$_4$ undergoes a sharp increase at 504 K \cite{15–17}, from $1.2 \times 10^{-5}$ to $9.0 \times 10^{-3}$ ohm$^{-1}$cm$^{-1}$ \cite{18}.

Despite extensive studies of high-temperature transitions in MX$_2$PO$_4$ (where M = K, Rb, Cs; X = H, D) during the past few years, the microscopic nature of the high-temperature phenomena in these crystals is still not completely understood. Under normal air conditions, their ionic conductivity is related to two competing processes: a polymorphic transition and chemical decomposition with partial polymerisation. Lee \cite{19}, Ortiz et al. \cite{16} and recently Park \cite{20}, attribute the increase of conductivity of the KDP compounds at high temperatures to the dehydration process starting on the sample surface and partial polymerisation. On the other hand, our previous powder X-ray investigations of CDP under humidified conditions \cite{6, 7} support Baranov’s et al. \cite{15} suggestion that the superprotonic phase of CDP is cubic and reversible with hysteresis on cooling. Recently, Boysen et al. \cite{18} and Otomo et al. \cite{21} reconfirmed the reversibility of the superionic phase transition in these crystals.

This paper presents the results of X-ray investigations of RbD$_2$PO$_4$ and CsH$_2$PO$_4$ over the temperature range from 288 K to 537 K and 507 K, respectively. In order to explain the nature of high-temperature phenomena in these crystals, detailed structure analyses were performed using a KM4-CCD diffractometer.

2. Experimental

Single-crystal measurements of RbD$_2$PO$_4$ and CsH$_2$PO$_4$ were carried out on a four circle X-ray KM4 diffractometer (Kuma Diffraction Company) equipped with a two-dimensional area CCD detector and a high-temperature attachment. MoK$\alpha$ graphite-monochromated radiation ($\lambda = 0.71073$ Å) was used for data collection. The investigated samples were heated in a sealed tube as well as under normal air conditions. Data used for the determination of the crystal structure of the RbD$_2$PO$_4$ high-temperature paraelectric phase were collected at $T = 430$ K. An omega scan with $\Delta \Omega = 1^\circ$ for each image was used for data collection. A series of 960 images in six different runs covered 89.5% of the Ewald sphere; 1764 reflections were recorded for RbD$_2$PO$_4$, which merged to give a total of 539 unique reflections. The lattice parameters were calculated from all the reflections measured. The structure of RbD$_2$PO$_4$ at 430 K was solved by the Patterson method using the SHELXS-97 program. Refine-
ment was carried out using SHELXL-97 [22]. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. The positions of hydrogen atoms were determined from difference Fourier maps and well refined. A correction for empirical absorption was applied for the observed reflections, and an extinction correction was introduced into the refinement.

3. Results and discussion

The temperature dependences of the lattice parameters for RbD$_2$PO$_4$ in the temperature range 288–537 K exhibit anomalies at 317 K and 377 K as well as structural changes at approximately 525 K (Fig. 1).

![Fig. 1. The temperature dependences of the lattice parameters in RbD$_2$PO$_4$.](image)

The structure analyses of these crystals confirmed that the ferrielectric phase has $P2_1$ symmetry, and that the paraelectric intermediate and high-temperature phases have $P2_1/c$ and $P2_1/m$ symmetry, respectively. X-ray diffraction CCD images obtained for RbD$_2$PO$_4$ in a sealed tube above 380 K prove that the high-temperature paraelectric phase of these crystals is stable up to approximately 525 K. Figure 2a presents the X-ray CCD image of a single-crystal sample of RbD$_2$PO$_4$ heated in a sealed tube from 380 K to 525 K. The CCD image of this sample taken at 527 K (Fig. 2b) demonstrates the disappearance of the single-crystal paraelectric phase of RbD$_2$PO$_4$ and the simultaneous polycrystallisation of the sample. Additionally, X-ray powder high-temperature measurements of RbD$_2$PO$_4$, performed in a sealed tube, confirmed that the monoclinic high-temperature paraelectric
phase of the crystals is stable up to approximately 525 K. Investigations under normal air conditions have shown that the paraelectric phase of RbD₂PO₄ is stable only up to about 510 K. Above this temperature, the crystal decomposes by dehydration. The CCD image obtained for RbD₂PO₄ at 515 K has revealed that in normal air the polycrystallisation process is complete at this temperature.

