

Article

High-Temperature Polymorphic Phase Transitions in MH_2PO_4 (M = K, Rb, Cs) Proton Conductors

Cristian E. Botez ^{1,*}, Zachary Musslewhite ¹, Alex D. Price ² and Chunqiang Li ² 

¹ Department of Physics and Astronomy, University of Texas at San Antonio, 1 UTSA Circle, San Antonio, TX 78249, USA; zachary.musslewhite@my.utsa.edu

² Department of Physics, University of Texas at El Paso, 500 W. University Avenue, El Paso, TX 79968, USA; adprice.c137@gmail.com (A.D.P.); cli@utep.edu (C.L.)

* Correspondence: cristian.botez@utsa.edu; Tel.: +1-210-458-8227

Abstract

We used powder X-ray diffraction (XRD) and ac impedance spectroscopy to investigate the polymorphic phase transitions undergone by the MH_2PO_4 (M = Cs, K, Rb) proton conductor series upon heating. High-pressure methods used in conjunction with energy dispersive XRD enhanced by synchrotron radiation allowed us to isolate a pure cubic (superprotonic) RbH_2PO_4 (RDP) polymorph (at $P = 1.2$ GPa and $T = 320$ °C) and collect data of enough quality to Rietveld refine its crystal structure. Our data and analysis reveal that cubic RDP (Pm-3m, $a = 4.76 \pm 0.01$ Å) is described by a unit cell where Rb and P atoms are in (0, 0, 0) and (0.5, 0.5, 0.5) positions, respectively, whereas O atoms are in (0.5, 0.234(5) 0.342(6)) positions having a multiplicity of 24 and an occupancy of 0.166. This results in dynamically disordered PO_4 tetrahedra that enables the superprotonic conduction in RDP, a mechanism like the one in the high-temperature cubic phase of the Cs-based compound CsH_2PO_4 (CDP). This is a notable behavior, as RDP and CDP are structurally different at room temperature—RDP is tetragonal (I-42d) and CDP is monoclinic ($P2_1/m$)—but following polymorphic modifications upon heating they both end up in superprotonic cubic phases that are isostructural to one another. On the other hand, we found that although the K-based phosphate KH_2PO_4 (KDP) has the same crystal structures as RDP at room and at intermediate temperatures, further heating does not lead to a cubic KDP phase. Overall, our results are significant from both the fundamental and applied perspective as superprotonic phosphates are promising materials for fuel cell electrolyte applications.

Keywords: polymorphism; phase transitions; proton conduction; high-pressure XRD



Academic Editor: Łukasz Szeleszczuk

Received: 16 July 2026

Revised: 3 August 2026

Accepted: 4 August 2026

Published: 6 August 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons](#)

[Attribution \(CC BY\)](#) license.

1. Introduction

Functional compounds that have the same chemical make-up but exhibit different crystal structures under different environments are of particular importance in materials science and engineering [1–4]. The lattice in which these polymorphs crystalize can be changed using external stimuli (e.g., temperature, pressure, light, pH), making them ideal candidates for applications where macroscopic properties need to be altered—quite dramatically in some cases—via minute changes in the sample environment [5,6]. Such polymorphic phase transitions are significant for a broad range of modern fields, including drug discovery [7,8], sustainable energy [9,10], actuators [11], electronic materials [12,13] and smart materials [14,15].

A particular case where understanding and controlling polymorphism is crucial for the proper operation of a functional material is represented by the phosphate-based solid

acid series MH_2PO_4 ($\text{M} = \text{Cs}, \text{K}, \text{Rb}$). These compounds are known to become highly efficient proton conductors when heated above a certain temperature threshold [16,17]. This allows them to function as fuel cell electrolytes at temperatures between 200 °C and 350 °C, a range that is of importance for automotive and space exploration applications but cannot be reached using polymer-based electrolytes that need constant hydration (as they conduct hydronium ions and not protons). CsH_2PO_4 (CDP) has been the most investigated member of the title series [18–20]. Its proton conductivity suddenly increases remarkably by three orders of magnitude when CDP is heated to 233 °C, but the microscopic details responsible for this so-called superprotonic behavior have been intensely debated for more than two decades. Some researchers attributed the superprotonic jump to a monoclinic $\rightarrow$ cubic polymorphic phase transition [20,21], while others ascribed it to chemical decomposition via dehydration [22,23]. While stronger evidence exists for the former scenario [16,17,20], the dehydration hypothesis has also received solid support [24]. The above-mentioned structural transition to a cubic CDP polymorph and this compound's chemical decomposition are not mutually exclusive. In fact, they both occur at temperatures in the immediate vicinity of the superprotonic conductivity onset threshold. This was confirmed by synchrotron X-ray diffraction measurements on CDP powders placed in a capillary holder [20], which demonstrated that the monoclinic $\rightarrow$ cubic transition precedes dehydration—in other words, it is the cubic CDP phase that dehydrates. Consequently, for a given time period (tens of minutes), the CDP sample was observed to be a mixture of cubic CDP and CDP dehydration products (e.g., $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$), so it is not possible to decide which of the two is responsible for the superprotonic behavior based just on this type of experiment. This situation was addressed through experiments where CDP powders were heated while kept under a saturated water vapor atmosphere [16,18] or under high pressure [20]. These conditions preserve the abrupt proton conductivity jump and the monoclinic $\rightarrow$ cubic structural transition upon heating above a critical temperature, but completely inhibit dehydration [17], which represent evidence that the cubic CDP polymorph enables the superprotonic conduction. In summary, there is irrefutable evidence of the existence of a high-temperature cubic CDP phase, but this polymorph is unstable and *does* decompose in minutes via dehydration unless the sample is kept under special high-humidity or high-pressure conditions [16–18,20,21].

Interestingly, the K- and Rb-based compounds KH_2PO_4 (KDP) and RbH_2PO_4 (RDP) differ structurally from their CDP counterpart at room temperature (KDP and RDP are tetragonal I-42d whereas CDP is monoclinic $\text{P}2_1/\text{m}$) but, upon heating, there are several observations of macroscopic property (proton conductivity) and microstructural behaviors of KDP and RDP similar to the ones observed in CDP. Yet, there is no conclusive evidence of a polymorphic transition to a *pure* superprotonic KDP or RDP phase despite findings of abrupt proton conductivity jumps in both of these phosphates [25], cubic structures in similar non-stoichiometric compounds (e.g., $\text{RbH}_{2-3y}(\text{PO}_4)_{1-y}$) [26,27], and a lattice that correctly indexes XRD patterns from RDP powders heated to 300 °C [28]. It is therefore important to investigate the evolution of the crystal structures of these phosphates upon heating with the overall goal of identifying polymorphic transitions, and a specific focus on isolating the high-temperature phases of KDP and/or CDP, determining their structures, and comparing them with the one responsible for the superprotonic behavior in CDP.

X-ray diffraction (XRD) enhanced by the use of synchrotron radiation is an ideal tool to study polymorphic phase transitions for several reasons. First, because unlike other methods (e.g., thermal analysis or X-ray spectroscopy), XRD results reveal not only that a transition occurred, but also detailed information about the crystal structures of the two polymorphs involved. Second, XRD data of enough quality (including data from crystalline powders) allow the full crystal structure of unknown polymorphs to be determined. In

addition, modern XRD setups include sample holders and chambers capable of producing the special sample environments and the stimuli needed to generate polymorphic phase transitions in the investigated materials. Finally, the high intensity of the beam and the ability to vary the X-ray wavelength, both specific to synchrotron radiation, allow rapid data collection and the use of diffraction geometries needed for highly specialized experiments (e.g., for high-pressure and high-temperature XRD).

