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

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The high-temperature behavior of KH_2PO_4 and RbH_2PO_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_2PO_4 and RbH_2PO_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_2PO_4 at 327 °C, at which the conductivity increased several orders of magnitude to a value of $6.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 340 °C. The activation energy for proton transport in the superprotonic phase is ΔH_a of 0.232 ± 0.008 eV and the pre-exponential factor A, $3.4 \pm 0.6 \times 10^3\ \Omega^{-1}\ cm^{-1}$ K. No superprotonic solid−solid phase transition was observed in KH_2PO_4. However, a sharp increase in conductivity to a value of $1.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 345 °C was observed upon melting ($T_m \sim 325$ °C). The liquid phase exhibited Arrhenius behavior comparable to that of superprotonic RbH_2PO_4, with $\Delta H_a = 0.227 \pm 0.004$ eV and $A = 5.2 \pm 0.5 \times 10^3\ \Omega^{-1}\ cm^{-1}$ K.

Introduction

MH_2PO_4-type compounds (M = alkali cation or NH_4) are comprised of hydrogen-bonded tetrahedral oxyanions, charge-balanced by monovalent cations. Several, chemically similar compounds in the $MHXO_4$ and $M_3H(XO_4)_2$ 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 $\sim 10^{-2}\ \Omega^{-1}\ cm^{-1}$. Dispute over the existence of such a phase transition in CsH_2PO_4, arising from the simultaneous occurrence of dehydration at ambient pressure,[1−7] has recently been resolved. It has been shown that, through either the use of pressure[8] or elevated water partial pressures,[9] a stable superprotonic phase can be observed in CsH_2PO_4. Thus, decomposition under ambient (dry) conditions does not preclude the existence of a superprotonic phase.

The potassium and rubidium members of the MH_2PO_4 family are isostructural with one another under ambient conditions, crystallizing in the tetragonal space group $I\bar{4}2d$[10] (referred to as phase II in the case of KH_2PO_4 and phase III for RbH_2PO_4). Cooling induces a well-documented ferroelectric transition in both compounds.[11,12] 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_2PO_4 indicated two polymorphic transitions, one at 180 °C,[13] to phase II′, and a second at 233 °C,[14] to phase I. More recent single-crystal diffraction studies have confirmed the existence of both transitions and have shown phase II′ to be triclinic ($P\bar{1}$), with entirely ordered phosphate groups, and phase I to be monoclinic ($P2_1/c$).[15] The existence of the II′ → I transition at 200−220 °C has been further confirmed by thermomechanical measurements, although little

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evidence for the transition at 180 °C was observed.[16] The structures of additional polymorphs that exist under atmospheric conditions have also been reported.[15,17]

Rubidium dihydrogen phosphate transforms quasi-irreversibly to a monoclinic phase (phase II) at a temperature somewhere between 80 and 120 °C, depending on the details of the experimental conditions.[3] The transition has been observed by numerous authors using primarily thermal analysis methods,[3,18−20] but also proton magnetic resonance and high-temperature powder X-ray diffraction.[20] The structure of RbH_2PO_4 phase II was determined from single-crystal X-ray studies to be monoclinic $P2_1/a$,[21] in agreement with the high-temperature powder diffraction studies.[20] Limited reports of a second transition to an as-of-yet unidentified phase I at higher temperatures have appeared.[13,22−24]

Despite these results, Park and co-workers have argued in a series of papers that none within the MH_2PO_4 class of compounds undergoes a polymorphic phase transition prior to decomposition/polymerization,[25,26] a position also held by Ortiz and co-workers.[27] 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 KH_2PO_4 and the II → I transition of RbH_2PO_4 transitions, has prevented accurate, electrical characterization of phase I in both of these phosphates.[5]

We show here thermal analysis results at ambient pressure, indicating that dehydration readily masks any transition to phase I in both KH_2PO_4 and RbH_2PO_4. Then using high-pressure electrical measurements, free from the ambiguities introduced by dehydration, the high-temperature phase behavior of both KH_2PO_4 and RbH_2PO_4 are characterized.

