High-temperature crystal structures and chemical modifications in RbH$_2$PO$_4$

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Abstract
We have used laboratory and synchrotron x-ray diffraction to investigate the structural and
chemical changes undergone by polycrystalline RbH$_2$PO$_4$ upon heating within the 30–250 °C
temperature interval. Our data show no evidence of the previously reported onset of partial
polymerization at $T = 96$ °C (Park *et al* 2001 *J. Phys.: Condens. Matter* **13** 9411) which was
proposed as an explanation for the high-temperature proton conductivity enhancement in
phosphate-based solid acids. Instead, we found that a tetragonal → monoclinic polymorphic
transition initiates at $T \approx 90$ °C. The transition is complete at $T \approx 130$ °C, and the new
monoclinic RbH$_2$PO$_4$ polymorph is stable upon further heating to $T = 200$ °C. Moreover, its
crystal structure is *isomorphic* to that of monoclinic CsH$_2$PO$_4$. This remarkable similarity
suggests that the microscopic structures and dynamics responsible for the high-temperature
superprotonic behavior of RbH$_2$PO$_4$ could be the same as those of its Cs-based counterpart.

1. Introduction

The fully hydrogen-bonded solid acids CsH$_2$PO$_4$ (CDP) and
RbH$_2$PO$_4$ (RDP) have been shown to exhibit an abrupt several-
order-of-magnitude jump in their proton conductivity upon
heating above a temperature threshold [1, 2]. Based on
this so-called 'superprotonic' behavior, CDP was successfully
used as a fuel-cell electrolyte at $T \approx 235$ °C [3], an
application that received a great deal of attention from both the
technological and the fundamental perspective. The ultimate
goal of the basic research on the high-temperature behavior
of these materials is to uncover the microscopic mechanisms
responsible for their enhanced proton conductivity. This
is particularly important, as theoretical studies of fully
hydrogen-bonded solid acids [4] have predicted that the proton
conduction mechanisms in these compounds are, in principle,
different from those in their half-hydrogen-bonded, sulfate-
based counterparts (e.g. CsHSO$_4$). Thus, an entirely new and
highly-efficient type of proton dynamics might be triggered by

heating in CDP and RDP. It is important to note, however, that
proposing realistic atomic-level scenarios of proton migration
requires a detailed knowledge of the chemical composition and
crystal structure of the phases present in these materials at
high temperatures. Yet, the mere nature of the microscopic
modifications that accompany the proton conductivity jump in
CDP and RDP has been under dispute for almost two decades.
Some research groups have attributed the proton conductivity
enhancement to polymorphic structural transitions to high-
temperature superprotonic CDP and RDP phases [1, 2, 5, 6],
while others have claimed that the heating-induced dehydration
and chemical decomposition of these compounds is, in fact,
responsible for their high-temperature behavior. Very recently,
high-pressure synchrotron x-ray diffraction [7] corroborated
with high-pressure ac-impedance spectroscopy experiments [1]
have conclusively shown that the superprotonic behavior
of CDP is indeed associated with a polymorphic structural
transition from the room-temperature monoclinic ($P2_1/m$)
phase of this material to a high-temperature dynamically-
disordered cubic ($Pm3m$) CDP phase. These findings were
shortly followed by neutron spectroscopy studies [8] which

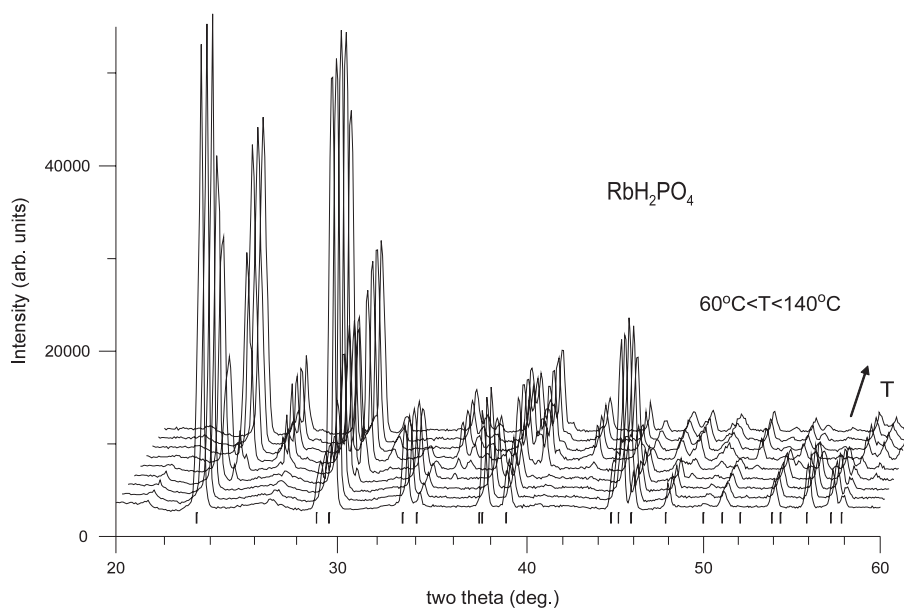[4] Author to whom any correspondence should be addressed.