Here we present a study where we used temperature-resolved synchrotron X-ray powder diffraction to study polymorphic transitions that occur in MH_2PO_4 ($\text{M} = \text{Cs}, \text{K}, \text{Rb}$) proton conductors as the temperature of these systems is raised toward their melting point. Two experimental methods were employed: (1) XRD in the transmission geometry where a fixed wavelength ($\lambda = 0.922\text{\AA}$) beam passes through a quartz capillary containing the sample and a flat detector perpendicular to the beam's direction intercepts the projections of the Debye–Scherrer diffraction cones, and (2) XRD in the reflectivity geometry where a “white” beam is incident on a sample placed in a high-pressure cell and the diffracted X-rays are intercepted by a multi-channel energy sensitive detector placed at a fixed 2θ angle. Our most significant result comes from high-pressure ($P = 1.2\text{ GPa}$) XRD measurements carried out on RDP at $320\text{ }^\circ\text{C}$. These data can be indexed to a single cubic ($\text{Pm}\text{-}3\text{m}$) phase, and most importantly, allowed us to carry out a full structural (Rietveld) refinement confirming that this is indeed an RDP polymorph where the Rb and P atoms are in $(0, 0, 0)$ and $(0.5, 0.5, 0.5)$ positions respectively, whereas O atoms are in $(0.5, 0.234(5), 0.342(6))$ positions having a multiplicity of 24 and an occupancy of 0.166. To the best of our knowledge, this is the first refinement of a pure RDP cubic phase that not only confirms its existence, but brings direct evidence of its crystal structure, including the dynamic disorder of the PO_4 tetrahedra which is most likely responsible for the superprotonic conduction. Another remarkable finding is that the high-temperature cubic RDP polymorph and its CDP counterpart are isomorphic (crystallographically identical) although at room temperature the two phosphates have different crystal structures (RDP is tetragonal ($\text{I}\text{-}42\text{d}$) and CDP is monoclinic ($\text{P}2_1/\text{m}$)). Finally, we found that the K-based compound, KDP, exhibits a different behavior upon heating. At room temperature, KDP has the same crystal structure as RDP (tetragonal, $\text{I}\text{-}42\text{d}$) and at $T = 220\text{ }^\circ\text{C}$ it undergoes a tetragonal $\rightarrow$ monoclinic polymorphic transition to a $\text{P}2_1/\text{m}$ structure that, again, is isomorphic with the intermediate-temperature RDP polymorph. Upon further heating KDP toward its melting point, however, we found no evidence of any other polymorphic transition, which is in agreement with previous predictions for ac impedance spectroscopy measurements [25]. Our results are significant because they clarify key aspects of the high-temperature polymorphic phase transitions in MH_2PO_4 ($\text{M} = \text{Cs}, \text{K}, \text{Rb}$) proton conductors, which, besides their fundamental importance, provide new insights likely to advance the use of these compounds as electrolytes in clean-energy fuel cell applications.

2. Materials and Methods

All MH_2PO_4 ($\text{M} = \text{Cs}, \text{K}, \text{Rb}$) crystalline powders used in this study were synthesized using a multistep precipitation-followed-by-recrystallization method. First, the metal carbonate MCO_3 (Alfa Aesar, Haverhill, MA, USA) ($\text{M} = \text{Cs}, \text{K}, \text{Rb}$) was mixed with phosphoric acid H_3PO_4 (85% aqueous solution, Alfa Aesar, Haverhill, MA, USA) as follows. H_3PO_4 was diluted to 10 wt% and then MCO_3 was added to achieve the proper stoichiometric ratio $\text{MCO}_3\text{:H}_3\text{PO}_4 = 1\text{:}2$. The carbonate dissolved quickly with effervescence and some heat release. Then, methanol was added dropwise as a precipitating agent. We used a mass of methanol equal to the mass of water used to dilute the phosphoric acid. The white precipitate was repeatedly washed and filtered, and eventually dried overnight at a temperature of $50\text{ }^\circ\text{C}$. The resulting powder was dissolved in de-ionized water and left

to recrystallize in open air for two weeks. The large crystals were finally crushed and thoroughly ground into a fine powder.

Two powder X-ray diffraction (XRD) methods were used. The first is based on synchrotron X-rays of wavelength $\lambda = 0.922 \text{ \AA}$ selected by a double-bounce monochromator. The sample was sealed in a capillary with a diameter of 1 mm mounted on a spinner and the temperature was controlled (to $\pm 1^\circ \text{C}$) by an air stream blower. A flat area detector perpendicular to the direction of the main beam was used in the transmission geometry to record the projections of the Debye–Scherrer cones that correspond to Bragg reflections from the polycrystalline powder. Software Fit2D [29] was used to convert the 2D datasets recorded by the area detector into one-dimensional I vs. 2θ powder diffraction patterns. The second method involved high-pressure measurements where a DIA-type large volume press was employed to compress the polycrystalline sample to a pressure up to 1.2 GPa. An energy dispersive method allowed us to record powder diffraction patterns within a fixed- 2θ geometry where a white incident beam collimated to dimensions $100 \times 100 \mu\text{m}^2$ was used together with a multichannel detector (MCD) placed at $2\theta = 6.480^\circ$. The pressure was transmitted through a mixture of amorphous boron and epoxy resin placed inside the cell. A layer of NaCl was also added to the mixture contained in the 1 mm diameter $\times$ 2 mm length boron nitride sample holder to allow an accurate determination of the pressure according to Decker’s equation [30]. The temperature was varied by an amorphous carbon furnace and measured using a W/Re thermocouple. The intensity, I , recorded as a function of the bin number of the MCD (which corresponds to a given wavelength within the white beam) was eventually converted to I vs. d -spacing powder diffraction data.

We also used ac impedance spectroscopy to confirm the connection between the superprotonic conductivity jump and the monoclinic ($P2_1/m$) $\rightarrow$ cubic ($Pm-3m$) polymorphic phase transition in CDP. Ac impedance spectroscopy measurements were carried out at $T = 190^\circ \text{C}$ and $T = 235^\circ \text{C}$ on cylindrical pellets pressed using CDP powders. Silver paint sprayed on both sides of the pellet and platinum mesh electrodes were used. The pellets were sealed in a 50 mL chamber filled with dry air and linked by feedthrough contacts to a Solartron 1260 impedance analyzer (AMETEK, Inc. Berwyn, PA, USA) operating at a 100 mV oscillating potential in a two point–four wire setup. At each temperature, both the in-phase and the out-of-phase components of the impedance, Z' and Z'' , were recorded at frequencies between 6 MHz and 100 Hz.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns recorded at room temperature ($T = 25^\circ \text{C}$) on (a) CDP, (b) KDP and (c) RDP powders within the 5° to 45° . 2θ range. For each of the three patterns, the black disks represent the data, whereas the solid line is a guide to the eye. The most relevant feature of the data is that the K- and Rb-based compounds have a similar tetragonal $I-42d$ symmetry, indicating that the room temperature KDP and RDP polymorphs are isostructural, whereas the XRD pattern from the Cs-based phosphate, CDP, is indexed by a different lattice symmetry, monoclinic $P2_1/m$. The three data sets also confirm the purity of the synthesized powders as all the observed peaks correspond to the Bragg reflection positions from the respective lattice.

