Investigations of the Phase Transition and Proton Dynamics in Rubidium Methane Phosphonate Studied by Solid-State NMR

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In search of new solid acid proton conductors, we prepared the solid acid rubidium methane phosphonate (RMP). These crystals have a monoclinic structure (P2_1/c; a = 9.3452, b = 9.3142, and c = 7.5021 Å; β = 101.12). The salt incorporates a hydrated lamellar structure. The 1H MAS NMR reveals two different types of acidic protons as well as the water protons in the lamella. The 1H VT MAS NMR of RMP·2H_2O single crystal shows a structural phase transition around 320 K, and the high-temperature phase exhibits significant proton dynamics. The proton proximities are established by solid state 1H DQF NMR. The dehydration of RMP crystal leads to structural collapse, and the resultant RMP powder is extremely hygroscopic. The proton environment and dynamics are examined using 1H DQF NMR, which reveals that the dehydrated RMP powder has rigid lattice, in contrast with the hydrated form. Further the 1H VT MAS NMR shows that dehydrated RMP powder has no phase transition, and no significant proton dynamics are observed in the temperature range of 250–350 K. The new hydrated crystal, RMP·2H_2O, shows high proton mobility at relatively low temperature (∼330 K) and a proton transport mechanism that uniquely relies on crystalline water.

Introduction

Fuel cells are promising candidates for clean and portable energy sources, because of their high efficiencies in electrical power generation and low pollution levels. The electrolyte membranes are indispensable for the development of fuel cells. Recently, Haile, et al. demonstrated that the inorganic solid acid proton conductors, such as CsH_2PO_4, can be used as solid electrolyte membrane in H_2/O_2 and direct methanol fuel cells, although several improvements are necessary before their practical application can be realized. These solid acids commonly noted as MH_2XO_4 (M = K, Cs, Rb, and X = P, Se) are comprised of hydrogen-bonded tetrahedral oxy-anions, charge-balanced by monovalent cations. Such materials undergo a structural phase transition to high-temperature phase commonly known as “superprotonic phase” in which high protonic conductivity through conduction of hydrogen bonded acid protons is observed. This transition is normally above 473 K, and for RbH_2PO_4 (hereafter called RDP), the superprotonic phase transition is around 543 K. The proton conductivity at ambient temperatures is a desirable property of fuel cell membrane materials, so it is essential to lower this transition temperature. One effective way to lower the structural phase transition is to decrease the strength of hydrogen bonding in the structure. It is known that substitution of alkane groups such as methyl and ethyl could lower lattice energy and hence lower the transition temperature. With this goal, we synthesized the solid acid rubidium methane phosphonate (hereafter called RMP) by substituting methyl group onto the acid group in rubidium dihydrogen phosphate.

To probe the structure and dynamics of this new material, the complementary techniques of solid-state nuclear magnetic resonance (NMR) and X-ray diffraction were used. While X-ray diffraction is useful for determining the positions of the heavy atoms, solid-state NMR can be used to study the proton dynamics and its local structure. In particular the two-dimensional NMR measurements could shed more light on the hydrogen-bonding structure, as well as providing a site-specific handle on the local dynamics. In this paper, the proton environments are investigated using 2D double quantum (DQ) 1H MAS NMR. This method combines the chemical shift resolution afforded by high-speed MAS with the ability to measure residual dipolar couplings and hence corresponding proton neighbors. The local dynamics of proton are also probed by proton spin–lattice relaxation (T_1) measurements.

Experimental Section

Single crystals of rubidium methane phosphonate (RMP) are obtained from a aqueous saturated solution of rubidium carbonate (Aldrich, 99.9%) and methyl phosphonic acid (Aldrich, 98%). Upon standing in a closed environment, the solutions produced good quality crystals that are transparent and colorless. The single-crystal X-ray diffraction data for the RMP was recorded at 100 K, using Cu Ka radiation with a wavelength of 1.54178 Å. The final R-factor for the structure solution was 2.82% with a space group of P2_1/c, and the details of the structure are available in the Supporting Information. The RMP·2H_2O single crystal is crushed into powder and dehydrated under vacuum heat treatment (350 K). This dehydrated powder is extremely hygroscopic and can be only handled in glove box. Hence, further experiments on RMP powder are done under tightly sealed inert atmosphere.

Rubidium dihydrogen phosphate (RDP) crystals are grown from aqueous solution of rubidium carbonate and phosphoric acid. The RDP crystals were crushed into powder and heat treated at 140 °C to remove any adsorbed water and produce high-temperature monoclinic phase. The diffraction of RDP
powder shows the formation of monoclinic $P\overline{2}1/a$, which agrees with previous reports.\textsuperscript{7} The monoclinic phase of RDP has been chosen here to provide a comparison with monoclinic structured RMP single crystal. $^1\text{H}$ MAS NMR was carried out using Bruker AV 500, 11.7 T magnet. The magnet has a proton Larmor frequency of 500.10 MHz and the $^1\text{H}$ pulse lengths were 2.5 $\mu$s. Rotors of 2.5 mm outer diameter, with a sample volume of 10 $\mu$L, were used to obtain MAS frequencies of 25 kHz. The $^1\text{H}$ chemical shifts were referenced to the solid external secondary sample adamantane ($\delta = +1.63$ ppm with respect to TMS $\delta = 0$ ppm). The $^{87}\text{Rb}$ MAS NMR measurements on RMP and RDP powder were carried out in Bruker AV 900 (21.1 T magnet) and AV 500 (11.7 T magnet) with rotors of 2.5 mm outer diameter and MAS frequencies of 25 kHz. The reported error values in the quadrupolar coupling constant ($C_Q$) are estimated from the fitting of the $^{87}\text{Rb}$ central transition spectra obtained at two different magnetic fields. The $^{87}\text{Rb}$ chemical shifts were referenced to saturated aqueous solution of rubidium nitrate chemical shift ($\delta$) 0 ppm. The $^1\text{H}-^2\text{H}$ double quantum filtered (DQF) experiments are carried out using the back to back (BaBa) pulse sequence$^9,10$ with spinning speed of 25 kHz. The spin lattice relaxation ($T_1$) measurements were done using a saturation recovery pulse sequence with a spinning speed of 25 kHz. It is known that for fast spinning speeds ($>20$ kHz) significant frictional heating occurs. The actual sample temperature was calibrated using the $^{119}$Sn resonance of $\text{Sm}_2\text{SnO}_3$ as a chemical shift thermometer.$^8$ The RMP single crystals are moisture sensitive and very delicate to handle, in particular during high-speed magic angle spinning ($>20$ kHz), the crystals shattered into tiny pieces inside the rotor. To avoid this, the RMP single crystal is wrapped in Teflon tape and placed inside the 2.5 mm rotor filled with anhydrous titanium oxide powder. The $^1\text{H}$ MAS NMR experiments on rotor with Teflon tape and titanium oxide were done, and no background signals are detected for this arrangement. However, during a long MAS NMR experiment ($>10$ h), even with this packing arrangement the crystal disintegrates. This precludes any long MAS NMR experiments, such as DQF sideband pattern experiments (will be discussed later) on this crystal. For other short experiments, the crystal is checked at regular intervals to make sure that it is not damaged. The crystals after the NMR experiments are kept not damaged. The crystals after the NMR experiments are kept.