Figure 1. Temperature-resolved XRD data collected upon heating a polycrystalline RDP sample in 10 °C steps from 60 to 140 °C (the data are vertically and horizontally shifted for clarity). The vertical bars indicate the 2θ positions of the Bragg reflections for the room-temperature tetragonal ($I\bar{4}2d$) RDP phase. The data show that the tetragonal phase changes into a lower-symmetry structure over the 90–130 °C temperature interval.

evidenced that the characteristics of the high-temperature CDP phase (e.g. its high-symmetry, and the six-fold dynamically-disordered PO_4 tetrahedra) have an important role in the enhancement of the proton conduction. Therefore, one could reasonably assume that the observed superprotonic behavior of RDP might also be due to a polymorphic transition similar to that of its Cs-based counterpart (e.g. monoclinic → cubic). Still, several aspects related to this conjecture require further clarification. First, the room-temperature phase of RDP is not monoclinic, but tetragonal ($I\bar{4}2d$). Although tetragonal RDP undergoes a first transformation at a temperature within the 80–120 °C interval (more than 100 °C below the superprotonic temperature threshold), and many authors have claimed this transformation to be a structural transition to a intermediate-temperature monoclinic RDP phase, the vast majority of these studies were based on thermal analysis methods which inherently lack the ability to provide crystal structure details. There is one x-ray diffraction study on RDP samples kept at 110 °C [9] that reveals a change in the in the XRD photograph with respect to its RT counterpart, but, as the authors indicate, precise structure determination attempts were not successful due to heating-induced twinning and crystal fragmentation. Consequently, the study could only conclude that the RDP modification at 110 °C is 'probably' isomorphic to KD_2PO_4, i.e. monoclinic $P2_1$ ($a = 7.37$ Å, $b = 14.73$ Å, $c = 7.17$ Å, and $\beta = 92°$). In view of these results, Ortiz *et al* made another attempt at uncovering the structural details of the above-mentioned transformation by carrying out XRD measurements of RDP powders previously kept at 150 °C [10]. These authors found new diffraction peaks in the XRD pattern (in addition to those of the RT tetragonal phase), but, surprisingly, the 2θ positions of these reflections did not match either the ones from the monoclinic RDP proposed in [9] or any other monoclinic structure claimed to represent the

intermediate-temperature RDP phase (e.g. the $P2_1/a$ RDP modification in [11]). Based on this observation, and following visual comparisons with the Bragg reflection positions in the powder XRD of the double salt $2RbH_2PO_4 \cdot Rb_2H_2P_2O_7$, Ortiz concludes that the transformation undergone by RDP near 100 °C is not a tetragonal-to-monoclinic polymorphic transition, but represents the sample's dehydration and chemical decomposition/polymerization via the reaction: $4RbH_2PO_4 \rightarrow 2RbH_2PO_4 \cdot Rb_2H_2P_2O_7 + H_2O$. These results are in agreement with observations by Park *et al* [12, 13], where optical microscopy, thermal analysis, and impedance spectroscopy methods were used to reach the same conclusion: the modification undergone by RDP at 96 °C represents the onset of partial polymerization according to the chemical reaction above. In addition, Park proposes a model [14] where the heating-induced enhanced proton conductivity in phosphate-based solid acids is attributed to the rapid braking and reforming of hydrogen bonds triggered by the above-mentioned dehydration/polymerization. This has an important implication for the microscopic nature of the superprotonic behavior of RDP, as the study that most clearly evidenced the proton conductivity jump upon heating RDP powders to 327 °C (under 1 GPa of pressure) [2] employed samples previously stored at 100 °C in an attempt at inducing the tetragonal-to-monoclinic transition prior to the experiment. Nonetheless, if Ortiz and Park's interpretation is correct, such thermal treatment resulted in the dehydration/polymerization of the RDP sample, and, consequently, the proton conductivity enhancement observed in [2] would not be due to the existence of a high-temperature superprotonic RDP phase, but to microscopic mechanisms related to chemical changes, as the ones proposed by Park. In the context of the previous findings on CDP [1, 7], however, this would mean that the same macroscopic phenomenon (the superprotonic behavior)