The CDP behavior upon heating is shown in Figure 2. First, results from the ac impedance spectroscopy were collected at two temperatures, (a) $T = 190^\circ \text{C}$ and (b) $T = 235^\circ \text{C}$, and presented in the form of Nyquist plots (Z' vs. Z'' at different frequencies ranging from 6 MHz to 100 Hz), showing a dramatic increase in the sample’s proton conductivity.

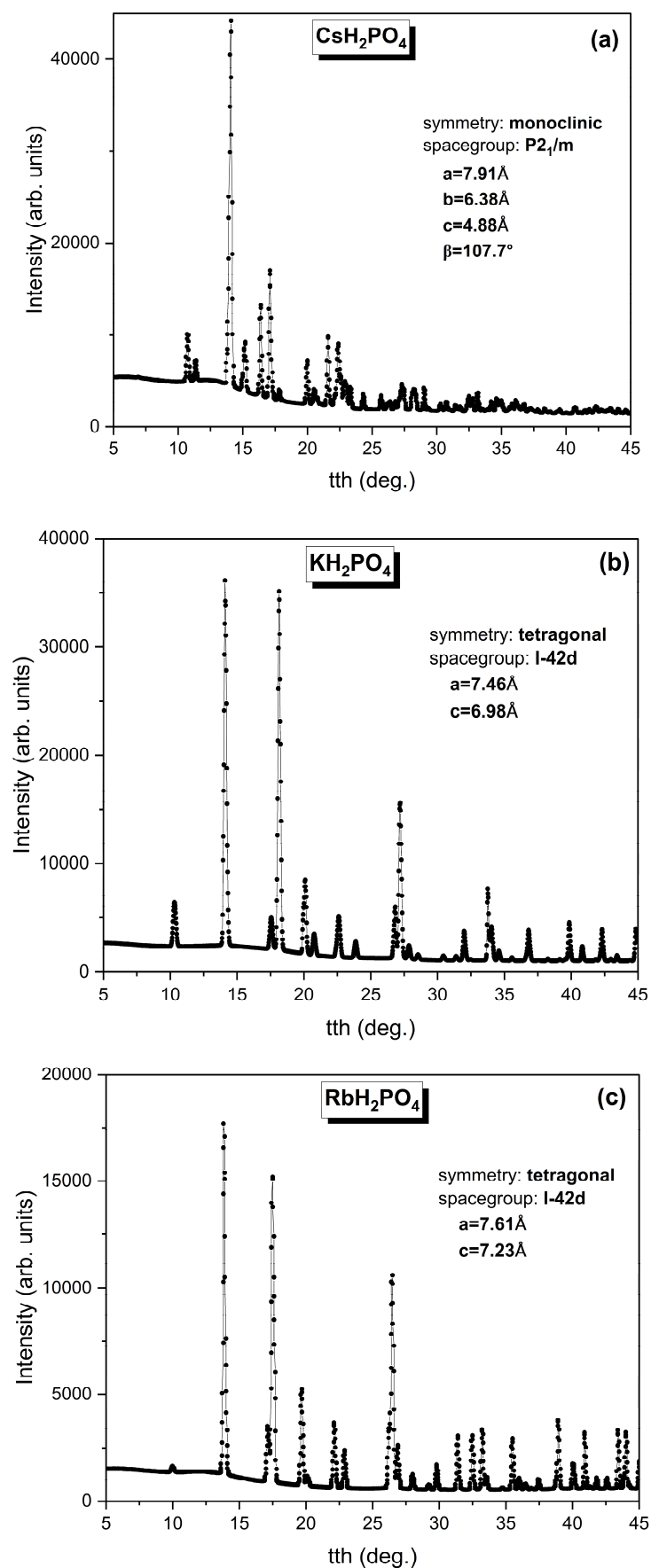


Figure 1. Powder X-ray diffraction (XRD) patterns recorded in transmission geometry using synchrotron radiation of wavelength $\lambda = 0.922 \text{ \AA}$ at room temperature ($T = 25 \text{ }^{\circ}\text{C}$) on the three solid acids used in this study, (a) CsH₂PO₄ (CDP), (b) KH₂PO₄ (KDP) and (c) RbH₂PO₄ (RDP).

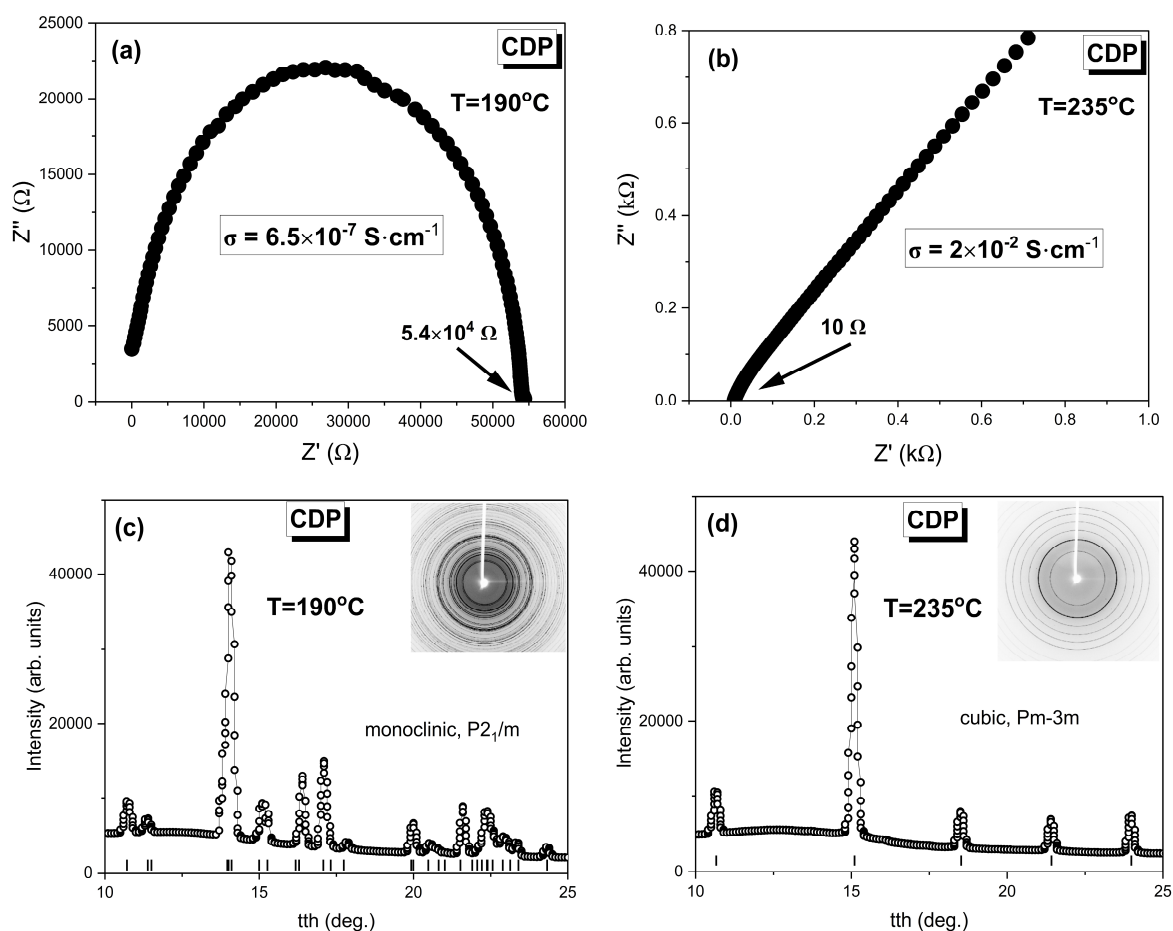


Figure 2. Frequency-resolved ac-susceptibility data collected on CDP pellets at (a) $T = 190\text{ }^{\circ}\text{C}$ and (b) $T = 235\text{ }^{\circ}\text{C}$ showing an abrupt jump in the proton conductivity (superprotonic behavior) upon heating, and powder XRD patterns collected at (c) $T = 190\text{ }^{\circ}\text{C}$ and (d) $T = 235\text{ }^{\circ}\text{C}$ indicating that a monoclinic ($P2_1/m$) $\rightarrow$ cubic ($Pm-3m$) polymorphic structural transition is responsible for the observed proton conductivity increase.