**Solid-State NMR Methods.** The dipolar coupling ($D_{ij}$) between protons $i$ and $j$ separated by a distance $r_{ij}$ is given by

$$D_{ij} = \frac{\mu_0 \gamma_i \gamma_j}{4\pi r_{ij}^3}$$

where $\mu_0$ is the vacuum permeability and $\gamma_i$ are the magnetic ratios of the interaction protons. To investigate $^1\text{H}-^1\text{H}$ dipole–dipole couplings directly, we make use of the BaBa double quantum (DQ) sequence, which allows us to distinguish between strongly and weakly dipolar coupled nuclei.$^9,10$ Strongly coupled systems can be used to generate double quantum coherences between pairs of protons. The relative intensity of the direct excitation (single pulse) MAS spectrum as compared to the 1D DQ filtered spectrum with increasing recoupling times could provide an immediate indication of the relative strengths of the dipolar couplings in the system.$^{11,12}$ The shorter the recoupling time needed to see a signal, the stronger is the coupling of the corresponding nuclei. Signals from such strongly coupled protons are subject to an ensuing decay at longer recoupling times due to the perturbing influence of further protons.$^{13}$ Combining these observations with our knowledge of the chemical structures, it is straightforward to identify those protons which are influenced by motional processes from those which are rigid on the time scale of our experiments.

A two-dimensional single quantum (SQ)-double quantum (DQ) correlation spectrum serves to identify the nature of the dipolar coupled pair, since the coupling partner of the directly detected spin can be identified in the indirect dimension, where the chemical shift is the sum of the shifts of the two involved protons. Auto peaks are located on the DQ diagonal.

The dipolar coupling strengths between different protons can be extracted by using rotor encoded DQF sideband measurements.$^{14}$ For an isolated spin-1/2 pair, the signal intensity of the DQ sidebands ($I_{\text{DQ}}$) is described by

$$I_{\text{DQ}}(t_1,t_2 = 0) = \cos(2\Delta \omega_{pc} t_1) \left[ \frac{3}{\tau} D_{eff} \sin(2\beta^0) \times \cos(\gamma^0 + \omega_{pc} t_1) N_T \right] \sin\left[ \frac{3}{\tau} D_{eff} \sin(2\beta^0) \cos(\gamma^0) N_T \right]$$

here $D_{eff}^\text{pp}$ is the effective dipolar coupling between protons $i$ and $j$, $\Delta \omega_{pc}$ is the frequency increment for States-TPPI, $t_1$ is the DQ evolution time increment, $\omega_{pc}(=2\pi\nu_{pc})$ is the spinning frequency, $N$ is the number of rotor periods in the excitation/reconversion portion of the BaBa sequence, $r_{\text{sg}}(=c_{\text{sg}})$ is the rotor period, $\beta^0$ and $\gamma^0$ are the Euler angles describing the orientation of the principal axis of the dipolar coupling tensor between spins $i$ and $j$ within the reference frame fixed to the rotor, and the symbol () represents the powder average. Fitting the observed sideband intensity to eq. 2, leads to the quantitative value of the dipolar coupling constant ($D_{ij}$), which in turn gives the distance between the atoms.$^{16,17}$ Here we demonstrate the use of side band patterns to determine the hydrogen-bonded proton–proton proximities in a new rubidium methane phosphonate.

**Results**

**Single-Crystal Structural Data.** The single-crystal X-ray diffraction data acquired on rubidium methane phosphonate (RMP) single-crystal reveal that it has a monoclinic structure with space group $P2_1/c$, and the details of the structural parameters are available in the Supporting Information. The unit cell parameters are $a = 9.3452$, $b = 9.3142$, and $c = 7.5021$ Å; $\beta = 101.12$, and the cell volume is 640.746 Å$^3$. The single-crystal X-ray studies at low temperature (100 K) and ambient temperature (296 K) show that the crystal holds the same space group with slightly different unit cell parameters which is probably due to thermal expansion of unit cell. This implies that the crystal has same monoclinic structure ($P2_1/c$) in the temperature range of 100–300 K. Unexpectedly the salt incorporates a hydrated lamellar structure, and the chemical composition of the single crystal is $\text{Rb}_2\text{H}_2(\text{CH}_3)_4(\text{PO}_3)_{12}\text{H}_2\text{O}$. The rubidium dihydrogen phosphate (RDP) is known to crystallize in the tetragonal system ($I4_2d$) at room temperature, whereas its deuterated analogue $\text{RbD}_2\text{PO}_4$ crystallizes in monoclinic phase ($P2_1$) similarly as $\text{KH}_2\text{PO}_4$.\textsuperscript{18–20} In the present study the undeuterated RMP crystallizes in monoclinic structure at room temperature.