observed in two systems that are chemically similar (CDP and RDP), would have microscopic origins that are *fundamentally different* from one another: a polymorphic structural transition for CDP, and thermal decomposition for RDP. As this is highly unexpected, further investigations of the real nature of the RDP transformation around 100 °C are worth carrying out.

We present a detailed x-ray diffraction study aimed at clarifying the structural transitions and chemical modifications undergone by polycrystalline RDP upon heating within the 30–250 °C temperature range. Powder x-ray diffraction methods, enhanced by the use of synchrotron radiation, are a powerful tool in the study of structural transitions for at least two reasons. First, the determination of a crystal structure allows a precise, direct, and equivocal identification of a given phase/polymorph [15]. Second, modern powder diffraction data analysis techniques permit the study of diffraction patterns from multiple-phase systems, where a mixture of different polymorphs can be identified, the contributions from each individual component can be isolated, and subsequently used for structure determination [16]. Our temperature-resolved data show that, upon heating, RDP undergoes a tetragonal → monoclinic structural transition that initiates at $T \approx 90$ °C and is complete at $T \approx 130$ °C. The new monoclinic RDP polymorph, which is stable upon further heating to $T \approx 200$ °C, crystallizes in spacegroup $P2_1/m$ (unit cell parameters $a = 7.694$ Å, $b = 6.199$ Å, $c = 4.774$ Å and $\beta = 109.02°$) and has a crystal structure that is strikingly similar to that of the room-temperature CDP phase. This strongly suggests that the superprotonic behavior in RDP might have the same microscopic origin as in CDP— a polymorphic transition from monoclinic $P2_1/m$ to a high-symmetry disordered superprotonic phase. Expectedly, however, a special environment is required to evidence such a transition and stabilize the superprotonic phase. Under ambient conditions we find that heating above 200 °C results in the slow and partial decomposition of RDP via dehydration.

2. Experimental procedure

RDP crystals were grown by slow evaporation from an aqueous solution prepared by mixing stoichiometric amounts of H_3PO_4 and Rb_2CO_3. The crystals were subsequently mechanically ground to a fine powder. Laboratory x-ray diffraction experiments were carried out using a Siemens D5000 diffractometer equipped with a Paar HTK high-temperature chamber and a Braun position sensitive detector. The sample was weighed and loaded in a flat-plate sample holder. During data collection, the RDP powder was exposed to an open atmosphere relative humidity of ~40%. Temperature-resolved XRD data were collected over the 30–250 °C range, in 10 °C steps; at each temperature, powder diffraction patterns corresponding to a 20°–60° 2θ-range (λ = 1.5406 Å) were recorded in the reflectivity geometry. The data collection time for each XRD pattern was approximately 90 min. The process was repeated several times to verify the reproducibility of the results. No significant differences between experimental runs were observed in the XRD patterns at any temperature. The synchrotron XRD measurements were
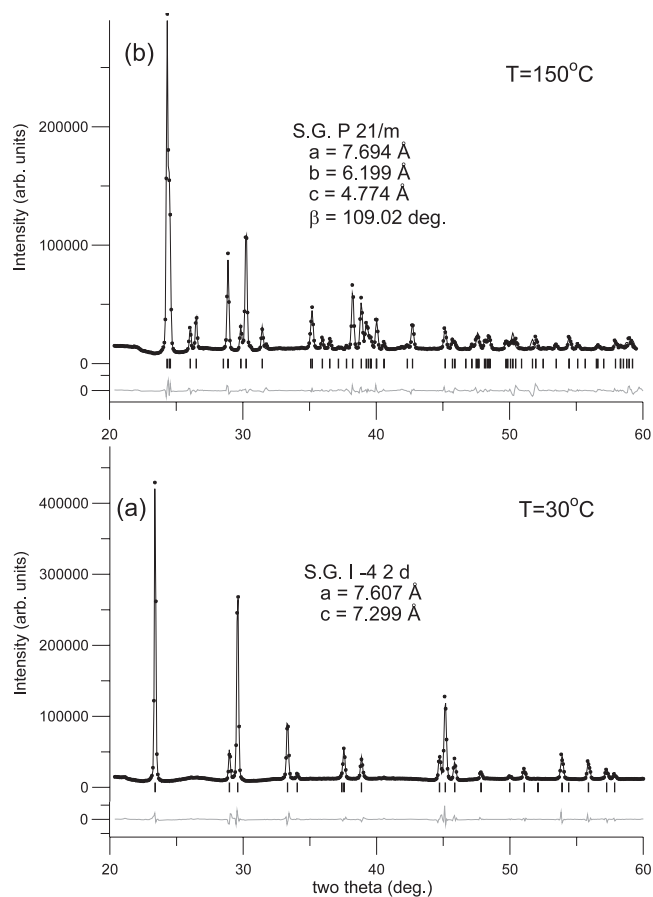