Indeed, the dataset collected at the lower temperature, $190\text{ }^{\circ}\text{C}$, exhibits a typical semicircular shape Nyquist plot which intersection with the Z' axis at low frequencies allows us to determine the proton conductivity of the sample as $6.5 \times 10^{-7}\text{ S}\cdot\text{cm}^{-1}$. At $T = 235\text{ }^{\circ}\text{C}$, however, the shape of the Nyquist plot changes dramatically into a straight line. Its intersection with the in-phase impedance axis yields a proton conductivity of $2 \times 10^{-2}\text{ S}\cdot\text{cm}^{-1}$, a value four orders of magnitude greater than its lower temperature counterpart. This superprotonic jump is associated with a polymorphic phase transition as indicated by the XRD data collected at the same temperatures (c) $T = 190\text{ }^{\circ}\text{C}$ and (d) $T = 235\text{ }^{\circ}\text{C}$. In both figures, the inset shows the raw data (the projection of the Debye-Scherrer cones onto the flat plate detector), while the open symbols are the corresponding I vs. 2θ powder XRD patterns. The vertical bars mark the 2θ positions of the Bragg reflections. These data show that the room temperature monoclinic $P2_1/m$ phase persists up to $T = 190\text{ }^{\circ}\text{C}$, but further heating to $T = 235\text{ }^{\circ}\text{C}$ leads to a new cubic $Pm-3m$ structure.

The data and analysis in Figure 3 confirm that the structure is indeed a CDP polymorph. The empty symbols here are the observed intensity I_{obs} recorded at different “detector” angles 2θ , whereas the red line is the calculated intensity I_{calc} via a Rietveld fit where the atom positions were allowed to vary together with the lattice constant and the profile parameters of the pseudo-Voigt function were used to model the peak shapes. The lower blue trace is the difference curve $I_{\text{calc}} - I_{\text{obs}}$. The fit yields a dynamically disordered

cubic structure described by a unit cell of lattice $a = 4.95 \pm 0.01 \text{ \AA}$, space group $Pm\text{-}3m$, and fractional coordinates (0, 0, 0) for the Cs atoms, (0.5, 0.5, 0.5) for the P atoms, and (0.5, 0.248(1) 0.322(2)) for the oxygen atoms which also have a multiplicity of 24 and an occupancy of 0.166.

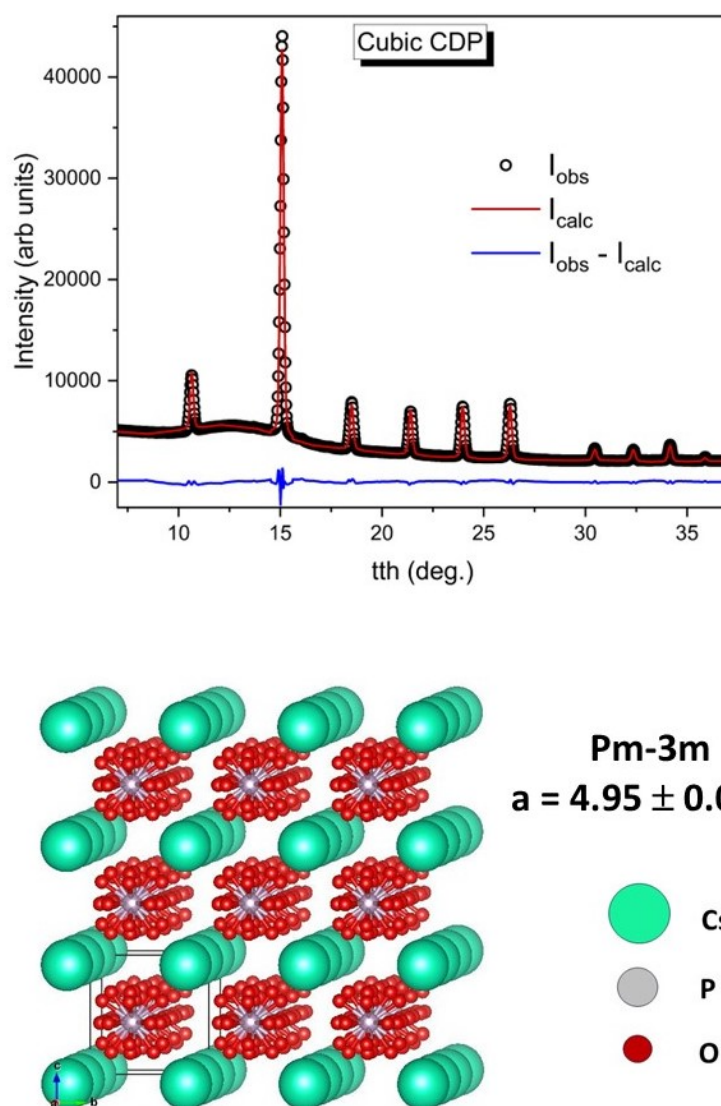


Figure 3. Rietveld refinement (red line) against powder XRD data recorded on CDP at $T = 235 \text{ }^{\circ}\text{C}$ (black circles) corresponding to a dynamically disordered cubic ($Pm\text{-}3m$, $a = 4.95 \pm 0.01 \text{ \AA}$) crystal structure where the Cs atoms (green) and P atoms (gray) are in (0, 0, 0) and (0.5, 0.5, 0.5) positions respectively, whereas the O atoms (red) occupy (0.5, 0.248(1) 0.322(2)) position with a multiplicity of 24 and an occupancy of 0.166.

Figure 4a shows the powder XRD pattern and the corresponding tetragonal ($I\text{-}42d$) crystal structure of KDP at $25 \text{ }^{\circ}\text{C}$. The Rb-based compound, RDP, has the same room temperature phase crystal structure [31]. As indicated above, an abrupt proton conductivity jump was reported at high temperatures and pressures ($\sim 325 \text{ }^{\circ}\text{C}$, 1 GPa) in both KDP and RDP. So, it might appear that even if this sudden proton conductivity increase was due to a polymorphic transition, such transition would not be of the monoclinic ($P2_1/m$) $\rightarrow$ cubic ($Pm\text{-}3m$) type (as the one observed in CDP). Interestingly, the data in Figure 4b brings a new perspective in this regard. It demonstrates that heating to intermediate temperatures ($220 \text{ }^{\circ}\text{C}$ in this case) leads to a phase transformation to a monoclinic $P2_1/m$ KDP polymorph that has lattice parameters $a = 7.581 \text{ \AA}$, $b = 6.206 \text{ \AA}$, $c = 4.530 \text{ \AA}$, and $\beta = 107.2 \text{ deg.}$ A

similar tetragonal $\rightarrow$ monoclinic transition was observed in RDP around 150 °C, where the existence of the monoclinic RDP polymorph was based on direct, stand-alone evidence, i.e., a full crystal structure (Rietveld) refinement against high-resolution X-ray diffraction data that allowed the precise determination of the space group, unit cell constants, fractional atom positions, and thermal parameters [31]. This is highly significant, because not only are the intermediate-temperature KDP and RDP polymorphs isomorphic to one another, but they are isomorphic (structurally identical) with the room temperature monoclinic CDP phase.

