Conductivity of Potassium and Rubidium Dihydrogen Phosphates at High Temperature and Pressure

Dane A. Boysen and Sossina M. Haile*
Keck Laboratories, Mail Code 138-78, California Institute of Technology, Pasadena, California 91125

Hongjian Liu and Richard A. Secco
Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

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The high-temperature behavior of KH$_2$PO$_4$ and RbH$_2$PO$_4$ has been investigated by several methods. Simultaneous differential scanning calorimetry and thermal gravimetry, combined with evolved gas analysis, was carried out from 25 to 500 °C under ambient pressure. The initial dehydration events in KH$_2$PO$_4$ and RbH$_2$PO$_4$ occur at 233 and 257 °C, respectively, with no indication of either solid—solid or solid—liquid transitions prior to weight loss. Application of pressure suppresses this dehydration. Impedance spectroscopy performed under 1 GPa revealed a highly reproducible superprotonic phase transition in RbH$_2$PO$_4$ at 327 °C, at which the conductivity increased several orders of magnitude to a value of 0.232 ± 0.008 eV and the pre-exponential factor A, 3.4 ± 0.6 × 10$^{-3}$ cm$^{-1}$ K. No superprotonic solid—solid phase transition was observed in KH$_2$PO$_4$. However, a sharp increase in conductivity to a value of 1.8 ± 10$^{-2}$ cm$^{-1}$ at 345 °C was observed upon melting (T$_m$ ~ 352 °C). The liquid phase exhibited Arrhenius behavior comparable to that of superprotonic RbH$_2$PO$_4$ with $\Delta H_\theta$ = 0.227 ± 0.004 eV and $A = 5.2 ± 0.5 × 10^3$ cm$^{-1}$ K.

Introduction

MH$_2$PO$_4$-type compounds (M = alkali cation or NH$_4$) are comprised of hydrogen-bonded tetrahedral oxy-anions, charge-balanced by monovalent cations. Several, chemically similar compounds in the MHXO$_4$ and M$_3$H- (XO$_4$)$_2$ families ($X = S, Se$) are known to exhibit a high-temperature, structural transition to a disordered state. At this so-called “superprotonic” transition the protonic conductivity increases by several orders of magnitude to values of $10^{-2}$ cm$^{-1}$. Dispute over the existence of such a phase transition in CsH$_2$PO$_4$, arising from the simultaneous occurrence of dehydration at ambient pressure, has recently been resolved. It has been shown that, through either the use of pressure or elevated water partial pressures, a stable superprotonic phase can be observed in CsH$_2$PO$_4$. Thus, decomposition under ambient (dry) conditions does not preclude the existence of a superprotonic phase.

The potassium and rubidium members of the MH$_2$PO$_4$ family are isostructural with one another under ambient conditions, crystallizing in the tetragonal space group I42d (referred to as phase II in the case of KH$_2$PO$_4$ and phase III for RbH$_2$PO$_4$). Cooling induces a well-documented ferroelectric transition in both compounds. In contrast, heating produces a distinct series of transitions for the two compounds, and in both cases, that sequence is of some debate in the literature.

Early studies of KH$_2$PO$_4$ indicated two polymorphic transitions, one at 180 °C to phase II, and a second at 233 °C to phase I. More recent single-crystal diffraction studies have confirmed the existence of both transitions and have shown phase II′ to be tridinic (P1), with entirely ordered phosphate groups, and phase I to be monoclinic (P2$_1$/c). The existence of the II′ → I transition at 200–220 °C has been further confirmed by thermomechanical measurements, although little

* Corresponding author. Telephone: (626) 395-2958. Fax: (626) 395-8868. E-mail: smhaile@caltech.edu.
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evidence for the transition at 180 °C was observed. The structures of additional polymorphs that exist under atmospheric conditions have also been reported.

Rubidium dihydrogen phosphate transforms quasi-reversibly to a monoclinic phase (phase II) at a temperature somewhere between 80 and 120 °C, depending on the details of the experimental conditions. The transition has been observed by numerous authors using primarily thermal analysis methods, but also proton magnetic resonance and high-temperature powder X-ray diffraction. The structure of RbH₂PO₄ phase II was determined from single-crystal X-ray studies to be monoclinic P2₁/a, in agreement with the high-temperature powder diffraction studies. Limited reports of a second transition to an as-of-yet unidentified phase I at higher temperatures have appeared.

Despite these results, Park and co-workers have argued in a series of papers that none within the M₂PO₄ class of compounds undergoes a polymorphic phase transition prior to decomposition/polymerization, but a position also held by Ortiz and co-workers. Both sets of authors conclude, primarily on the basis of thermal analyses, that all anomalies in high-temperature properties can be attributed to a decomposition process, which involves phosphate condensation and polymerization. Indeed, thermal dehydration, which initiates at temperatures close to the II′ → I transition of KH₂PO₄ and the II → I transition of RbH₂PO₄ transitions, has prevented accurate, electrical characterization of phase I in both of these phosphates.