Figure 2. Le Bail fits to x-ray powder diffraction patterns measured at (a) 30 °C and (b) 150 °C. The solid symbols are the observed intensities (I_{obs}), the solid line is the best fit (I_{calc}), and the lower trace is the difference curve ($I_{obs} - I_{calc}$). For both phases, the vertical bars indicate the Bragg reflection positions. The newly observed high-temperature phase is indexed by monoclinic spacegroup $P2_1/m$ and lattice parameters $a = 7.694$ Å, $b = 6.199$ Å, $c = 4.774$ Å, and $\beta = 109.02°$.

performed on the X7B beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory using x-rays of wavelength 0.922 Å selected by a double flat-crystal monochromator. A Mar345 flat-plate detector was employed in the transmission geometry to detect the diffracted beam. The powder sample was contained in a glass capillary during the data collection. Images were collected upon heating RDP polycrystals in 10 °C steps from room temperature to 250 °C. An exposure time of 45 s was used at each temperature. Eventually, the images were processed by integrating over the projections of the Debye–Scherrer cones onto the flat detector using the FIT2D software [17].

3. Results and discussion

Figure 1 shows powder XRD patterns measured over the 20°–60° 2θ-range at nine different temperatures upon heating a RDP sample from 60 to 140 °C (data are shifted both laterally and vertically for clarity). The vertical bars indicate the 2θ positions corresponding to the Bragg reflections from
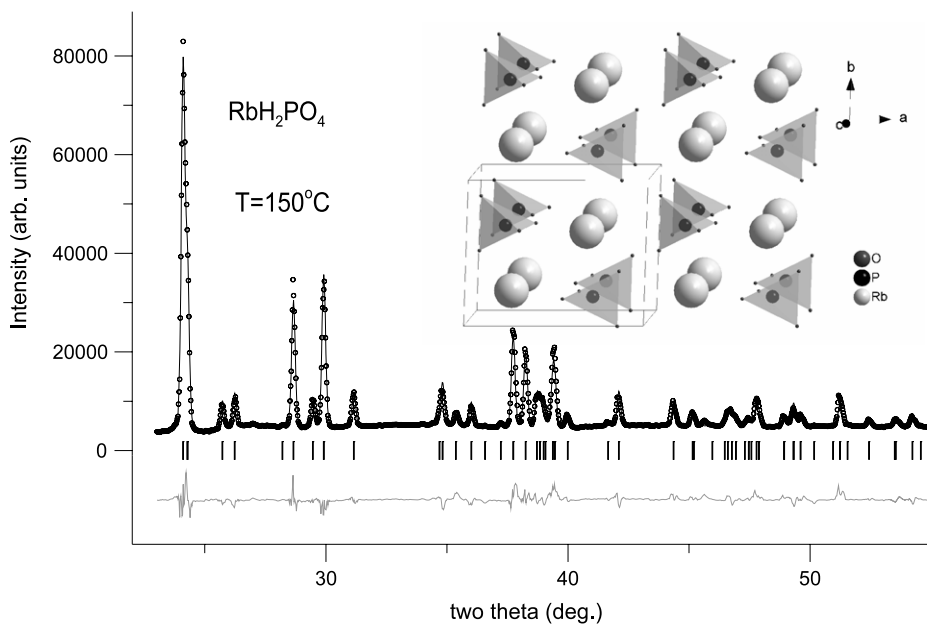
Figure 3. Rietveld refinement of the monoclinic RDP phase. The empty symbols represent the measured scattered intensity as a function of the diffraction angle, while the solid line is the calculated pattern. The lower trace shows the difference between the observed and the calculated patterns and the vertical bars are the Bragg reflection markers. The inset shows the Rietveld refined positions of the non-hydrogen atoms in the crystal structure of monoclinic RDP.

