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# High-temperature dehydration behavior and protonic conductivity of RbH<sub>2</sub>PO<sub>4</sub> in humid atmosphere

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#### 1. Introduction

Rubidium dihydrogen phosphate, RbH<sub>2</sub>PO<sub>4</sub>, is one of the members in KH<sub>2</sub>PO<sub>4</sub> family which is composed of monovalent cation and hydrogen-bonded tetrahedral oxy-anion. Its ambient and sub-ambient phases have been well characterized: it has an orthorhombic structure with space group Fdd2 below its ferroparaelectric phase transition at  $T_c = -126$  °C, and a tetragonal structure (phase III) with space group  $I\bar{4}2d$  at room temperature [1]. However, its high-temperature (HT) phases are less certain. From X-ray diffraction (XRD) experiments Blinc et al. found that it transforms from tetragonal to monoclinic symmetry (phase II) at  $T_p = 86 \degree C$  [2] although the measured transition temperature  $T_p$ varied by wide margin between  ${\sim}80$  and  ${\sim}120\,^\circ\text{C}$  strongly depending on the experimental conditions [1]. However, based on the dielectric constant, thermal analysis, thermo-microscopy data, X-ray and so on, Ortiz et al. [3-5], Park and Lee [10,6-9] suggested that the changes in  $RbH_2PO_4$  around  $T_p$  were entirely due to thermal dehydration:

$$n\text{RbH}_2\text{PO}_4(s) \rightarrow \text{Rb}_n\text{H}_2\text{P}_n\text{O}_{3n+1}(s) + (n-1)\text{H}_2\text{O}(\nu), \quad n \ge 1$$
 (1)

where *n* denotes the number of molecules participating in the thermal decomposition; the letter *s* and *v* enclosed in parenthesis, the solid and vapor states, respectively. They contended that the term HT phase transition around  $T_p$  should be replaced by the one onset of particular polymerization at reaction sites on the surface.

#### ABSTRACT

The high-temperature (HT) properties of RbH<sub>2</sub>PO<sub>4</sub> have been investigated here by several methods. Two anomalies at  $T_p$  (~109 °C) and  $T'_p$  (~276 °C) in differential scanning calorimetry (DSC) measurement are due to structural transition from tetragonal (phase III) to monoclinic (phase II) and monoclinic to an unidentified phase I, respectively. The initial dehydration event in RbH<sub>2</sub>PO<sub>4</sub> occurs at ~250 °C, leading to the formation of dimer crust (Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) on the external surface of crystal particles which decelerates the further dehydration process. The conductivity measurement was performed under a highly humidified N<sub>2</sub> condition  $P_{H_2O} \approx 0.56$  atm to suppress its dehydration. It revealed two reversible superprotonic phase transition at  $T_p$  and  $T'_p$ . For the one at  $T'_p$ , the conductivity increases sharply by ~2 orders of magnitude and the high-conductivity phase I was stable till melting. However, the other one at  $T_p$  shows a relatively small jump in conductivity.

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A recent report has resolved the huge controversy over the behavior of RbH<sub>2</sub>PO<sub>4</sub> at  $T_p$ . Botez et al. published the crystal structure of RbH<sub>2</sub>PO<sub>4</sub> in monoclinic phase above  $T_p$  on the basis of XRD data [11]. There are, additionally, limited reports of another transition from the monoclinic phase to an as-of-yet unidentified phase I at  $T'_n \approx 280$  °C [12–15].

From the point of view of conductivity measurement of RbH<sub>2</sub>PO<sub>4</sub> at HT, Baranov et al. reported that the conductivity increases abruptly by about twice when heating it through the tetragonal-monoclinic phase transition at  $T_p$  [16], however, this transition was observed only on heating. Therefore, the microscopic nature of RbH<sub>2</sub>PO<sub>4</sub> at HT is still not completely understood yet. The main difficulty seems to be that the HT phase transition occurs very close to the region where strong thermal decomposition sets in and even two effects are overlapping to a certain extent. A chemically similar compound in this family, CsH<sub>2</sub>PO<sub>4</sub>, is known to exhibit a HT, structural transition to a disordered state. At this so-called "superprotonic" transition the proton conductivity increases by several orders of magnitude [16-21]. The dispute over the existence of such a phase transition in CsH<sub>2</sub>PO<sub>4</sub>, arising from the simultaneous occurrence of dehydration, has recently been resolved via the use of high pressure [22] or elevated water partial pressure [23]. Indeed, thermal dehydration, which initiates at temperature close to the phase II-I transition of CsH<sub>2</sub>PO<sub>4</sub> and RbH<sub>2</sub>PO<sub>4</sub>, has prevented accurate, electrical characterization of phase I in both phosphates. Very recently, Boysen and Haile [24] employed high pressure during conductivity measurements, with the aim of suppressing dehydration and enabling complete characterization of its HT phase, then concluded that at 1 GPa pressure

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 $RbH_2PO_4$  does exhibit a superprotonic phase transition prior to melting.

In this paper we first reported a study of the phase and dehydration behavior of  $RbH_2PO_4$  above room temperature, using thermal measurements and HT XRD analysis. In the second portion of study, we employed a new method, i.e., highly humidified  $N_2$  flow, to suppress its dehydration, which has not been reported before. To demonstrate the superprotonic phase transition of  $RbH_2PO_4$  at  $T'_p$ , we carried out its conductivity measurements under this condition, free from the ambiguities introduced by dehydration in the heating process.