We show here thermal analysis results at ambient pressure, indicating that dehydration readily masks any transition to phase I in both KH₂PO₄ and RbH₂PO₄. Then using high-pressure electrical measurements, free from the ambiguities introduced by dehydration, the high-temperature phase behavior of both KH₂PO₄ and RbH₂PO₄ is characterized.

**Experimental Methods**

**Sample Preparation.** Granular KH₂PO₄ was obtained from commercial sources (Alfa Aesar, 99.9%). RBH₂PO₄ was prepared in powder form by combining the starting reagents of Rb₂CO₃ (Alfa Aesar, 99.8%) and H₃PO₄ (ACS, 85% w/w aqueous solution) in a molar ratio of 1:2 in aqueous solution. Solid State Commun. 2000, 113, 627.

Experimental methods, thermal, dehydration, phase transitions, high pressure, phase characterization.

**Results and Discussion**

**Thermal Analysis at Ambient Pressure.** Thermal analysis results obtained upon heating powders of KH₂PO₄ and RbH₂PO₄ to 500 °C are presented in Figure 1. The DTG and mass spectroscopy results correspond well to one another and show multiple dehydration events, with two major events occurring at 233/320 °C and 257/340 °C, respectively. Only one rather broad endothermic event observed from the DSC measurements for KH₂PO₄ at 241 °C and RbH₂PO₄ at 261 °C is perhaps the result of the multiple overlapping dehydration events.

observed by DTG and mass spectroscopy. The absence of a transition for KH$_2$PO$_4$ at $\sim$180 °C, well before dehydration begins, cannot be readily explained, but suggests that the II $\rightarrow$ II' transformation is highly dependent on the details of sample preparation and experimental conditions.

The existence of multiple dehydration events for both compounds indicates a multistep process, occurring via the formation of polyphosphite intermediates. Nevertheless, the overall dehydration can be described by the following reaction,

$$\text{MH}_2\text{PO}_4(s) \rightarrow \text{MPO}_3(s) + \text{H}_2\text{O}(g)$$

where M = K, Rb. This reaction results in a 13.2 and 9.9% loss of mass for KH$_2$PO$_4$ and RbH$_2$PO$_4$, respectively—precisely that observed by TG, Figure 1. Furthermore, samples recovered after thermal analysis were identified by powder X-ray diffraction as MPO$_3$. No evidence of either polymorphic solid--solid or melting transitions was observed under ambient pressures. The use of finely ground powder samples thus results in high-temperature behavior that is dominated by thermal decomposition, as has been shown for CsH$_2$PO$_4$.8

**High-Pressure Electrical Characterization.** In Figure 2, P--T phase diagrams for (a) KH$_2$PO$_4$ and (b) RbH$_2$PO$_4$, adapted from references 22 and 31, indicate the path over which ac impedance data were performed. Typical Nyquist plots of ac impedance spectra are presented in Figure 3 for selected temperatures. At low temperatures (top panels) well-resolved semicircles were obtained. The real resistance of both compounds at low temperatures is determined by fitting to an $RQ$ equivalent circuit model, where $R$ is a resistor and $Q$ is a constant phase element. In contrast, for both compounds at high temperatures, only an electrode response was

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**Figure 1.** Simultaneous differential scanning calorimetry (DSC), thermal gravimetry (TG), and corresponding differential thermal gravimetry (DTG) of KH$_2$PO$_4$ and RbH$_2$PO$_4$ powders upon heating to 500 °C at 10 °C min$^{-1}$ under flowing 40 cm$^3$ min$^{-1}$ dry N$_2$ gas. H$_2$O in the evolved gas is identified by mass spectroscopy (Mass Spec), m 18.00.

**Figure 2.** Pressure--temperature (P--T) phase diagrams of (a) KH$_2$PO$_4$ and (b) RbH$_2$PO$_4$ adapted from refs 22 and 31, indicating the path over which ac impedance measurements were performed.
The conductivities obtained from the high-pressure impedance measurements are presented in Arrhenius plots in Figure 4. The arrows indicate the direction of temperature change between data collections. The regions of phase stability expected from the P–T phase diagrams of Figure 2 are overlaid and indicated by dashed lines.

As synthesized, KH$_2$PO$_4$ crystallizes in phase II (tetragonal, I$\text{4}_1\text{4}_2\text{d}$). Application of pressure (at 25 °C) induces a transition to phase IV; however, the position of the II–IV phase boundary has not been determined and the exact phase present at the initiation of the high-pressure conductivity measurements is thus not known. Regardless of this ambiguity, one expects KH$_2$PO$_4$ to transform to phase I at 250 °C upon heating under 1 GPa (Figure 2a). The conductivity, Figure 4a, increases smoothly through this temperature; there is no sharp increase that would be characteristic of a superprotonic phase transition. This behavior is entirely in agreement with the reported monoclinic structure of phase I. Upon further heating, one expects phase I to melt at 325 °C, and here the conductivity increases by more than 2
Conductivity of KH₂PO₄ and RbH₂PO₄

orders of magnitude to a value of \(~1.8 \times 10^{-2} \ \Omega^{-1} \text{cm}^{-1}\) at 345 °C. Recovery of the KH₂PO₄ sample from the ball drop experiment confirmed that this was a solid–liquid transition and not a solid–solid superprotonic transition.