the room-temperature tetragonal RDP phase, which, as the data indicate, is the only phase present in the sample up to 80 °C. At $T = 90$ °C, however, the diffracted intensities from this phase start decreasing, and they completely vanish upon further heating to 130 °C. Concomitantly, new robust peaks appear in the XRD patterns indicating that the tetragonal RDP undergoes a complete transformation over the 90–130 °C temperature interval. Heating above 130 °C (up to about 200 °C) results in no further changes in the XRD profile.
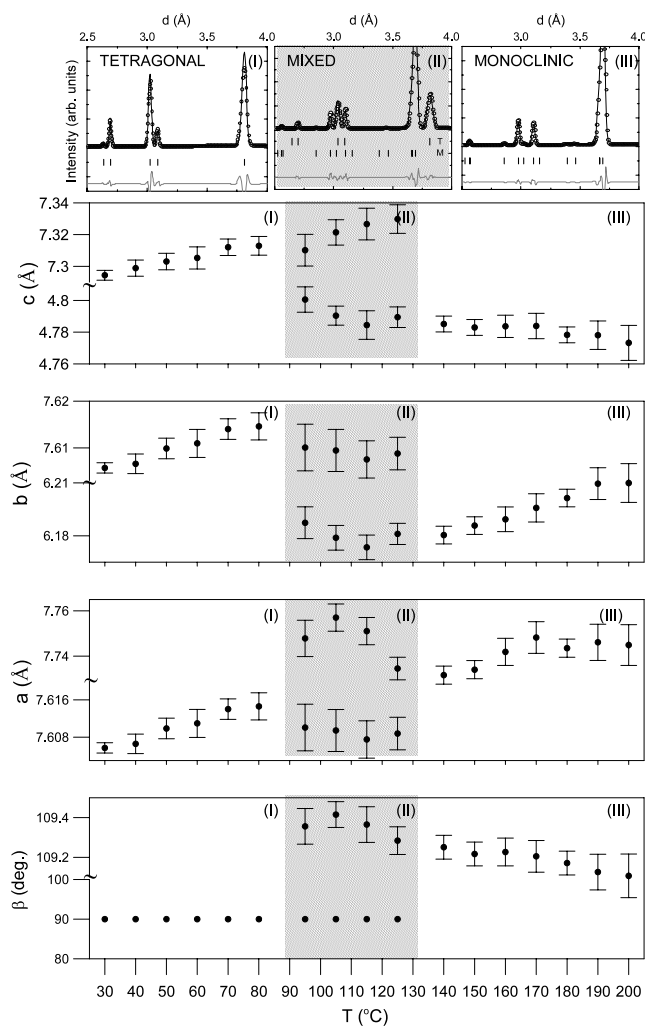
An important question at this point of our analysis is whether the above-described RDP transformation results in a single phase or in multiple phases. We managed to index the data collected at $T = 150$ °C to a single crystallographic phase with spacegroup $P2_1/m$ and unit cell parameters $a = 7.694$ Å, $b = 6.199$ Å, $c = 4.774$ Å and $\beta = 109.02°$. Figure 2 shows full profile (Le Bail) fits to (a) the room-temperature RDP phase and (b) the above-mentioned monoclinic $P2_1/m$ phase. In both cases the solid symbols represent the diffracted intensity observed at a given angle 2θ, the solid line is the best fit, the lower trace is the difference curve between the observed and the calculated intensities, and the vertical bars are the positions of the Bragg reflections. In a Le Bail fit the unit cell parameters, the diffracted intensities, and the peak profile parameters are iteratively adjusted to give the best agreement with the data. The fits in figure 2 were obtained using this procedure implemented in the program FULLPROF [18]. For the room-temperature RDP phase the starting unit cell parameters and spacegroup were taken from the Powder Diffraction File 84-0115, whereas for the higher-temperature phase we used the unit cell information obtained from the indexing of the $T = 150$ °C data. The peak profiles were modeled in both cases by pseudo-Voigt