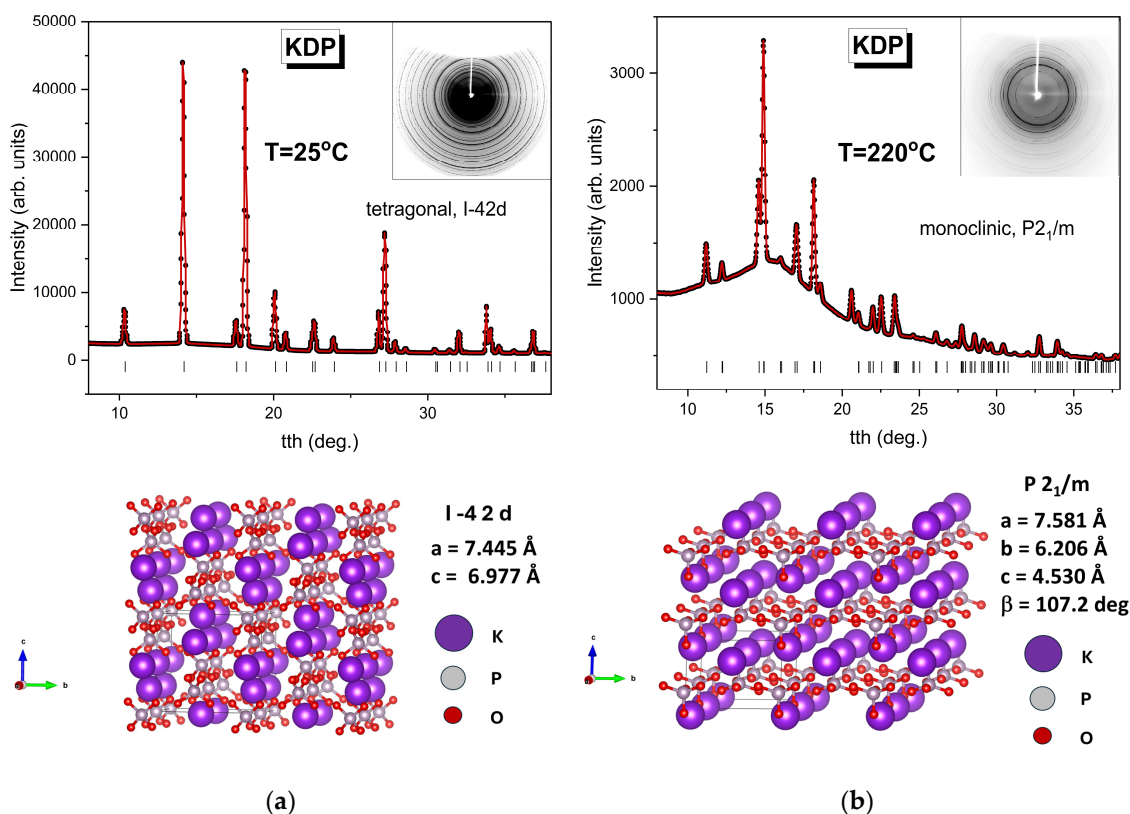


Figure 4. (a) Powder XRD collected on KDP at room temperature $T = 25\text{ }^{\circ}\text{C}$ and the corresponding tetragonal crystal structure (I-42d, $a = 7.445\text{ }\text{\AA}$ and $c = 6.977\text{ }\text{\AA}$), and (b) powder XRD collected on the same KDP sample at $T = 220\text{ }^{\circ}\text{C}$ and the corresponding crystal structure demonstrating a polymorphic transition to an intermediate-temperature monoclinic phase ($P2_1/m$, $a = 7.581\text{ }\text{\AA}$, $b = 6.206\text{ }\text{\AA}$, $c = 4.530\text{ }\text{\AA}$, and $\beta = 107.2\text{ deg.}$).

The observations above lead into the situation schematically presented in Figure 5. CDP crystallizes in a monoclinic ($P2_1/m$) symmetry at room temperature and upon heating to 240 °C (under ambient humidity and pressure conditions) this phase changes into a cubic ($Pm-3m$) one, which, based on extensive evidence, is responsible for the superprotonic behavior of CDP. The other two phosphate solid acids, KDP and RDP, crystallize in a tetragonal symmetry at room temperature, but both undergo the same tetragonal (I-42d) $\rightarrow$ monoclinic ($P2_1/m$) polymorphic phase transition when heated to intermediate temperatures. This is an interesting finding as it appears that, at room temperature, it deviates from the predictions of the radius ratio rule which predicts that increasing the cation size leads to higher symmetry crystals. The most likely explanation for the observed behavior is that KDP, RDP, and CDP are salts based on large, non-spherical and polarized oxyanions, while the radius ratio rule was developed taking into account just basic sphere-geometry considerations.

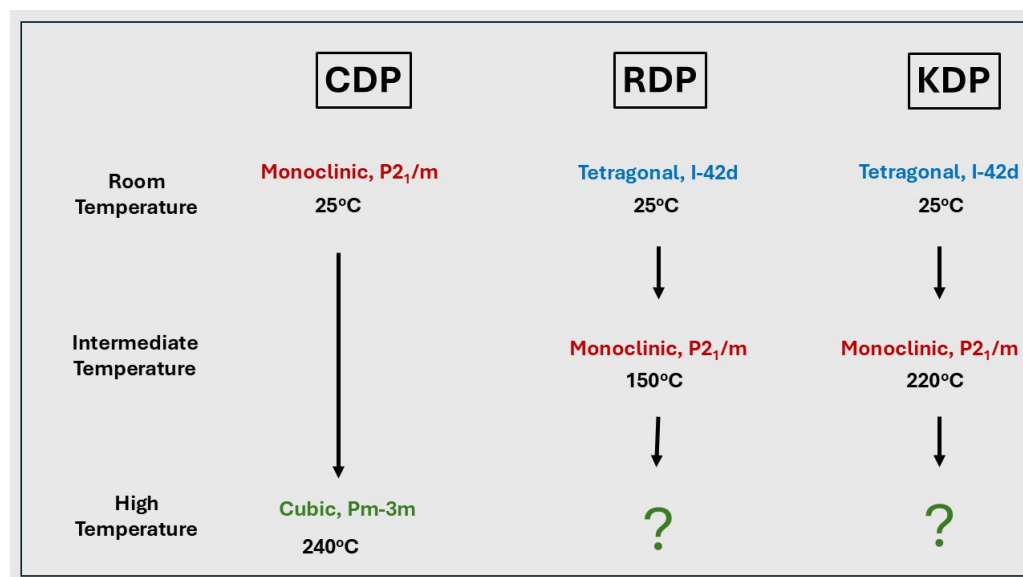


Figure 5. Schematic representation of the polymorphic phase transitions in MH_2PO_4 ($M = Cs, K, Rb$) proton conductors emphasizing the possibility that superprotonic KDP and RDP phases similar to their CDP counterpart exist at high temperatures.