Experimental Methods

Sample Preparation. Granular KH_2PO_4 was obtained from commercial sources (Alfa Aesar, 99.0%). RbH_2PO_4 was prepared in powder form by combining the starting reagents of Rb_2CO_3 (Alfa Aesar, 99.8%) and H_3PO_4 (ACS, 85% w/w aqueous solution) in a molar ratio of 1:2 in aqueous solution. Rapid precipitation of RbH_2PO_4 was induced by the introduction of methanol to the solution, and the resultant solids were then filtered from the mother solution. Single crystals of both KH_2PO_4 and RbH_2PO_4 were grown by slow evaporation of H_2O under ambient conditions from an aqueous solution of the respective powders. Crystals were stored in an oven at ∼100 °C prior to all measurements to avoid condensation of moisture. Phases were identified by both single-crystal X-ray diffraction (Syntex $P2^1$ 4-circle, Mo Kα radiation) and powder X-ray diffraction (Siemens D 500 powder, Cu Kα radiation).

Characterization. Thermal analysis was carried out on powders ground from single crystals using a Netzsch STA 449C thermal analyzer in which differential scanning calorimetry (DSC) and thermal gravimetry (TG) were simultaneously performed. Evolved H_2O (m 18.00) was monitored with a Pfeiffer Thermal Star mass spectrometer. Measurements were made under flowing 40 $cm^3\ min^{-1}$ dry N_2 gas, while heating at a rate of 10 °C min^{-1}.

To suppress dehydration and observe possible superprotonic phases, high-pressure ac impedance spectroscopy was employed. Single crystals were lightly ground and subsequently packed into a boron nitride (BN) cup with Pt electrodes on top and bottom. The cup was then placed into a high-pressure cell composed of an oversized pyrophyllite cube in which a Nb foil served as a heater and a Pt/Pt10%Rh thermocouple was employed for monitoring temperature. The high-pressure cell was placed into a large-volume 1000-ton cubic anvil hydraulic press (H.T. Hall Inc.) in which a quasi-hydrostatic pressure of 1.0 ± 0.2 GPa was maintained by the extrusion of the pyrophyllite to form 12 gaskets along the edges of the cube. Each anvil, in electrical isolation from the other, makes contact through the faces of the cube with the electrodes, thermocouple, and heater, respectively. The details of the experimental apparatus are given elsewhere.[28,29] A pressure−temperature calibration was applied to the readings from the Pt/Pt10%Rh thermocouple.[30] Alternating current (ac) impedance spectra were collected using a Solartron SI 1260 impedance/phase gain analyzer over the frequency range 10 Hz to 1 MHz with an applied voltage of 1.0 V. Data analysis was performed using the commercial software package ZView (Scribner & Associates). Samples were repeatedly heated and cooled from 25 to 350 °C while making electrical measurements.

Because the sample cannot be directly observed in the high-pressure ac impedance cell, one must establish whether measured changes in conductivity are due to melting of the sample or to a true solid−solid transition. To achieve this, a ball-drop experiment was performed. A ruby sphere 0.5 mm in diameter and a tungsten carbide sphere 0.6 mm in diameter, with 1 atm/22 °C densities of 4.0 and 14.9 g/cm^3, respectively, were placed on top of the sample in a BN cup. The BN cup was then loaded into a high-pressure cell analogous to that used for the high-pressure electrical characterization, pressurized to 1.0 ± 0.2 GPa, heated to 350 °C, held for 10 min, and cooled back to room temperature. Recovered samples were examined to determine whether the WC or ruby balls fell to the bottom of the cell, thereby indicating a solid−liquid transition.