functions. Besides allowing a precise determination of the lattice parameters, the high-quality (low-residual) Le Bail fits shown in figure 2 clearly demonstrate that tetragonal RDP transforms into a *single* monoclinic ($P2_1/m$) phase that is stable at $T = 150$ °C. No change in the sample's weight was detected upon heating to this temperature. Below, we show that this new phase is, indeed, a RDP polymorph.

To verify the nature of the observed monoclinic structure we carried out Rietveld refinements [19] against the $T = 150$ °C XRD data using the General Structure Analysis System (GSAS) [20]. In a Rietveld refinement one adjusts not only the parameters governing the unit cell dimensions and the peak profile shape, but also the atomic coordinates and thermal parameters to obtain the best agreement with the data. The results of this analysis are shown in figure 3, where the solid line is the best Rietveld fit, the empty symbols represent the scattered intensity measured as a function of the diffraction angle, the lower trace is the difference curve (between the observed and calculated patterns), and the vertical bars are reflection markers for the Bragg reflections. The starting parameters for the Rietveld fit included the lattice constants, spacegroup, and peak-shape parameters yielded by the Le Bail analysis above. We also assumed that the phase at $T = 150$ °C is a RDP polymorph whose structure is isomorphic with the room-temperature monoclinic ($P2_1/m$) CDP—this gave us the starting positions for the non-hydrogen atoms. Soft constraints were imposed on the P–O bond distances and the O–P–O bond angles in the PO_4 tetrahedra. The refinement converges upon the simultaneous variation of 15 parameters to a whole-pattern residual $R_{wp} = 7.6\%$. The resulting fractional coordinates of the non-hydrogen atoms and the isotropic thermal parameters are presented in table 1, and the corresponding crystal structure

Table 1. Fractional atomic coordinates and thermal parameters of the monoclinic RDP phase. Numbers in parentheses are statistically estimated standard deviations (ESDs) from the Rietveld fit.

	Fractional coordinates and thermal parameters						
Atom	X	Y	Z	Multiplicity	Wyckoff letter	Occupancy	U_{iso}
Rb	0.2623(6)	0.25	0.0604(8)	2	e	1	0.0377(23)
P	0.2456(17)	0.75	0.5319(25)	2	e	1	0.0377(23)
O(1)	0.4156(26)	0.75	0.4132(33)	2	e	1	0.0377(23)
O(2)	0.3451(23)	0.75	0.8736(44)	2	e	1	0.0377(23)
O(3)	0.1289(35)	0.5482(51)	0.4203(42)	4	f	1	0.0377(23)

Figure 4. Temperature dependence of the lattice parameters of the (I) tetragonal, (II) mixed (tetragonal + monoclinic), and (III) monoclinic phases of RDP. At each temperature the lattice parameters were obtained from Le Bail fits to synchrotron x-ray diffraction data. The upper panels show fits to the (I) 30 °C, (II) 110 °C, and (III) 150 °C data.

tetrahedra are slightly distorted; the O(1)–P–O(2) angle, for example, is reduced to 101.10° from its theoretical value of 109.44°. Yet, the most important result of the Rietveld analysis is that the crystal structure of the monoclinic RDP polymorph is almost identical to its CDP counterpart. This is demonstrated by the results in table 2 which presents a comparison between the two monoclinic (CDP and RDP) phases. As previously mentioned, monoclinic CDP is the room-temperature phase of this compound, which changes into the disordered cubic (superprotonic) CDP phase when heated to ∼235 °C. It is therefore remarkable that, upon heating, room-temperature tetragonal RDP transforms into an intermediate-temperature monoclinic polymorph whose crystal structure is essentially the same as monoclinic CDP *before* exhibiting the superprotonic jump at about 300 °C. This strongly suggests that the proton conductivity enhancement observed in RDP might have a microscopic origin similar to the one in its Cs-based counterpart, i.e. a polymorphic structural transition to a high-symmetry disordered phase.