The crystal structure of RMP.2H$_2$O is shown in Figure 1. The water in the lamellar structure holds the two phosphate anions together and four such phosphate anions along with four rubidium atoms and four acid protons form a unit cell. The RMP.2H$_2$O unit cell contains two pairs of acid protons.
which are separated by 7.537 Å along the $a$ axis. In the pair, two acid protons are separated by 3.534 Å along the $b$ axis (see Figure 1). However, the single-crystal X-ray measurements are inadequate to distinguish subtle differences in the acid proton environments, whereas the $^1$H MAS NMR measurements will give a more detailed view of the acid proton environments. So further studies to explore the proton environments and its dynamics were carried out by high resolution $^1$H MAS NMR measurements.

**Thermal Analysis.** Thermal analysis by differential scanning calorimetry (DSC) for RMP$\cdot$2H$_2$O single crystal is shown in Figure 2. Two endothermic peaks are observed around 330 and 340 K. However, there is no significant weight loss observed in the thermogravimetric analysis (TGA) during this temperature range (not shown here). Therefore, dehydration of the crystals can be neglected. This indicates, rather, a possible structural phase transition in the RMP$\cdot$2H$_2$O single crystal. The thermal analysis during cooling cycle of DSC shows the absence of these peaks and simply a flat curve (not shown here). This indicates the quasi-irreversible nature of this phase transition. This quasi-

irreversible phase transition is common in crystals of KDP type (KH$_2$PO$_4$, where $K$ = Rb, Cs, or NH$_4$).$^{21}$ The parent compound RDP has quasi-irreversible phase transition around 390 K, and the CsH$_2$PO$_4$ has similar a quasi-irreversible phase transition around 500 K.$^{22}$ Further, the visual inspection of crystals during heating affirms that the crystal is not melted, and there are no significant changes at this temperature range (up to 370 K). More detailed insight into the phase transition is provided by the $^1$H MAS NMR measurements in the low temperature and high-temperature structures.

$^1$H MAS NMR. Figure 3 shows the $^1$H MAS NMR of RDP, RMP$\cdot$2H$_2$O single crystal, and RMP powder acquired with spinning speed of 25 kHz. The chemical shift value of each resonance sheds light on the different hydrogen-bonding environments. The proton chemical shift scales for different environments are well documented in the literature.$^{23,24}$ It has been demonstrated that, for H-bonded anions, inorganic acid, metal hydrates, and carboxylic acids, there is a linear decrease in the proton isotropic chemical shift with increasing H-O hydrogen bond length.$^{24}$ Hence, a general correlation can be used between the observed $^1$H chemical shifts and the hydrogen bond lengths in these materials.

Normally the acid protons are expected to have a chemical shift in the range of 10–15 ppm, due to the influence of strong hydrogen bonds. The methyl protons have relatively low chemical shifts (0–2 ppm). The proton resonance for the physisorbed water would be between 4 and 7 ppm. With this chemical shift scale, we can label the $^1$H resonances observed for RDP and RMP. The $^1$H MAS NMR of high-temperature phase RDP powder (Figure 3a) shows two resonances at higher chemical shifts at 14.2 and 12.0 ppm corresponding to the two different acid protons, which coincides with the well-known crystal structural data.$^{18}$ There is also a broad and low-intensity peak at 6.4 ppm, which is due to the physisorbed water in the RDP powder. The RDP system has been well studied by thermal analysis methods, high-temperature powder X-ray diffraction methods,$^{18}$ NMR,$^{25}$ and NQR,$^{26}$ so here after, we will concentrate on the RMP$\cdot$2H$_2$O single crystal and the RMP powder. The $^1$H MAS NMR of the RMP$\cdot$2H$_2$O single crystal shows (Figure 3c) three major proton resonances which can be generally classed as acid protons, methyl protons, and water protons. The two overlapping resonances at 13.5 ppm (peak A1) and 12.8 ppm (peak A2) represent the two slightly different acid protons. The full width at half-maxima ($\Delta$) of peaks A1 and A2 are 345 and 280 Hz, respectively. The peak at 1.2 ppm ($\Delta$ ≈ 710 Hz) represents methyl protons (peak M), and the sharp
powder. The water peak is very weak and broad (\( \Delta f = 740 \text{ Hz} \)) representing methyl protons (peak M) and acid proton (peak A) resonances at 1.2 ppm (\( \Delta f = 290 \text{ Hz} \)) and 12.3 ppm (\( \Delta f = 10 \text{ kHz} \)) respectively. The water peak is dehydrated under vacuum heat treatment, exhibits resonances at 1.2 ppm (\( \Delta f = 740 \text{ Hz} \)) and 12.3 ppm (\( \Delta f = 490 \text{ Hz} \)) representing methyl protons (peak M) and acid proton (peak A) respectively. The water peak is very weak and broad (\( \Delta f = 2150 \text{ Hz} \)), indicating the very small amount of water in RMP powder.

\(^1\text{H} \text{ MAS DQF Spectra.}\) Beyond the general assignment of the \(^1\text{H} \text{ MAS NMR spectra, we can explore the proton environment and dynamics by using 1D double quantum filtered (DQF) } \(^1\text{H} \text{ NMR spectra. Figure 4 shows a comparison of single pulse } \(^1\text{H} \text{ MAS NMR spectra with DQ filtered spectra with increasing recoupling times for both RMP powder and crystal. The RMP powder shows (Figure 4b) that both methyl and acid protons are successfully recoupled in the DQF spectra for all recoupling times, which implies that both methyl and acid protons have strong dipolar couplings. On the other hand, the RMP-2H_2O single crystal (Figure 4a) shows the absence of the water peak in all DQF spectra, which reveals that the water molecules in the lamellar structure of the RMP-2H_2O single crystal are highly dynamic. However the methyl and acid protons of the RMP-2H_2O single crystal are successfully recoupled for all recoupling times, suggesting the strong dipolar coupling among the protons in the framework of the material.