Results and Discussion

Thermal Analysis at Ambient Pressure. Thermal analysis results obtained upon heating powders of KH_2PO_4 and RbH_2PO_4 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 KH_2PO_4 at 241 °C and RbH_2PO_4 at 261 °C is perhaps the result of the multiple overlapping dehydration events

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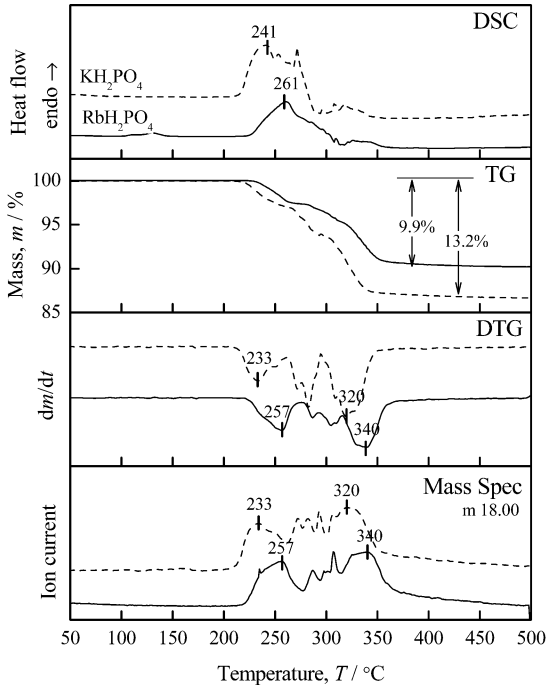

Figure 1. Simultaneous differential scanning calorimetry (DSC), thermal gravimetry (TG), and corresponding differential thermal gravimetry (DTG) of KH_2PO_4 and RbH_2PO_4 powders upon heating to 500 °C at 10 °C min^{-1} under flowing 40 cm^3 min^{-1} dry N_2 gas. H_2O in the evolved gas is identified by mass spectroscopy (Mass Spec), m 18.00.

observed by DTG and mass spectroscopy. The absence of a transition for KH_2PO_4 at ~180 °C, well before dehydration begins, cannot be readily explained, but suggests that the II → 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,

$$MH_2PO_4(s) \rightarrow MPO_3(s) + H_2O(g) \qquad (1)$$

where M = K, Rb. This reaction results in a 13.2 and 9.9% loss of mass for KH_2PO_4 and RbH_2PO_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_2PO_4.[8]

High-Pressure Electrical Characterization. In Figure 2, *P*−*T* phase diagrams for (a) KH_2PO_4 and (b) RbH_2PO_4, adapted from references 22 and 31, indicate the region over which ac impedance data were collected. 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