This raises the question if further heating of the monoclinic KDP and/or RDP phases leads to another phase transition, possibly to a cubic phase like the one in their CDP counterpart. It is important to indicate that the high-temperature cubic CDP phase has not only been observed under ambient conditions where it is known to be transient [20], but also under a saturated water vapor atmosphere [18], high pressure [20,32], and a small volume of sealed dry air [9], conditions under which it is stable. For KDP and RDP an abrupt increase in proton conductivity was only observed under special conditions, particularly under high pressure [25]. Finally, there is solid evidence that the proton conductivity jump that occurs upon heating KDP's monoclinic phase under high pressure ($\sim 1\text{GPa}$) is due to melting [25], which would obviously be inconsistent with any type of transition from one crystalline phase to another. Consequently, we will focus our analysis below on the Rb-based compound, RDP.

A superprotonic behavior was not observed in RDP when the temperature was increased under ambient conditions. Accordingly, several studies have shown that the RDP monoclinic polymorph chemically decomposes via dehydration when its temperature is raised toward RDP's melting point [33], unless a special sample environment is used [25]. Consequently, instead of the powder XRD method used so far in our study, we searched for a possible second polymorphic transition in RDP based on a different setup where RDP powders kept under high pressure ($\sim 1.2\text{GPa}$) are heated up to $\sim 350^\circ\text{C}$ and XRD data are collected at different temperatures using an energy dispersive method.

Figure 6 shows two of such datasets recorded on RDP in the high-pressure cell as the temperature is raised from $T = 270^\circ\text{C}$ to $T = 320^\circ\text{C}$. There are three notable features of these data. First, the intensity, I , is reported as a function of the d -spacing as the detector angle 2θ is fixed at 6.480° . The energy sensitive detector records raw data as I vs. “bin number” (on 2040 bins corresponding to different energy values/wavelengths within the main white beam) and then the bin numbers are converted to d -spacing values. Second, despite being different from one another the two XRD patterns contain reflections that occur at the same d -spacing values (shown in the red rectangles). These are false reflections coming from the pressure-cell materials, the W/Re thermocouple and from Rb fluorescence, and will be ignored in the structural analysis below. Finally, the datasets show a significant change

in the Bragg reflections d-spacing positions as the temperature increases from 270 °C to 320 °C. We believe this observation indicates a polymorphic transition of monoclinic RDP to a higher symmetry phase (as evidenced by the reduction in the number of reflections).

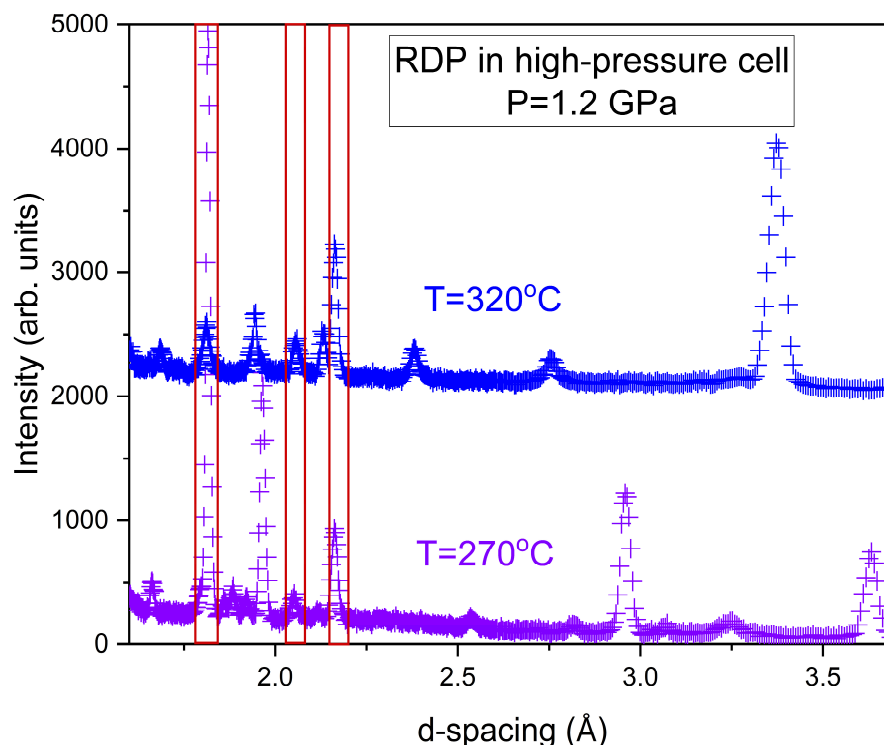


Figure 6. Energy dispersive powder XRD patterns collected on RDP under high pressure ($P = 1.2$ GPa) at $T = 270$ °C and $T = 320$ °C, indicating that structural modifications occur upon heating within this temperature range. The spurious peaks in the red boxes correspond to Rb fluorescence and Bragg reflections from materials used in the high-pressure cell.

Figure 7 shows a quantitative analysis of the powder XRD data recorded on RDP at $T = 320$ °C and $P = 1.2$ GPa (blue crosses). The small vertical bars represent the d-spacing positions of the Bragg reflections from a cubic Pm-3m structure that has a lattice parameter $a = 4.76$ Å. Even more importantly, the green curve shows the I vs. d profile calculated based on the best Rietveld fit that yields the fractional positions, occupancy, and multiplicity of the Rb, P, and O atoms in the unit cell, as well as their isotropic Debye–Waller factors. The lower black trace is the difference between the observed and calculated I vs. d curves. The fit converges ($\chi^2 = 2.24$) upon the independent variation in eight independent parameters related to the unit cell (O atom positions, peak profile, and histogram scale) and yields a disordered cubic phase described by a unit cell where Rb and P atoms are in (0, 0, 0) and (0.5, 0.5, 0.5) positions, respectively, whereas O atoms are in (0.5, 0.234(5) 0.342(6) position having a multiplicity of 24 and an occupancy of 0.166. The positions of the non-hydrogen atoms in the unit cell (including the six possible orientations of the PO_4 tetrahedra) are schematically shown in the lower panel, while more detailed information is presented in Table 1. This is an important result because it represents conclusive evidence of the existence of a monoclinic $\rightarrow$ cubic polymorphic phase transition in RDP.

As already mentioned, previous studies have shown a similar behavior in non-stoichiometric compounds [26,27], but our present study demonstrates that a stable *pure* RDP polymorph exists at $T = 320$ °C and $P = 1.2$ GPa and reveals its crystal structure. Second, we found that the cubic polymorph is structurally identical (isomorphic) with its CDP counterpart. This is significant because it implies that the same highly efficient proton conduction mechanism enabled by the PO_4 tetrahedral disorder is responsible

for the superprotonic conduction in both phosphates, CDP and RDP. Furthermore, an ac impedance spectroscopy study carried out on RDP under 1 GPa of pressure uncovered a superprotonic conductivity jump at about 327 °C [25], conditions nearly identical to those under which we observed the phase transition to cubic RDP. These observations corroborate and represent strong evidence that the abrupt increase in the proton conduction that occurs upon heating RDP toward its melting point is indeed due to a monoclinic $\rightarrow$ cubic polymorphic phase transition and not due to chemical modifications.