In order to have more insight into the local structure of the RMP-2H_2O single crystal, we performed the 2D \(^1\text{H} \text{ DQ correlation spectra.}\) The 2D \(^1\text{H} \text{ DQ correlation spectrum of RMP-2H_2O single crystal using BaBa pulse sequence with two rotor period recoupling time (i.e, } t_r = 80 \text{ } \mu\text{s} \) is shown in Figure 5. The diagonal peaks (at 2 and 13 ppm in the single quantum dimension) represent the dipolar coupling of like methyl protons and acid protons, respectively. The DQ diagonal peak of the methyl protons is observed with an integral intensity of about half that of the DQ signal of the acid protons. This is caused by the longer excitation times used (\( t_r = 80 \text{ } \mu\text{s} \)) in this data set. The cross-peaks observed at off diagonal frequencies represents the dipolar coupling between the acid protons and methyl protons. More significant in terms of probing the structures are the correlations among the two slightly different acid protons (A1 and A2) whose resonances occur in the lower left quadrant of the DQ spectrum. An expansion of this region is given as insert in the Figure 5. The expanded DQ spectrum shows that the acid proton resonances A1 and A2 have strong cross-peaks and relatively weak diagonal peak. The weak diagonal peak is due to the relatively weaker coupling between like protons A1\(-\)A1 and A2\(-\)A2. This indicates that the like protons are spatially well separated. The strong cross-peaks, which represent the correlation between different acid protons (A1 and A2), indicates the strong dipolar coupling and correlated proximity of the two acid protons (A1 and A2). These findings allow us to uniquely identify acid protons (A1 and A2) in the single-crystal structure data, and will be discussed in detail in forthcoming structural analysis section.

The 2D \(^1\text{H} \text{ DQ correlation spectrum of dehydrated RMP powder at 300 K using BaBa pulse sequence with two rotor period recoupling time (i.e, } t_r = 80 \text{ } \mu\text{s} \) is shown in Figure 6. The 2D DQ spectrum exhibits two auto peaks in the DQ diagonal which arise from self-correlations of like methyl (CH_3) and acid protons (O\(\cdots\)H) of RMP powder. More interesting, however are the intense and well resolved cross-peaks between methyl and acid protons. The cross-peaks implies the methyl and acid protons are closely spaced which results in strong dipolar coupling between them.

**DQ Sideband Analysis.** Molecular geometries and packing motifs can be determined by measuring the exact dipolar coupling strengths between different functional groups, which in turn give the distances between the observed atoms. The dipolar coupling strengths between different protons can be extracted by using rotor encoded DQ sideband measurements.\(^{14}\)

Using such rotor encoded DQ sideband measurements, we can obtain structural insight for RMP powder, for which crystal structure is not available. The spinning sideband patterns that arise from the acid protons at 13 ppm are shown in Figure 7. The DQ spinning sideband patterns are recorded using rotor encoded BaBa DQF sequence. Figure 7a exhibits the sideband pattern of acid protons in dehydrated RMP powder by applying a \( t_i \) increment of \( \Delta t_{i} = t_i/40 = 1 \mu\text{s} \), with spinning frequency of 25 kHz and four rotor periods (4\( t_r = 160 \mu\text{s} \)) of recoupling for DQ excitation and recoversion. Figure 7b exhibits the sideband pattern of acid protons in dehydrated RMP powder by applying a \( t_i \) increment of \( \Delta t_{i} = t_i/100 = 1 \mu\text{s} \), with spinning frequency of 10 kHz and two rotor periods (2\( t_r = 200 \mu\text{s} \)) of recoupling for DQ excitation and recoversion. Both side band pattern (Figure 7a,b) only shows the first order and third-order spinning side band, which can be easily fitted with an isolated spin pair interaction. This suggests that the remote couplings to the next neighbor acid protons are negligible, due to the spatial separation of acid protons in the unit cell. The fitting of...
the experimental spectrum, using an isolated spin pair assumption, yields the dipolar coupling ($D_{ij}$) of 3950 Hz for four rotor periods ($\tau_r = 160$ ms) spectra (Figure 7a) and 4250 Hz for two rotor periods ($\tau_r = 200$ ms) spectra (Figure 7b). Hence, the average dipolar coupling ($D_{ij}$) between the acid protons in dehydrated RMP powder is 4000 Hz, which corresponds to the distance of 3.1 Å. This distance represents the spatial separation of two nearest acid protons (labeled as peak A in Figure 3b) in dehydrated RMP powder.

$^{87}$Rb MAS NMR. $^{87}$Rb is a quadrupolar nuclei ($I = 3/2$) and $^{87}$Rb MAS NMR spectra is known to be very sensitive to any structural changes in the $^{87}$Rb nuclei environment. Hence, analysis of $^{87}$Rb MAS spectra could shed light on the local structure of these materials. Figure 8a shows the $^{87}$Rb MAS NMR of RDP measured at 21.1 T with a spinning speed of 25 kHz. A fit of this spectrum requires two quadrupolar powder line shapes with the quadrupolar constant ($C_Q$) of 7.4 ± 0.2 and 8.4 ± 0.2 MHz and asymmetry factor ($\eta$) of 0.35 and 0.60, respectively. These two quadrupolar line shapes have equal relative integral intensity, suggesting that dehydrated RMP powder has two Rb sites in the crystal structure. Figure 9 exhibits the static $^{87}$Rb NMR of RMP-$2H_2O$ single crystal at both temperatures shows a single Gaussian type peak, indicating only one Rb site in both the room temperature and the high-temperature phase. The significance of variable temperature static $^{87}$Rb NMR of RMP-$2H_2O$ single crystal will be discussed latter.

Variable Temperature $^1$H MAS. It is interesting to study the thermally activated proton dynamics in this new material. The variable temperature (VT) $^1$H MAS NMR is a simple and effective tool to provide a snapshot of the thermally activated proton dynamics in solids. The VT $^1$H MAS NMR measurements were acquired under fast MAS (25 kHz) conditions for better spectral resolution. The VT $^1$H MAS NMR single pulse spectra of dehydrated RMP powder are shown in Figure 10. The $^1$H single pulse MAS NMR of RMP powder data set (Figure 10) does not show any coalescence or significant line narrowing in the temperature range of our experiments.