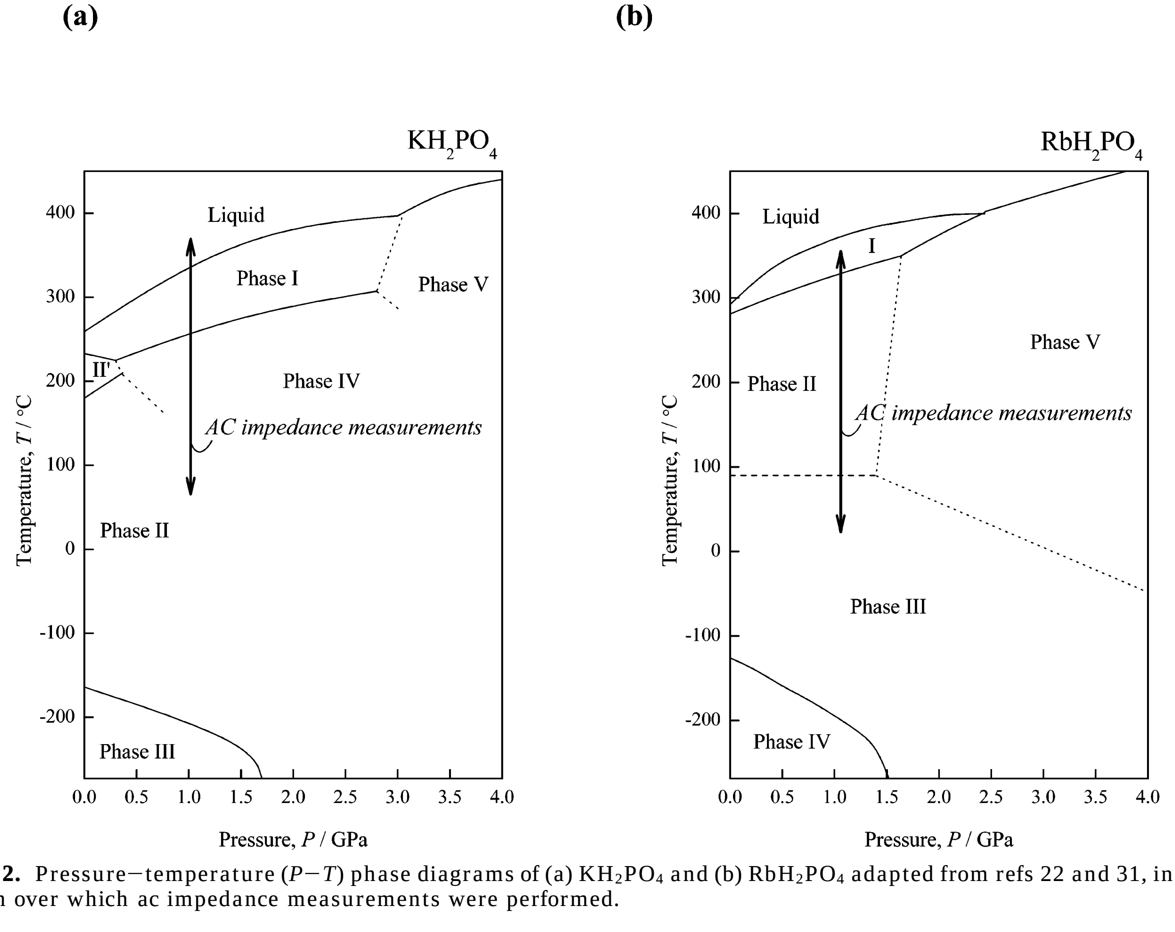

Figure 2. Pressure−temperature (*P*−*T*) phase diagrams of (a) KH_2PO_4 and (b) RbH_2PO_4 adapted from refs 22 and 31, indicating the path over which ac impedance measurements were performed.