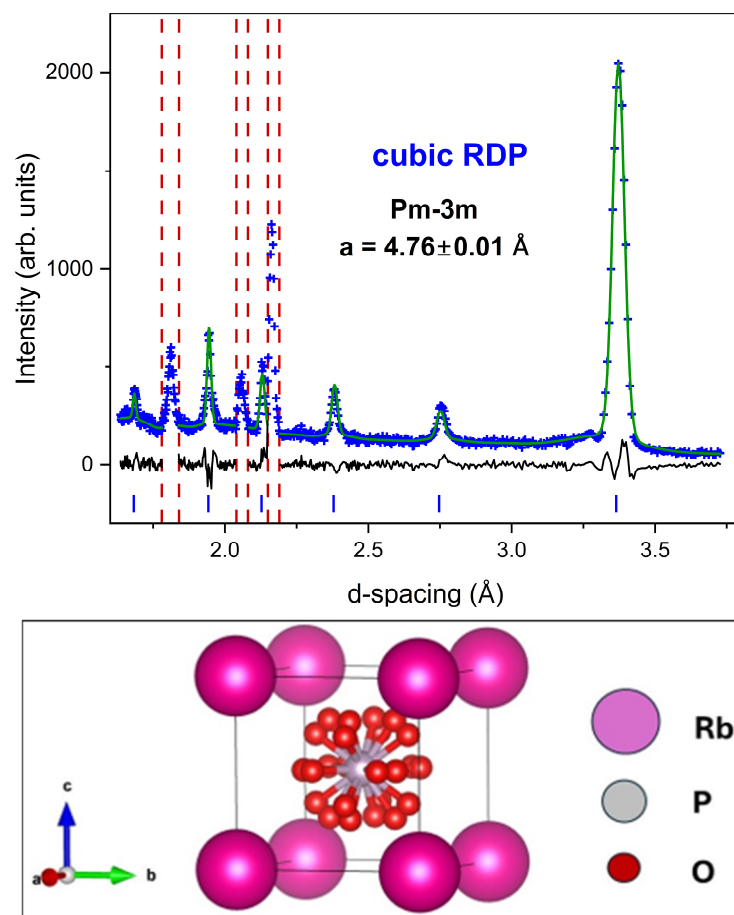


Figure 7. Rietveld refinement against high-pressure ($P = 1.2$ GPa) XRD data collected on RDP powders at $T = 320$ °C. The blue crosses are the observed intensities corresponding to different d-spacing values, I_{obs} ; the green line is the calculated intensity, I_{calc} , and the lower black trace is the difference curve $I_{\text{obs}} - I_{\text{calc}}$. The vertical bars mark the positions of the Bragg reflections from the cubic (Pm-3m, $a = 4.76$ Å) unit cell. The lower panel shows the unit cell atom positions, demonstrating the isomorphism between the superprotonic RDP and CDP polymorphs.

Table 1. Types, positions, and isotropic Debye–Waller factors of the atoms in the Pm-3m cubic RDP unit cell. Numbers in parentheses are statistical estimated standard deviations from the fit.

Atom Type	x	y	z	Fraction	Symmetry	Multiplicity	U_{iso}
Rb	0	0	0	1	m3m	1	0.025
P	0.5	0.5	0.5	1	m3m	1	0.025
O	0.5	0.234(5)	0.342(6)	0.166	m(x)	24	0.025

4. Summary

We used powder XRD and ac impedance spectroscopy to investigate the polymorphic phase transition undergone by the MH_2PO_4 ($M = \text{Cs}, \text{K}, \text{Rb}$) proton conductor series upon

heating and clarify their connection with the crystal structures and dynamic mechanisms that enable the dramatic proton conductivity increase in these materials at high temperatures. We found that although CDP and RDP crystalize in different lattice symmetries at room temperature—RDP is tetragonal (I-42d) and CDP is monoclinic ($P2_1/m$)—the two compounds become isomorphous at high temperatures where they both crystallize as dynamically disordered cubic ($Pm-3m$) polymorphs. Our most significant result is the finding that cubic RDP is stable at $T = 320\text{ }^{\circ}\text{C}$ under a pressure of 1.2 GPa. We used powder XRD data collected under these conditions to determine the structure of this polymorph: space group $Pm-3m$, lattice constant $a = 4.76 \pm 0.01\text{ \AA}$, and a unit cell where Rb and P atoms are in (0, 0, 0) and (0.5, 0.5, 0.5) positions respectively, whereas O atoms are in (0.5, 0.234(5) 0.342(6)) position having a multiplicity of 24 and an occupancy of 0.166. We also determined that the isomorphism between KDP and RDP persists to intermediate temperatures as demonstrated by a tetragonal (I-42d) $\rightarrow$ monoclinic ($P2_1/m$) polymorphic phase transition. Yet, unlike RDP, the K-based phosphate, KDP, shows no evidence of a cubic, superprotonic polymorph. This is consistent with previous results from ac impedance spectroscopy measurements [25]. Besides their fundamental significance, our results are important for clean-energy applications as phosphate-based solid acids are materials that can function as fuel cell electrolytes based on their transition to high-temperature superprotonic phases.

Author Contributions: C.E.B., conceptualization, methodology, investigation, project administration, formal analysis, and writing—original draft; C.L., investigation, project administration, formal analysis, and writing—review and editing; Z.M. and A.D.P., formal analysis, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded in part by the Donors of the American Chemical Society Petroleum Research Fund under research grant no. 45854-GB10.

Data Availability Statement: The data presented in this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Manjón, F.J.; Errandonea, D. Pressure-induced structural phase transitions in materials and earth sciences. *Phys. Status Solidi (B)* **2009**, *246*, 9–31.
- Bernstein, J. Polymorphism—A Perspective. *Cryst. Growth Des.* **2011**, *11*, 632–650. [[CrossRef](#)]
- Barber, J.; Revolinsky, P.; Bhagatji, J.; Pedrazzoli, D.; Kravchenko, S.; Kravchenko, O. Polymorphism and Mechanical Behavior in Hot-Pressed 3D-Printed Polyamide Composite: Effects of Pressure and Temperature. *Polymers* **2025**, *17*, 922. [[CrossRef](#)] [[PubMed](#)]
- Desiraju, G.R. Crystal Engineering: From Molecule to Crystal. *J. Am. Chem. Soc.* **2013**, *135*, 9952–9967. [[CrossRef](#)] [[PubMed](#)]
- Wang, Q.; Yan, H.-Z.; Zhao, X.; Wang, C.-M. Polymorphic Phase Transition and Piezoelectric Performance of BaTiO_3 - CaSnO_3 Solid Solutions. *Actuators* **2021**, *10*, 129. [[CrossRef](#)]
- Valeeva, A.A.; Sadovnikov, S.I.; Gusev, A.I. Polymorphic Phase Transformations in Nanocrystalline Ag_2S Silver Sulfide in a Wide Temperature Interval and Influence of Nanostructured Ag_2S on the Interface Formation in $\text{Ag}_2\text{S}/\text{ZnS}$ Heteronanostructure. *Nanomaterials* **2022**, *12*, 1668. [[CrossRef](#)] [[PubMed](#)]
- Chistyakov, D.; Sergeev, G. The Polymorphism of Drugs: New Approaches to the Synthesis of Nanostructured Polymorphs. *Pharmaceutics* **2020**, *12*, 34. [[CrossRef](#)] [[PubMed](#)]
- Higashi, K.; Ueda, K.; Moribe, K. Recent progress of structural study of polymorphic pharmaceutical drugs. *Adv. Drug Deliv. Rev.* **2017**, *117*, 71–85. [[CrossRef](#)] [[PubMed](#)]
- Botez, C.E.; Martinez, I.; Price, A.D. Stability of Superprotonic CsH_2PO_4 Hermetically Sealed in Different Environments. *Materials* **2022**, *15*, 4969. [[CrossRef](#)] [[PubMed](#)]
- Holley, R., III; Burlingame, Q.C.; Loo, Y.-L. Mapping the polymorphic phase transformations of CsPbI_3 perovskite thin films. *J. Mater. Chem. C* **2025**, *13*, 19654–19659. [[CrossRef](#)]
- Zhu, L.-F.; Zhang, B.-P.; Zhao, X.-K.; Zhao, L.; Yao, F.-Z.; Han, X.; Zhou, P.-F.; Li, J.-F. Phase transition and high piezoelectricity in $(\text{Ba,Ca})(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ lead-free ceramics. *Appl. Phys. Lett.* **2013**, *103*, 072905. [[CrossRef](#)]