The response to heating of the RMP-$2H_2O$ single crystal, however, is dramatically different than the dehydrated RMP powder. As seen in Figure 11a, $^1$H VT MAS (25 kHz) spectra
show significant line narrowing in both the methyl and water protons as the temperature is increased. The $^1$H VT MAS spectra of the RMP–$^2$H$_2$O crystal up to 320 K show all the three resonances representing methyl, acid, and water protons. Around 305 K the water proton resonances narrow and increase in intensity at the expense of acid proton resonance. Above 320 K, the acid proton resonances (A1 and A2) totally vanished leaving only sharp methyl and water proton resonances of RMP–$^2$H$_2$O single crystal. It is worthwhile to mention that this is not coalescence of the acid proton and water proton peaks, which could be observed due to proton exchange. The main characteristic feature of coalescence is the change of isotropic chemical shift observed when two peaks, representing two different chemical sites, move toward each other. As we can see (Figure 11a), there is no significant change in the isotropic chemical shift of either the acid proton and water proton peaks with in the temperature range studied. This clearly indicates that the
abrupt change in the $^1$H MAS spectra of RMP·2H$_2$O single crystal around 320 K is due to a structural phase transition. It is important to point out that, during cooling cycle of the VT $^1$H MAS measurement, the high-temperature spectral features persisted after the crystal had been cooled to room temperature, however, the sample return to the low-temperature phase after a period of time (about a week), as indicated by the reappearance of the initial $^1$H NMR spectrum. This suggests that the reverse phase transition (i.e., from high temperature to low-temperature phase) is a slow process. This slow reverse phase transition is also observed in rubidium dihydrogen phosphate (RDP), where it changes from the high-temperature monoclinic phase to the room-temperature tetragonal phase. Interestingly, the transition temperature observed by NMR is slightly lower than the phase transition temperature observed by DSC (Figure 2). This could be due to the different heating rate between NMR and DSC. Further, NMR is very local probe, whereas the DSC observes the bulk properties and hence observes a higher temperature for the onset of the phase transition.

To extract more detail about the phase transition mechanisms, we deconvoluted the VT $^1$H MAS lines of RMP·2H$_2$O crystal with Gaussian and Lorentzian line shapes. Above 305 K the methyl proton resonance shows two components, a broad ($\Delta \approx 1300$ Hz) Gaussian type peak and sharp ($\Delta \approx 380$ Hz) Lorentzian type peak indicating low temperature and high-temperature phase methyl protons respectively. These two components in the methyl resonances are observed in the temperature range of 305−320 K, and after 320 K, only a sharp lorentizan line is observed indicating the complete phase transition. This reveals that the structural phase transition of RMP·2H$_2$O single crystals are starts with methyl groups around 305 K. This result coincides with the variable temperature studies discussed below. The integral intensities of acid proton and water protons are normalized to the integral intensity of methyl protons, assuming that methyl protons’ intensity should be unchanged during the phase transition. Figure 11b shows the variation of water proton and acid protons integral intensities in RMP·2H$_2$O crystal. The normalized integral intensities of both acid protons (A1 and A2) and water protons remain constant up to 300 K, indicating that there is no significant proton exchange in this temperature range. Above 300 K, acid proton intensity drops, whereas the water proton intensity increases, and around 330 K, the acid proton resonances vanish and the normalized intensity of water protons above this temperature remains constant. This reveals that, during the phase transition, the acid protons migrate to the lamellar structure. In the high-temperature phase of RMP·2H$_2$O single crystal, there is no hydrogen bonded acid protons observable on the NMR time scale; however, there are highly dynamic water protons in lamellar structure.

Protons Spin Lattice Relaxation Measurement. To explore the proton dynamics and its role in the high-temperature phase transition of RMP·2H$_2$O single crystal, the temperature-dependent proton spin lattice relaxation ($T_1$) has been measured using the saturation-recovery pulse sequence. Figure 12 shows the temperature-dependent proton $T_1$ relaxation of the dehydrated RMP powder. The methyl proton has nearly four times lower $T_1$ ($1.38 \pm 0.02$ s) compared with acid protons ($7.43 \pm 0.13$ s) at ambient temperature (300 K). The low $T_1$ value of methyl proton is due to the rotation of the methyl group. Interestingly the acid protons have long $T_1$, indicating the rigid structure and less dynamics of acid protons in this material. The temperature-dependent $T_1$ measurements shows both the methyl and acid proton $T_1$ values gradually increase with increasing temperature and there are no significant changes observed over the temperature range studied.

More significant changes are seen in the spin lattice relaxation ($T_1$) of the RMP·2H$_2$O single crystal shown in Figure 13. The $T_1$ value of acid protons and water protons are shown in Figure 13a. The two acid protons A1 and A2, have the same $T_1$ values, which is not surprising considering the almost equivalent chemical environment for these protons. The spin lattice relaxation of water protons decreases rapidly during the phase transition (280−310 K), and after phase transition the $T_1$ value

Figure 12. Temperature dependence of $^1$H spin–lattice relaxation $T_1$ for dehydrated RMP powder measured using saturation recovery pulse sequence under 11.7 T magnetic field with MAS spinning frequency of 25 kHz. The open circle represents hydrogen bonded acid protons and closed circle represents methyl protons. The lines are provided as a guide to the eye.