![Fig. 2. X-ray diffraction CCD image of RbD₂PO₄ heated in a sealed tube at: a) 515 K, b) 527 K](image)

Table 1. Crystal data and structure refinement for RbD₂PO₄ at 430 K

<table>
<thead>
<tr>
<th>Identification code</th>
<th>rbd430</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>RbD₂PO₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>184.47</td>
</tr>
<tr>
<td>Temperature</td>
<td>430(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system space group</td>
<td>monoclinic P2(1)/M</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>4.8040(10) Å</td>
</tr>
<tr>
<td>b</td>
<td>6.2020(12) Å</td>
</tr>
<tr>
<td>c</td>
<td>7.7366(15) Å</td>
</tr>
<tr>
<td>β</td>
<td>109.08(3) deg</td>
</tr>
<tr>
<td>Volume</td>
<td>217.84(7) Å³</td>
</tr>
<tr>
<td>Z/Calculated density</td>
<td>2.812 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>11.606 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>172</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.21×0.25×0.29 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.31 to 28.41 deg</td>
</tr>
<tr>
<td>Index ranges</td>
<td></td>
</tr>
<tr>
<td>–6 ≤ h ≤ 6</td>
<td></td>
</tr>
<tr>
<td>–8 ≤ k ≤ 4</td>
<td></td>
</tr>
<tr>
<td>–9 ≤ l ≤ 10</td>
<td></td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>1764/539 (R(int) = 0.0669)</td>
</tr>
<tr>
<td>Completeness to 2theta</td>
<td>28.41 89.5%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>539/0/42</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.295</td>
</tr>
<tr>
<td>Final R indices (P&gt;σ(F))</td>
<td>R₁ = 0.0334, wR₂ = 0.0683</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0372, wR₂ = 0.0694</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.078(2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.519 and –0.566×10⁻³</td>
</tr>
</tbody>
</table>
The crystal structure of the high-temperature paraelectric phase of RbD₂PO₄ is similar to that of CsH₂PO₄ at room temperature [14] having a monoclinic symmetry with the space group \( P2_1/m \) and two chemical units in the unit cell. Nevertheless, the atomic coordinates of RbD₂PO₄ were determined independently. Crystal data and details of data collection and refinement for RbD₂PO₄ at 430 K are shown in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters, with ESDs in parentheses, calculated for this crystal are presented in Table 2 (\( U_{eq} \) is defined as one third of the trace of the orthogonalised \( U_{ij} \) tensor).

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters for RbD₂PO₄ at 430 K

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq} )</th>
</tr>
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<tbody>
<tr>
<td>Rb(1)</td>
<td>7081(1)</td>
<td>7500</td>
<td>7622(1)</td>
<td>48(1)</td>
</tr>
<tr>
<td>P(1)</td>
<td>2102(1)</td>
<td>2500</td>
<td>7452(1)</td>
<td>32(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>5054(2)</td>
<td>2500</td>
<td>9007(2)</td>
<td>44(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2102(2)</td>
<td>517(2)</td>
<td>6307(2)</td>
<td>84(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>–197(2)</td>
<td>2500</td>
<td>8341(2)</td>
<td>99(1)</td>
</tr>
<tr>
<td>D(1)</td>
<td>6620(4)</td>
<td>2500</td>
<td>8820(3)</td>
<td>70(6)</td>
</tr>
<tr>
<td>D(2)</td>
<td>1160(6)</td>
<td>70(6)</td>
<td>5510(5)</td>
<td>98(12)</td>
</tr>
</tbody>
</table>

Figure 3 presents the projection of the atom arrangement in the unit cell of the RbD₂PO₄ crystal along the \( b \) axis. Some interatomic distances and angles in RbD₂PO₄ are shown in Table 3. Large values of the anisotropic displacement parameters of all oxygen atoms indicate that the structure of RbD₂PO₄ crystals is dynamically disordered. The refinement of the crystal structure revealed the isomorphism of the crystals RbD₂PO₄ at 430 K and CsH₂PO₄ at room temperature.

![Fig. 3. The projection of the atoms arrangement in RbD₂PO₄ along the b axis at 430 K](image-url)

Our previous powder and single-crystal diffraction investigations of CsH₂PO₄ revealed that the paraelectric phase of these crystals is stable up to approximately 504 K and that at this temperature a structural phase transition from the paraelectric phase to
the superionic phase occurs [5–8]. The superionic phases of these crystals are unstable under normal air due to dehydration.