Once we determined the identity and the crystal structure of the intermediate-temperature phase obtained by heating polycrystalline RDP, we carried out further temperature-resolved XRD experiments to clarify the details of the tetragonal → monoclinic transition and investigate the stability of the monoclinic RDP polymorph upon heating above 150 °C. We used synchrotron x-rays and a flat-plate detector, which significantly reduced the data collection time at each temperature to about 45 s. The temperature was increased in 10 °C increments, and, at each temperature step, full profile analysis of the XRD data was used to accurately determine the unit cell parameters of the phase or phases present in the sample. Figure 4 shows the results obtained at temperatures within the 30–200 °C temperature range. Three distinct regions are observed: (I) between 30 and 90 °C, (II) between 90 and 130 °C, and (III) between 130 and 200 °C. The three upper panels show Le Bail fits to data collected within these three regions. The fits demonstrate that tetragonal RDP is the only phase present within region (I), a mixture of tetragonal and monoclinic RDP coexists within region (II), and pure monoclinic RDP is present in region (III). The lower panels show the temperature dependence of the lattice parameters of the two RDP polymorphs obtained from Le Bail fits to XRD data. A smooth variation of these parameters is observed, which indicates that no other structural or chemical modifications (except for the tetragonal → monoclinic polymorphic transition) occur in the 30–200 °C temperature range. Most importantly, the data and

is shown in the inset of figure 3. The structure consists of alternating rows of PO$_4$ tetrahedra and Rb atoms that run parallel to the *c* axis. Each tetrahedron is hydrogen bonded at all four corners so that there are two types of hydrogen-bond chains zig-zagging along the *a* and *c* axes. The Rietveld refinement also reveals that the PO$_4$
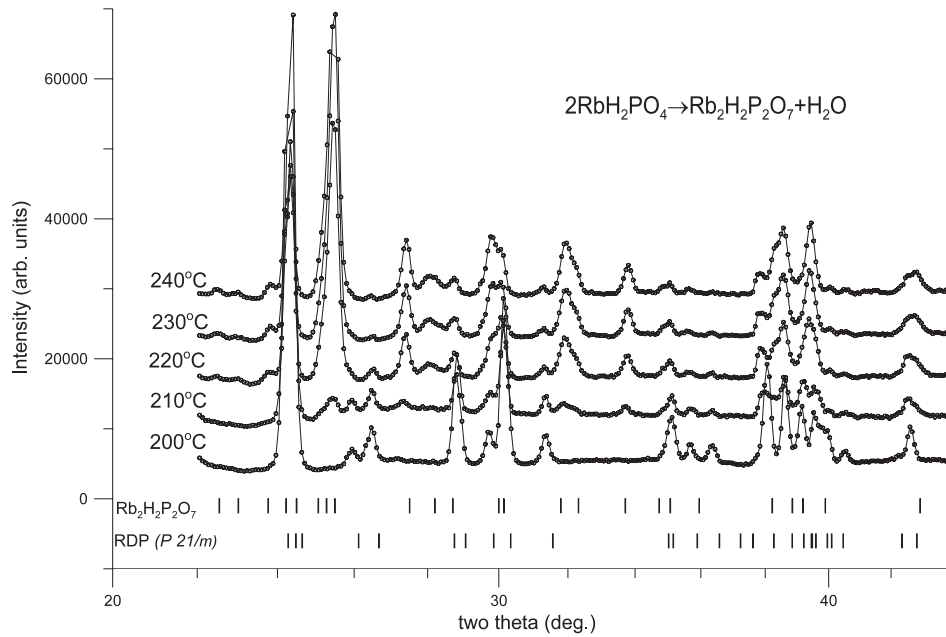
Figure 5. Temperature-resolved x-ray powder diffraction patterns of RDP measured within the 200–240 °C interval. The data shows the decomposition of the monoclinic RDP upon heating, according to the reaction $2RbH_2PO_4 \rightarrow Rb_2H_2P_2O_7 + H_2O$.

Table 2. Comparison between unit cell parameters and PO_4 tetrahedral bond distances and angles in the monoclinic phases of rubidium- and cesium-dihydrogen phosphate.