Figure 13. Temperature dependence of $^1$H spin–lattice relaxation ($T_1$) for RMP·2H$_2$O single crystal measured using saturation recovery pulse sequence under 11.7 T magnetic field with MAS spinning frequency of 25 kHz (a) spin–lattice relaxation ($T_1$) of acid protons and water protons, the open circle represents hydrogen bonded acid protons and closed circle represents water protons. (b) spin–lattice relaxation ($T_1$) methyl protons. The lines are provided as a guide to the eye.
is an order of magnitude less than in the low-temperature phase. In contrast, the $T_1$ value of acid protons gradually increases up to the phase transition point and, after phase transition, the resonance totally vanishes. Similarly, the $T_1$ value the methyl proton also undergoes an order of magnitude decrease after phase transition, as shown in Figure 13b. The $T_1$ values and also the line width of $^1$H MAS NMR spectra change remarkably above 320 K. The methyl protons also show a drop in $T_1$ over the phase transition. The decrease in $T_1$ is not sudden at the phase transition temperature (330 K) in this case, but rather, it starts decreasing at 300 K and completes its decline around 320 K. Another significant observation is the biexponential nature of the magnetization curve during this phase transition temperature (305–320 K). The confidence limit of the fitting greatly improves with the use of biexponential function, compared with the single-exponential function. This biexponential fit gives two different $T_1$ components in the order of 9 and 0.1 s which represents the rigid and mobile methyl components, respectively. These two $T_1$ components indicate the presence of two different phases representing the low temperature and high-temperature phase of RMP-2H$_2$O single crystal in the temperature range of 305–320 K. This behavior is also observed in the variable temperature $^1$H MAS spectra (Figure 11a), as a broad Gaussian type peak and sharp lorentizan type peak of methyl resonances. The weight factor at 300 K, for these two $T_1$ starts from 80% and 20% for high $T_1$ and low $T_1$ components respectively. At the end of phase transition (i.e., at 320 K), the low $T_1$ value (i.e., ~0.1 s) regains 90% weighting factor, and high $T_1$ value has only 10% weighting factor. This variation of $T_1$ weighting factor of rigid and mobile methyl components well agrees with the integral intensity of Gaussian type peak and sharp lorentizan type peak, observed in the variable temperature $^1$H MAS spectra (Figure 9a) between 305–320 K. This implies, the phase transition actually starts around 305 K and is complete around 330 K. The temperature-dependent spin lattice relaxation measurement is direct measure of ion mobility in the crystal, and will be further discussed in the proton dynamics section below.

**Discussion**

**Structural Analysis.** The $^1$H MAS NMR (Figure 3c) revealed that the RMP-2H$_2$O single crystal has three different type of protons namely, methyl protons, water protons and acid protons. Based on the RMP-2H$_2$O single-crystal structure data this water molecule can be assigned to the water molecules incorporated in lamellar structure of the single crystal. Further, the two overlapping acid proton peaks reveal that acid protons have two slightly different environments. Since the chemical shift is directly related with hydrogen bond length, the two different chemical shifts might arise from two distinct hydrogen bond lengths. The assignment of these two slightly different acid protons can be done using the two-dimensional $^1$H DQ MAS correlation spectrum. The DQ spectrum of acid protons (Figure 5) shows that the acid proton resonances A1 and A2 have weak auto correlations indicating weaker coupling between like protons A1−A1 and A2−A2 resulting in low intensity in the diagonal peaks. This indicates that the like protons are spatially well separated. However, the cross-peaks which represents the correlation between the two slightly different acid protons A1−A2, are much stronger than the diagonal resonances, indicating that the two acid protons (A1 and A2) are in close proximity to each other. As was discussed earlier, the unit cell of RMP-2H$_2$O single-crystal structure contains two pairs of acid protons and the identical protons in each pair are separated by a distance of 4.8 Å along the $a$ axis. If we assume the two protons in the pair have slightly different environment and correspond to the resonances A1 and A2, then we can expect the strong dipolar coupling between the two acid protons A1 and A2, due to the relatively smaller spatial separation of 3.53 Å (see Figure 1). This relatively stronger dipolar coupling ($D_{ij} = 2700$ Hz) will give strong cross-peak in the DQ spectra. The distance between the like protons (i.e., A1−A1 and A2−A2) are separated by 4.8 Å along the $a$ axis resulting in weaker dipolar coupling ($D_{ij} = 1090$ Hz), and hence gives weaker diagonal peak in the DQ spectra. As we see in DQ spectra (insert in Figure 5), the cross-peaks are stronger and the diagonal peaks are weaker, our assignment of two proton resonances A1 and A2 to the two unique acid protons is valid.

Unlike the RMP-2H$_2$O single crystal, the dehydrated RMP powder has only one acid proton resonance which has relatively lower chemical shift than the RMP-2H$_2$O single crystal (Figure 3). The decrease in chemical shift of acid proton resonance in RMP powder indicates that the $\text{H}^+\cdot\text{O}$ hydrogen bond of acid proton is longer than the RMP-2H$_2$O single crystal. Further, the acid proton resonance of dehydrated RMP powder is relatively broader than the acid proton resonances of RMP-2H$_2$O single crystal. This suggests the local structure around acid protons may be disordered, and certainly differs from the structure of the RMP-2H$_2$O single crystal. This has been confirmed by investigating the dipolar coupling strengths of acid protons by rotor encoded sideband NMR measurements. The fitting of sideband pattern of acid protons (Figure 7) gives the distance between the acid protons as 3.1 ± 0.1 Å. This value is significantly lower than the distance between nearest acid protons in RMP-2H$_2$O crystals (3.534 Å), based on the single-crystal structural data. This clearly indicates that upon dehydration the lamellar structure of the RMP-2H$_2$O crystal is collapsed and attains a new structure. The deconvolution of the $^1$H MAS spectra of dehydrated RMP powder using Gaussian line shapes gives a ratio for the acid protons and methyl protons as 1:3 within the experimental error. This ratio matches the chemical composition data, which is expected to have three methyl protons and one acid proton for each anion.