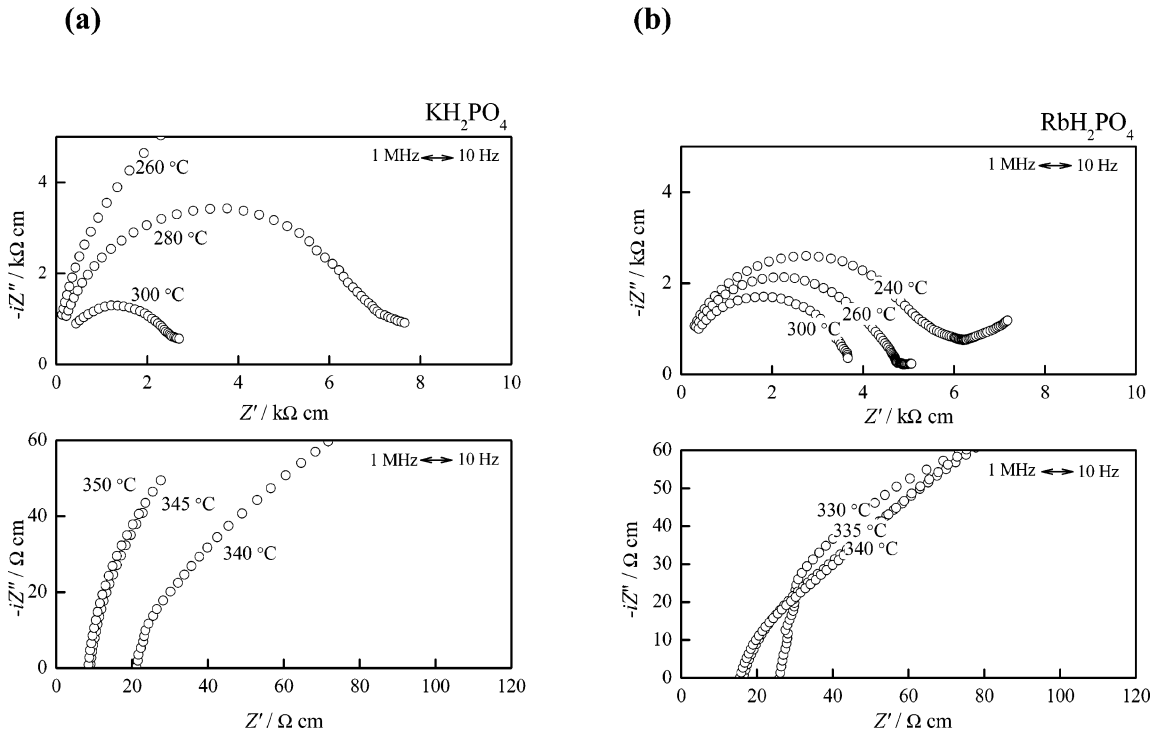

Figure 3. Sample Nyquist plots at various temperatures upon heating of measured real (Z') and imaginary ($-iZ''$) ac impedance response (1 Hz to 1 MHz) under 1.0 ± 0.2 GPa of pressure for (a) KH_2PO_4 and (b) RbH_2PO_4.

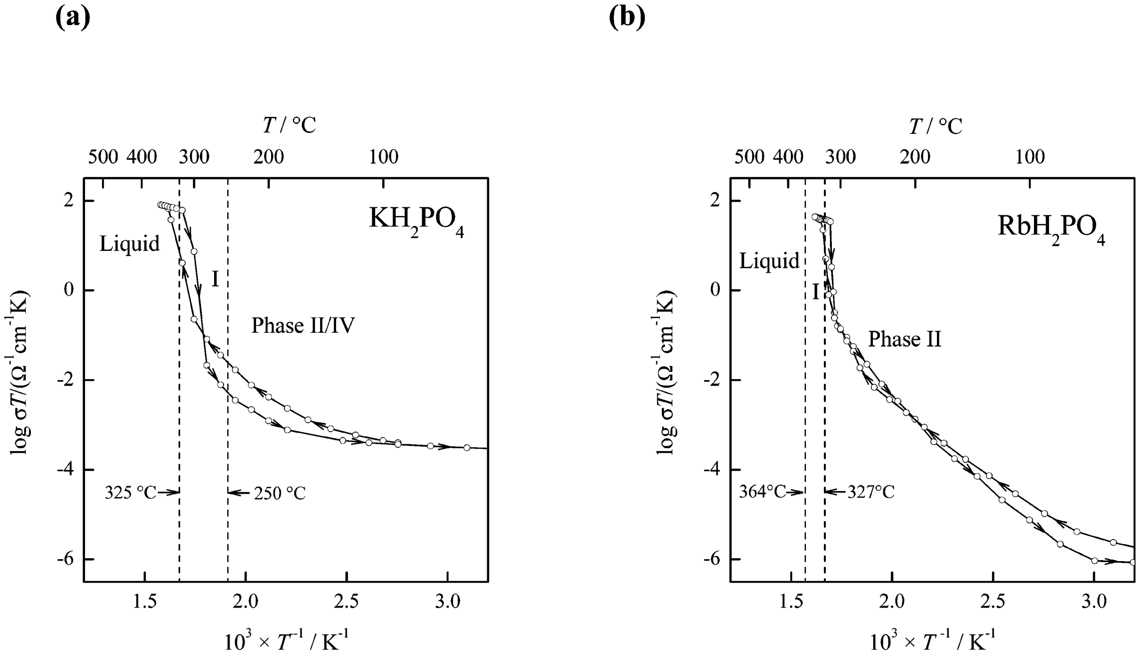

Figure 4. Arrhenius plots of the conductivity (σ) results from ac impedance measurements performed upon heating and cooling from 25 to 350 °C under 1.0 ± 0.2 GPa of pressure for (a) KH_2PO_4 and (b) RbH_2PO_4.

observed (bottom panels), and the intercept with the real axis (Z') is the estimated resistance of the sample.