	RDP	CDP [7]
Unit cell		
Spacegroup	$P2_1/m$	$P2_1/m$
a (Å)	7.868(6)	7.912(2)
b (Å)	6.299(5)	6.383(1)
c (Å)	4.871(4)	4.8802(8)
β (deg)	109.15(3)	107.73(2)
Phosphate group tetrahedral bond distances and angles		
P–O(1) (Å)	1.622(19)	1.565(6)
P–O(2) (Å)	1.590(18)	1.481(5)
P–O(3) (Å)	1.558(7)	1.529(4)
O(1)–P–O(2) (deg)	101.1(9)	107.0(3)
O(1)–P–O(3) (deg)	109.6(6)	106.1(2)
O(2)–P–O(3) (deg)	113.4(6)	113.6(2)
O(3)–P–O(3) (deg)	109.4(7)	109.9(2)

analysis undeniably demonstrate that the monoclinic RDP phase is stable up to 200 °C. In addition, our finding of a temperature region over which the two RDP polymorphs (tetragonal and monoclinic) coexist is significant because it reveals why the temperature at which the tetragonal RDP phase transforms could not be unambiguously determined (many authors have previously indicated that the transition occurs at *a* temperature somewhere in the 80–120 °C range,

depending on the sample and experimental conditions [21]). Finally, we observed that heating above 200 °C under ambient pressure and humidity conditions does lead to the partial dehydration of the monoclinic RDP polymorph via the reaction $2RbH_2PO_4 \rightarrow Rb_2H_2P_2O_7 + H_2O$. This is demonstrated in figure 5, where the open symbols represent XRD patterns collected at five different temperatures between 200 and 240 °C. The lower and the upper vertical bars indicate the

2θ positions of the Bragg reflections from monoclinic RDP and di-rubidium dihydrogen pyrophosphate ($Rb_2H_2P_2O_7$), respectively. While the $200\,°C$ data is fully indexed by the monoclinic RDP unit cell, further heating leads to new robust peaks in the XRD pattern that correspond to $Rb_2H_2P_2O_7$. At $240\,°C$ the pyrophosphate phase is dominant, but well-defined reflections from monoclinic RDP are still present in the data. This partial chemical decomposition is not unexpected, and is the likely reason for which a potential transition to a superprotonic RDP phase cannot be observed upon heating under ambient conditions. This is somewhat similar to the behavior of CDP, with the exception that the onset of the decomposition and the superprotonic transition in CDP occur at almost the same temperature [7], whereas RDP starts dehydrating at about $210\,°C$, which is about one hundred degrees below the temperature where the jump in proton conductivity was observed. Consequently, if the superprotonic behavior of RDP is indeed due to a polymorphic transition from monoclinic to a high-temperature superprotonic phase (similar to that in CDP), experiments where the heating is carried out under a special environment (high-pressure or saturated water vapor atmosphere) are needed to uncover this structural transformation. These measurements are currently underway.

4. Summary

We used laboratory and synchrotron x-ray diffraction to investigate the crystal structure modifications and chemical changes that occur upon heating polycrystalline RDP within the 30–$250\,°C$ temperature interval. Our data and analysis show that RDP does not start dehydrating/polymerizing at $T = 96\,°C$, as previously proposed [13], but undergoes a polymorphic transition from its room-temperature tetragonal phase to an intermediate-temperature monoclinic phase. The transition begins at $T \approx 90\,°C$ and is complete at $T \approx 130\,°C$, with a mixture of the two RDP polymorphs being present in the sample in between these temperatures. The new monoclinic RDP phase crystallizes in spacegroup $P2_1/m$ with unit cell parameters $a = 7.694$ Å, $b = 6.199$ Å, $c = 4.774$ Å and $\beta = 109.02°$. Its crystal structure is nearly identical to that of monoclinic CDP, which hints to the possibility that similar structural transitions and proton conduction mechanisms are responsible for the superprotonic behavior observed in both these phosphate-based solid acids. Upon further heating under ambient pressure and humidity conditions, the monoclinic RDP polymorph is stable up to $200\,°C$, temperature above which it starts dehydrating via the reaction $2RbH_2PO_4 \rightarrow Rb_2H_2P_2O_7 + H_2O$.

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