The $^{87}$Rb MAS NMR of dehydrated RMP powder (Figure 8b) is significantly different from the $^{87}$Rb MAS NMR of RDP (Figure 8a). The dehydrated RMP powder shows two Rb sites with nearly three times larger $C_0$ values (7.6 and 8.5 MHz), compared with single Rb site in monoclinic RDP with small $C_0$ value (2.7 MHz). The $C_0$ value of the $^{87}$Rb NMR is very sensitive to the local coordination of the Rb nuclei. Both RDP and RMP-2H$_2$O single crystal has monoclinic symmetry with Rb$_2$O$_5$ polyhedral coordination. The relatively larger $C_0$ in dehydrated RMP powder clearly indicates that the dehydrated RMP powder has less symmetric Rb co-ordination environment and different crystal structure than the monoclinic RDP and RMP-2H$_2$O single crystal. So, the dehydrated RMP powder exhibits a new structure which is different from both RMP-2H$_2$O single crystal and RDP. However, the crystal structure of the RMP powder is not known and our attempts to measure the X-ray diffraction measurements are unsuccessful so far, mainly due to extremely high moisture sensitivity of RMP powder.

**Phase Transition.** The variable temperature $^1$H MAS spectra of RMP-2H$_2$O single crystal (Figure 11a) shows a phase transition around 325 K. During this phase transition, the water proton resonance and methyl proton resonance undergo signifi-
cant line narrowing. Another interesting observation from the VT $^1$H MAS spectrum is the absence of the acid protons in the high-temperature phase (>325 K). The analysis of integral intensities of acid protons and water protons (Figure 11b) through the phase transition shows that water proton intensities are increasing at the expense of acid proton intensities. Above phase transition temperature, both acid proton intensities (A1 and A2) are fully transferred to water proton intensities, which reveal that the acid protons are moved to the water protons in the lamellar structure and become highly mobile in the interlayer structure. In the high-temperature phase of the RMP-$^2$H$_2$O single crystal, there are no hydrogen bonded acid protons, and only methyl and water protons are observed. This phase transition is also observed in the spin lattice relaxation ($T_1$) measurements (Figure 13) of RMP-$^2$H$_2$O single crystal. The methyl and water proton (Figure 13) show an order of magnitude drop in $T_1$ around 325 K, which suggests the structural phase transition. Further, the observation of two $T_1$ components, i.e., rigid (~9 s) and mobile (0.1 s) of methyl protons well before the phase transition temperature (325 K) indicates that the methyl group plays vital role in the structural phase transition. The methyl unit can be thought of as “grease” which lowers the lattice energy of the salt. Therefore it is not surprising that these domains sense the onset of the phase transition before the hydrogen bonds. This lends support to our hypothesis (discussed in introduction) of introducing phase transition before the hydrogen bonds. This lends support to our hypothesis (discussed in introduction) of introducing methyl group in order to reduce the phase transition temperature and thereby facilitate the proton dynamics. The variable temperature $^{87}$Rb static NMR (Figure 9) could provide more information about the structural phase transition of RMP-$^2$H$_2$O single crystal. The $^{87}$Rb static NMR of RMP-$^2$H$_2$O single crystal measured at 300 K shows single Gaussian type peak which coincides with the single Rb site observed in the single-crystal XRD crystal structure of RMP-$^2$H$_2$O. Interestingly, the high-temperature (330 K) $^{87}$Rb NMR spectra of the RMP-$^2$H$_2$O single crystal also shows single Gaussian peak, which reveals that the high-temperature phase has also only one Rb site similar to its low-temperature phase. Further, this suggests that the high-temperature phase of the RMP-$^2$H$_2$O single crystal also different from the dehydrated RMP powder, where two Rb sites are observed. The significant result from the variable temperature $^{87}$Rb NMR is the peak width at high-temperature (330 K), of about 13 kHz, which clearly confirms that the phase transition around 325 K in RMP-$^2$H$_2$O single crystal is not simple melting of crystal, but a structural phase transition.

In the case of dehydrated RMP powder both variable temperature $^1$H MAS (Figure 10) and $T_1$ measurement (Figure 12) do not show any significant changes in the temperature range of 250–340 K. This confirms that, unlike RMP-$^2$H$_2$O single crystal, the dehydrated RMP powder does not have any phase transition in the temperature range of our study.

**Proton Dynamics.** Constraints on the timescales of proton dynamics between different chemical sites can be extracted from the chemical shift differences of proton resonances. In the absence of the onset of coalescence or line-broadening, the rate of chemical exchange (in Hz) between different chemical sites can be concluded to be much less than the chemical shift (in Hz) difference of the respective proton resonances. For the low-temperature phase of the RMP-$^2$H$_2$O single crystal, the $^1$H MAS spectra of low-temperature phase RMP-$^2$H$_2$O single crystal at 310 K (Figure 3c) shows two distinct resonances for acid protons (peaks A1 and A2), with isotropic chemical shift difference of 370 Hz ($\Delta \delta = 0.75$ ppm). This indicates that frequency of any chemical exchange between these two different acid proton sites (A1 and A2, see Figure 1) should be much less than 370 Hz, otherwise exchange broadening of the acid proton peaks would be observed. Similarly the isotropic chemical shift difference between the water protons (peak B) and acid protons (peaks A1 and A2) is about 3500 Hz ($\Delta \delta = 7$ ppm), which reveals that any chemical exchange between these sites should be much less than 3500 Hz. On the other hand, the proton dynamics between identical chemical sites can be extracted from the 1D DQF measurements. In particular, the DQF measurement with different recoupling times give the direct evidence of the proton dynamics in each chemical site. If the proton dynamics is faster than the recoupling time, then the proton resonances will be filtered out in the DQF measurement, and a lower limit on the rate of the dynamic process can be established. Conversely, if the resonances are recoupled at even the shortest recoupling times, an upper limit on the rate of any dynamic process can be determined. The room-temperature 1D DQF spectra of the low-temperature phase RMP-$^2$H$_2$O single crystal (Figure 4a) shows the acid protons are successfully recoupled even at high recoupling time (8$\tau_r = 320$ $\mu$s, i.e., 3125 Hz) of DQF measurements, which reveal that any internal chemical exchange within the acid proton sites should be less than 3125 Hz. Hence, both the chemical shift difference and higher recoupling time DQF measurements clearly indicate that the acid protons in the low-temperature phase of the RMP-$^2$H$_2$O single-crystal experience a relatively rigid lattice environment and have no significant chemical exchange between themselves or with water protons. On the contrary, in the 1D DQF spectra of RMP-$^2$H$_2$O single crystal (Figure 4a) the water protons are filtered out by the DQ filter, even for the short recoupling time (0.5$\tau_r = 20$ $\mu$s, i.e., 50 kHz), which indicates that the dynamics of water protons (peak B) in the low-temperature phase of the RMP-$^2$H$_2$O single crystal is faster than 50 kHz. This suggests that the water molecules in the low-temperature phase of RMP-$^2$H$_2$O crystal are highly dynamic and possibly moving inside the interlayer lamellar structure. Interestingly, this situation changes in the high-temperature phase of RMP-$^2$H$_2$O single crystal. The VT $^1$H MAS spectrum (Figure 11a), shows that at the high-temperature phase (>320 K) the water protons and methyl protons show significantly sharpened lines ($\Delta \lambda = 170$ and 160 Hz, respectively). This indicates that, both water protons and methyl protons are highly dynamic at this high-temperature phase. We also performed the 1D DQF spectra of RMP-$^2$H$_2$O single crystal at 330 K (not shown here), and both methyl and water protons are absent in the DQ spectra, with recoupling time of 20 $\mu$s (i.e, 0.5$\tau_r = 20$ $\mu$s, i.e., 50 kHz), revealing that the proton dynamics are much faster than 50 kHz. This suggests that the acid and methyl protons are highly dynamic in the high-temperature phase.