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_2PO_4 crystallizes in phase II (tetragonal, $I\bar{4}2d$). 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_2PO_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 orders of magnitude to a value of ~$1.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 345 °C. Recovery of the KH_2PO_4 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,

$$\sigma T = A e^{-\Delta H_a / kT} \qquad (2)$$

where σ is conductivity, T is temperature, A is a pre-exponential factor, ΔH_a is the activation enthalpy, and k is Boltzmann's constant, yields a ΔH_a of 0.227(4) eV and an A of $5.2(5) \times 10^3\ \Omega^{-1}\ cm^{-1}$ K. Upon cooling KH_2PO_4, 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.

The behavior of RbH_2PO_4 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 RbH_2PO_4 in phase II closely resembles that of CsH_2PO_4 ($P2_1/m$).[32] Upon heating RbH_2PO_4 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 ~$6.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ 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 RbH_2PO_4. Reproducible Arrhenius behavior of the superprotonic phase I was observed, with a ΔH_a of 0.232(8) eV and an A of $3.4(6) \times 10^3\ \Omega^{-1}\ cm^{-1}$ K, values fairly typical of superprotonic conductors.[33] Upon cooling, there was some hysteresis (~10 °C). Like that of KH_2PO_4, the electrical behavior was somewhat irreproducible between heating and cooling cycles in phase II, but much more Arrhenius in nature with a ΔH_a of 0.77(2) eV and an A of $3(2) \times 10^5\ \Omega^{-1}\ cm^{-1}$ K.

A summary of the activation enthalpies and pre-exponential factors for KH_2PO_4 and RbH_2PO_4 phases measured here are given in Table 1. The proton transport properties of RbH_2PO_4 are quite comparable to those of CsH_2PO_4,[8] from which one can readily conclude that phase I of RbH_2PO_4 shares the same cubic structure in which phosphate groups are highly rotationally disordered.[6] It is noteworthy that the activation enthalpy of the liquid phase of KH_2PO_4 is quite similar to that of the superprotonic phase I of RbH_2PO_4 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 KH_2PO_4 and superprotonic RbH_2PO_4.

Table 1. Summary of Activation Enthalpies, ΔH_a, and Pre-exponential Factors, A, for Protonic Transport of the Various Phases of KH_2PO_4 and RbH_2PO_4 Measured upon Heating and Cooling from 25 to 350 °C under 1.0 ± 0.2 GPa of Pressure

compound	phase	ΔH_a/eV	$A/\Omega^{-1}\ cm^{-1}$ K
KH_2PO_4	liquid	0.227(4)	$5.2(5) \times 10^3$
RbH_2PO_4	I	0.232(8)	$3.4(6) \times 10^3$
	II	0.77(2)	$3(2) \times 10^5$

We have additionally conducted preliminary high-pressure ac impedance measurements on LiH_2PO_4 and NaH_2PO_4, which suggest that these compounds do not exhibit superprotonic phase transitions. Combined with the absence of a superprotonic phase transition in KH_2PO_4, this indicates a clear cation size effect in which MH_2PO_4 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.

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 KH_2PO_4 and RbH_2PO_4 examined in powder form.

2. At 1 GPa pressure KH_2PO_4 *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 RbH_2PO_4 *does* exhibit a superprotonic phase transition prior to melting.

4. The existence of a superprotonic transition in RbH_2PO_4 and not KH_2PO_4, 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 $MHXO_4$ family of compounds.[34]

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