Table 3. Selected bond lengths [Å] and angles [deg] for RbD₂PO₄ at 430K

<table>
<thead>
<tr>
<th>Bond/Pair</th>
<th>Length [Å]</th>
<th>Angle [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb(1)--O(2)#1</td>
<td>2.9437(11)</td>
<td></td>
</tr>
<tr>
<td>P(1)--O(3)</td>
<td>1.4798(16)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(3)#3</td>
<td>2.9898(17)</td>
<td></td>
</tr>
<tr>
<td>P(1)--O(2)</td>
<td>1.5158(11)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(1)#3</td>
<td>3.0988(14)</td>
<td></td>
</tr>
<tr>
<td>P(1)--O(2)#1</td>
<td>1.5158(11)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(3)#5</td>
<td>3.3407(7)</td>
<td></td>
</tr>
<tr>
<td>P(1)--O(1)</td>
<td>1.5304(11)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(2)#7</td>
<td>3.4188(14)</td>
<td></td>
</tr>
<tr>
<td>O(1)--D(1)</td>
<td>0.81(2)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(2)#4</td>
<td>3.4582(13)</td>
<td></td>
</tr>
<tr>
<td>O(2)--D(2)</td>
<td>0.69(3)</td>
<td></td>
</tr>
<tr>
<td>Rb(1)--O(1)</td>
<td>3.5205(8)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Rotation CCD image of CsH₂PO₄ heated in a sealed tube at: a) 410 K, b) 509 K

X-ray rotation and oscillation CCD pictures (Fig. 4) of CsH₂PO₄ have reconfirmed that the paraelectric phase of these crystals is stable up to 504 K. At this temperature, a clear structural phase transition from the monoclinic \( P2_1/m \) paraelectric phase to the cubic superionic phase has been observed. Figure 4a shows an X-ray rotation CCD image of a single-crystal sample of CsH₂PO₄ heated in a sealed tube from 288 K to
410 K. The rotation CCD image of this sample taken at 509 K (Fig. 4b) demonstrates an essential structural change accompanied by the superionic phase transition in the crystal.

The oscillation CCD pictures for CsH₂PO₄ around the a-axis taken at room temperature and 510 K are shown in Figure 4. These results unequivocally establish a cubic $Pm-3m$ symmetry ($a = 4.952(1) \, \text{Å}$) for the superionic phase of CsH₂PO₄. Upon cooling, CsH₂PO₄ remains in the cubic phase down to a temperature of approximately 464 K. The reversible nature of the superionic transformation (with a 40° hysteresis) in CsH₂PO₄ is a strong evidence for the polymorphic character of this solid–solid transition. Detailed data of the crystal structure of the cubic superionic phases of CsH₂PO₄ and CsD₂PO₄ will be published in a following paper.

4. Conclusions

The temperature dependences of the lattice parameters of RbD₂PO₄ have revealed anomalies, which correspond to successive phase transitions at 317 K and 377 K, as well as an anomaly at approximately 525 K. The ferrielectric phase has the $P2₁$ symmetry (with $2a, b, 2c, Z = 8$) and the paraelectric intermediate phase has $P2₁/c$ symmetry (with $a, b, 2c, Z = 4$). The high-temperature paraelectric phase of RbD₂PO₄ has the $P2₁/m$ symmetry with the basis lattice parameters and $Z = 2$. The refinement of the crystal structure of RbD₂PO₄ at 430 K proves that the high-temperature paraelectric phase of the crystal is isomorphous with the paraelectric phase of CsH₂PO₄ at room temperature. The high-temperature paraelectric phase is stable up to approximately 525 K. At this temperature, the polycrystallisation of the single-crystal line samples and polymerisation due to their decomposition was observed.

The paraelectric phase of CsH₂PO₄ is stable up to 504 K. At this temperature, a structural phase transition from the monoclinic $P2₁/m$ paraelectric phase to the superionic phase was observed. These results undoubtedly prove the $Pm-3m$ cubic symmetry of the superionic phase of the crystals studied. The cubic phase is stable upon cooling over the 40-degree temperature regime. The reversible nature of the superionic transformation (with a 40-degree hysteresis) in CsH₂PO₄ is a strong evidence for a polymorphic character of this solid–solid transition.

References


Received 10 December 2004
Revised 10 September 2005