Further, the spin lattice relaxation ($T_1$) measurement (Figure 13) also shows both the water and methyl protons experience an order of magnitude drop in $T_1$ during the phase transition. The origin of $^1$H MAS NMR line widths arise mainly from the residual homonuclear dipolar coupling between protons, which would be averaged by proton dynamics. On the other hand, the $T_1$ originates from dipolar and/or chemical shift interactions of proton. In principle, the line shape of an individual resonance is sensitive to the motion of the order of the line width (170 Hz), whereas $T_1$ is sensitive to the motion of the order of the $^1$H resonance frequency (500 MHz). In the present case, we observe a significant decrease in both line shape and $T_1$ relaxation; hence, we can conclude that the same motion contributes to the sharp line shape and the lower $T_1$ relaxation. This implies that the water protons in high-temperature phase
of RMP-2H2O single crystal are highly mobile and possibly hopping between sites, which cause averaging of the dipolar interactions. On the other hand, the sharp methyl peaks represents the fast rotation of methyl protons about its C3 axis. It is interesting to note that the water protons in the lamellar structure are highly mobile, whereas the acid protons appear to migrate to the lamellar structure, based on the relative intensities of 1H resonances (Figure 11b). This proton conduction mechanism is significantly different from the superprotonic MHx−XO4-type solid acids (where M = monovalent cation, X = S, Se, P, As, and n = 1, 2), where the hydrogen bonded acid protons are the conducting species, which moves through the reorientation of oxy-anions (XO4)32,33. On the other hand, the conventional organic polymer electrolyte membranes (PEM), made of perfluoropolymer, operate under humid conditions, i.e., proton transport relies on the presence of liquid water. Recently Abe et.al reported the proton conducting glasses which include hydrogen-bonded protons as well as molecular water, where the molecular water is the key component for the high proton conductivity.34,35 In these cases, the proton conductivity is due to the mobility of acid protons with significant support from the water molecules. In the polymer electrolyte membranes, the proton conduction is mediated through the formation and dynamics of hydronium ions (H3O+)36,37. However, the exact nature and chemical identity of charge carriers in the high-temperature phase of the RMP-2H2O single crystal is intriguing and needs further study. Nevertheless, the high proton dynamics at relatively low temperature indicates that RMP-2H2O is a promising candidate as electrolyte for fuel cells. To support this molecular-level study of dynamics, macroscopic conductivity measurements using impedance spectroscopy are essential. Unfortunately, due to the sensitive nature of the crystals, with respect to humidity, as yet such measurements have not been possible.

The dehydrated RMP powder does not show any significant changes in either VT 1H MAS NMR (Figure 10) and spin lattice relaxation T1 (Figure 12) in the temperature range of 250−350 K. We also performed the variable temperature 1D DQF spectra (not shown here), where both methyl and acid proton peaks are successfully recoupled at all temperatures, suggesting the consistently strong dipolar interactions within the rigid lattice of the RMP powder. From this we conclude that the ions in dehydrated RMP powder remain rigid and there are no significant proton dynamics in the temperature range of study. Moreover, the absence of coalescence, chemical shift changes or narrowing of the hydrogen-bonded acid protons in the VT 1H MAS NMR is a clear indication that these protons are fixed in their positions and unable to contribute to either local proton mobility or long-range proton transport. Hence, it is unlikely to have any appreciable proton conductivity in the dehydrated RMP powder in the temperature ranges of 250−350 K.

Conclusions

Single crystals of the hydrated rubidium methane phosphonate (RMP-2H2O) have been grown by slow evaporation method. The double quantum filtered (DQF) 1H NMR sequences removes water signal, which indicates that water in the lamellae have rapid local motion. The variable temperature 1H MAS NMR spectra shows a structural phase transition around 320 K, during phase transition the acid protons are moved to lamellae water protons. On the other hand, the efforts to remove the lamellae water by means of dehydration under heat treatment results in structural collapse. The variable temperature 1H DQF and spin lattice relaxation measurement on dehydrated RMP powder reveals it has rigid lattice. Further, unlike RMP-2H2O single crystal, there is no structural phase transition observed for the dehydrated RMP powder. In summary, the new material, lamellar structured hydrated rubidium methane phosphonate (RMP-2H2O) shows significant proton dynamics in the high-temperature phase. The role of water molecules in the phase transition and its dynamics are intriguing, and warrant further study. This new crystal is of great promise as electrolyte membrane, especially because of the high proton mobility at relatively low temperature and the proton transport uniquely relies on crystalline water.

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Supporting Information Available: The crystal structure of the RMP-2H2O single crystal measured at 70 K, included as CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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