Fitting the conductivity of the liquid phase to the Arrhenius relationship,

$$\sigma(T) = A e^{-\Delta H_a/kT}$$

where \(\sigma\) is conductivity, \(T\) is temperature, \(A\) is a pre-exponential factor, \(\Delta H_a\) is the activation enthalpy, and \(k\) is Boltzmann's constant, yields a \(\Delta H_a\) of 0.227(4) eV and an \(A\) of \(5.2(5) \times 10^3 \ \Omega^{-1} \text{cm}^{-1} \ K\). Upon cooling KH₂PO₄ some hysteresis (~20 °C) from the melt phase and rather irreproducible electrical behavior in the low-conductivity solid phases were observed. It was not possible to distinguish between phases I, II, and IV from these electrical measurements, and the conductivity is highly non-Arrhenius in the low-temperature regime.

Highly non-Arrhenius in the low-temperature regime.

The behavior of RbH₂PO₄ is markedly different. Storing the sample at 100 °C induces a transformation from phase III to phase II and the latter is the phase present at the initiation of the high-pressure conductivity experiments. Though not identical, the structure of RbH₂PO₄ in phase II closely resembles that of CsH₂PO₄ (P₂₁/m). Upon heating RbH₂PO₄ above 327 °C, a II–I phase transition is expected (Figure 2b). From the ac impedance results presented in Figure 4b, a sharp "jump" in the conductivity to a value of \(~6.8 \times 10^{-2} \ \Omega^{-1} \text{cm}^{-1}\) at 340 °C is evident, indicative of a superprotonic phase transition. The solid–solid nature of this transition was confirmed by the ball drop experiment performed on RbH₂PO₄. Reproducible Arrhenius behavior of the superprotonic phase I was observed, with a \(\Delta H_a\) of 0.232(8) eV and an \(A\) of \(3.4(6) \times 10^3 \ \Omega^{-1} \text{cm}^{-1} \ K\), values fairly typical of superprotonic conductors. Upon cooling, there was some hysteresis (~10 °C). Like that of KH₂PO₄, the electrical behavior was somewhat irreproducible between heating and cooling cycles in phase II, but much more Arrhenius in nature with a \(\Delta H_a\) of 0.77(2) eV and an \(A\) of \(3.2(10) \ \Omega^{-1} \text{cm}^{-1} \ K\).

A summary of the activation enthalpies and pre-exponential factors for KH₂PO₄ and RbH₂PO₄ phases measured here are given in Table 1. The proton transport properties of RbH₂PO₄ are quite comparable to those of CsH₂PO₄ from which one can readily conclude that phase I of RbH₂PO₄ shares the same cubic structure in which phosphate groups are highly rotationally disordered. It is noteworthy that the activation enthalpy of the liquid phase of KH₂PO₄ is quite similar to that of the superprotonic phase I of RbH₂PO₄ and the overall difference in conductivity between the two is less than a factor of 2. This points to similar mechanisms for ionic transport between liquid KH₂PO₄ and superprotonic RbH₂PO₄.

We have additionally conducted preliminary high-pressure ac impedance measurements on LiH₂PO₄ and NaH₂PO₄, which suggest that these compounds do not exhibit superprotonic phase transitions. Combined with the absence of a superprotonic phase transition in KH₂PO₄, this indicates a clear cation size effect in which MH₂PO₄ compounds with cations of size Rb⁺ and larger (Cs⁺) can exhibit superprotonic phase transitions, whereas for cations smaller than Rb⁺ (K⁺, Na⁺, Li⁺) melting precludes a superprotonic phase transition.

### Table 1. Summary of Activation Enthalpies, ΔH\(_a\), and Pre-exponential Factors, A, for Protonic Transport of the Various Phases of KH₂PO₄ and RbH₂PO₄ Measured upon Heating and Cooling from 25 to 350 °C under 1.0 ± 0.2 GPa of Pressure

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>ΔH(_a)/eV</th>
<th>A/(\Omega^{-1} \text{cm}^{-1} \ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>Liquid</td>
<td>0.227(4)</td>
<td>5.2(5) \times 10³</td>
</tr>
<tr>
<td>RbH₂PO₄</td>
<td>I</td>
<td>0.232(8)</td>
<td>3.4(6) \times 10³</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.77(2)</td>
<td>3.2(10) \times 10³</td>
</tr>
</tbody>
</table>

### Summary

The results of this study can be summarized as follows:

1. Under a dry atmosphere and ambient pressure, dehydration dominates the high-temperature behavior of both KH₂PO₄ and RbH₂PO₄ examined in powder form.
2. At 1 GPa pressure KH₂PO₄ does not exhibit a superprotonic phase transition prior to melting. Thus, the reported transition at 325 °C is not accompanied by rotational disordering of the phosphate groups.
3. At 1 GPa pressure RbH₂PO₄ does exhibit a superprotonic phase transition prior to melting.

The existence of a superprotonic transition in RbH₂PO₄ and not KH₂PO₄, despite their identical structure types at room temperature, indicates that cation size plays a major role in the presence or absence of such transitions, as has been observed in the MHXO₄ family of compounds.

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