12. Wang, X.; Wei, Q.; Luo, J.; Jia, X.; Zhang, M.; Zhu, X.; Wei, B. Pressure-Induced Phase Transitions and Electronic Structure Evolution of Ba₄Au. *Materials* **2025**, *18*, 3728. [[CrossRef](#)] [[PubMed](#)]
13. Rowińska, M.; Stefańska, D.; Bednarchuk, T.J.; Zareba, J.K.; Jakubas, R.; Gagor, A. Polymorphism and Red Photoluminescence Emission from 5s² Electron Pairs of Sb(III) in a New One-Dimensional Organic–Inorganic Hybrid Based on Methylhydrazine: MHy₂SbI₅. *Molecules* **2024**, *29*, 455. [[CrossRef](#)] [[PubMed](#)]
14. Alrefaee, S.H.; Ahmed, H.A.; Khan, M.T.; Al-Ola, K.A.; AL-Refai, H.; El-Atawy, M.A. New Self-Organizing Optical Materials and Induced Polymorphic Phases of Their Mixtures Targeted for Energy Investigations. *Polymers* **2022**, *14*, 456. [[CrossRef](#)] [[PubMed](#)]
15. Parthasarathy, G.; Santosh, M. Pressure Induced Polymorphic Phase Transition of Natural Metamorphic Kalsilite; Electrical Resistivity and Infrared Spectroscopic Investigations. *Minerals* **2015**, *5*, 647–653. [[CrossRef](#)]
16. Haile, S.M.; Chisholm, C.R.; Sasaki, K.; Boysen, D.A.; Uda, T. Solid acid proton conductors: From laboratory curiosities to fuel cell electrolytes. *Faraday Discuss.* **2007**, *134*, 17–39. [[CrossRef](#)] [[PubMed](#)]
17. Paschos, O.; Kunze, J.; Stimming, U.; Maglia, F. A Review on Phosphate Based, Solid State, Protonic Conductors for Intermediate Temperature Fuel Cells. *J. Phys. Condens. Matter* **2011**, *23*, 234110. [[CrossRef](#)] [[PubMed](#)]
18. Boysen, D.A.; Uda, T.; Chisholm, C.R.; Haile, S.M. High-performance solid acid fuel cells through humidity stabilization. *Science* **2004**, *303*, 68–70. [[CrossRef](#)] [[PubMed](#)]
19. Ponomareva, V.G.; Shutova, E.S. High-temperature behavior of CsH₂PO₄ and CsH₂PO₄–SiO₂ composites. *Solid State Ion.* **2007**, *178*, 729–734. [[CrossRef](#)]
20. Botez, C.E.; Hermosillo, J.D.; Zhang, J.; Qian, J.; Zhao, Y.; Majzlan, J.; Chianelli, R.R.; Pantea, C. High-temperature phase transitions in CsH₂PO₄ under ambient and high-pressure conditions: A synchrotron x-ray diffraction study. *J. Chem. Phys.* **2007**, *127*, 194701. [[CrossRef](#)] [[PubMed](#)]
21. Mohammad, N.; Mohamad, A.B.; Kadhum, A.A.H.; Loh, K.S. A review on synthesis and characterization of solid acid materials for fuel cell applications. *J. Power Sources* **2016**, *322*, 77–92. [[CrossRef](#)]
22. Ortiz, E.; Vargas, R.A.; Mellander, B.E. On the high-temperature phase transitions of CsH₂PO₄: A polymorphic transition? A transition to a superprotonic conducting phase? *J. Chem. Phys.* **1999**, *110*, 4847–4853. [[CrossRef](#)]
23. Park, J.-H. Possible origin of the proton conduction mechanism of CsH₂PO₄ crystals at high temperatures. *Phys. Rev. B* **2004**, *69*, 054104. [[CrossRef](#)]
24. Park, J.-H.; Kim, C.-S.; Choi, B.-C.; Moon, B.K.; Seo, H.-J. Physical properties of CsH₂PO₄ crystal at high temperatures. *J. Phys. Soc. Jpn.* **2003**, *72*, 1592–1593. [[CrossRef](#)]
25. Boysen, D.A.; Haile, S.M.; Liu, H.; Secco, R.A. Conductivity of Potassium and Rubidium Dihydrogen Phosphates at High Temperature and Pressure. *Chem. Mater.* **2004**, *16*, 693–697. [[CrossRef](#)]
26. Xiong, G.; Wang, L.S.; Haile, S.M. Superprotonic conductivity in RbH_{2–3y}(PO₄)_{1–y}: A phosphate deficient analog to cubic CsH₂PO₄ in the (1 – x)RbH₂PO₄–xRb₂HPO₄ system. *Mater. Horiz.* **2023**, *10*, 5555–5563. [[CrossRef](#)] [[PubMed](#)]
27. Gaydamaka, A.A.; Ponomareva, V.G.; Bagryantseva, I.N. Phase composition, thermal and transport properties of the system based on the mono- and dihydrogen phosphates of rubidium. *Solid State Ion.* **2019**, *329*, 124–130. [[CrossRef](#)]
28. Botez, C.E.; Price, A.D. Structural and Proton Conduction Modifications in RbH₂PO₄ Crystals upon Heating Under Different Environments. *Crystals* **2026**, *16*, 147. [[CrossRef](#)]
29. Hammersley, A.P.; Svenson, S.O.; Hanfland, M.; Fitch, A.N.; Hauserman, D. Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High Press. Res.* **1996**, *14*, 235–248. [[CrossRef](#)]
30. Decker, D.L. High-Pressure Equation of State for NaCl, KCl, and CsCl. *J. Appl. Phys.* **1971**, *42*, 3239–3244. [[CrossRef](#)]
31. Botez, C.E.; Martinez, H.; Tackett, R.J.; Chianelli, R.R.; Zhang, J.; Zhao, Y. High-temperature crystal structures and chemical modifications in RbH₂PO₄. *J. Phys. Condens. Matter* **2009**, *21*, 325401. [[CrossRef](#)] [[PubMed](#)]
32. Boysen, D.A.; Haile, S.M.; Liu, H.; Secco, R.A. High-temperature behavior of CsH₂PO₄ under both ambient and high pressure conditions. *Chem. Mater.* **2003**, *15*, 727–736. [[CrossRef](#)]
33. Li, Z.; Tang, T. High-temperature dehydration behavior and protonic conductivity of RbH₂PO₄ in humid atmosphere. *Mater. Res. Bull.* **2010**, *45*, 1909–1915. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.