#### 2. Experimental

#### 2.1. Sample preparation

 $RbH_2PO_4$  under study was obtained from aqueous solutions of rubidium carbonate ( $Rb_2CO_3$ ) and phosphorous acid ( $H_3PO_4$ ), in which the  $Rb:PO_4$  molar ratio was set at 1:1 according to  $Rb_2CO_3 + 2H_3PO_4 \rightarrow 2RbH_2PO_4 + CO_2 + H_2O$ . Rapid precipitation was induced by the introduction of methanol, and the precipitate then filtered out. The resulting powder was kept in an oven at 80 °C for at least 6 h, in view of their hygroscopicity, this drying process was repeated prior to any experiment.

#### 2.2. Materials characterization

The as-synthesized  $RbH_2PO_4$  products were characterized by scanning electron microscopy (SEM) and energy dispersive

analysis of X-ray (EDX) with a LEO 1530 at an accelerating voltage of 5 kV. Powder X-ray diffraction (XRD) patterns of the product were recorded in a Rigaku Rotaflex RU-200B diffractometer using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.5418 Å), to confirm their identity. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer Diamond DSC, and thermogravimetry analysis (TGA), with a Pyris-6 instrument. In both types of thermoanalytical experiments the sample was sat in a platinum pan, then heated at the same rate of 10 °C/min, to 475 °C, in a dynamic atmosphere of dried N<sub>2</sub> flowing at 50 ml/min.

#### 2.3. Impedance measurements

Pellets for electrical analysis were fabricated from dried powder, that was mechanically ground in an agate mortar for 1 h, then loaded at 7 tons for 5 min. A pressed pellet, of 10 mm in diameter and 1 mm in thickness, had its flat faces coated with silver via vapor deposition before silver paint applied, then stayed inside a tube furnace. Its humidification was maintained by flowing N<sub>2</sub> that had bubbled through water heated to around 90 °C; the relative humidity at the gas outlet was read from a sensor and held near 80%, corresponding to water partial pressure at  $\sim$ 0.56 atm. Sample temperature was monitored with a PICO TC-08 thermocouple and, during a measurement, either kept constant or raised stepwise from 25 to 285 °C. An HP 4284A Precision LCR Meter performed impedance measurements in the frequency range of 20 Hz to 1 MHz. Impedance spectra were analyzed using the commercially available software package, Zview (Scribner Associates Inc.). The conductivity,  $\sigma$ , of the pellet sample was





Fig. 1. (a) Panoramic SEM image of the as-synthesized RbH<sub>2</sub>PO<sub>4</sub> products. (b) Enlarged SEM image of RbH<sub>2</sub>PO<sub>4</sub> particles with different sizes. (c) EDX spectrum taken from the particles above.

determined from the frequency dependence of the real and imaginary part of the impedance plotted in the complex plane (Cole–Cole plot), i.e.,  $\sigma = L/(AR)$ , where *L* and *A* are thickness of the pellet and electrode surface area, respectively.

#### 3. Results and discussion

#### 3.1. Phase transition at $T_n$

The general morphologies of the as-synthesized polycrystalline RbH<sub>2</sub>PO<sub>4</sub> powder are examined by SEM observation in Fig. 1(a) and (b). As can be seen from the panoramic image, the sample consists of a large quantity of particles with different sizes. Most of them have an average dimension of about  $6 \,\mu m$  in diameter. Moreover, EDX result shown in Fig. 1(c) indicates that the sample under investigation is composed of O, P and Rb, and their atomic ratio is about 71.92:13.68:14.40, no other elements exist except these three ones. In fact, it should be noteworthy that H atom cannot be detected in the EDX analysis. The typical thermoanalytical results have been presented in our previous report [25]. From the DSC pattern of RbH<sub>2</sub>PO<sub>4</sub> in Fig. 2(a), one can observe two strong endothermic peaks at  $\sim$ 123 and  $\sim$ 276 °C, respectively. The former has been confirmed as a structural transition signal from tetragonal to monoclinic phase [11,25], the later corresponds to a potential transition from monoclinic to an unidentified phase [12–15]. The other peaks with star are attributed to dehydration



**Fig. 2.** (a) DSC thermogram of RbH<sub>2</sub>PO<sub>4</sub> upon heating to 475 °C at 10 °C/min under flowing 50 ml/min dry N<sub>2</sub> gas. (b) Influence of several selected heating-rates on the DSC curves near  $T_p$ . Inset: Peak temperatures ( $T_{peak}$ ) of the phase transition at  $T_p$  as a function of heating-rate ( $\Phi$ ).

(a)  $(1) 235^{\circ}C$ (2) 265°C  $\mathbf{\nabla}$ : RbH<sub>2</sub>PO<sub>4</sub>  $: Rb_2H_2P_2O_7$ (3) 265°C for 10 h ntensity / a.u. (4) 285°C  $(5) 450^{\circ}C$ 10 20 30 40 50 60  $2\theta$  / degrees 100 (b) RbH<sub>2</sub>PO<sub>4</sub> 98 Mass, m/ % 96 Rb2H2P2O7 (4.9%) 94 92 RbPO<sub>3</sub> (9.9%) 90 200 300 100 400 Temperature, T/ºC

**Fig. 3.** (a) Evolution of the XRD patterns of powdered  $RbH_2PO_4$  as a function of annealing temperature: (1) 235 °C for 1 min; (2) 265 °C for 1 min; (3) 265 °C for 10 h; (4) 285 °C for 1 min; (5) 450 °C for 1 min. (b) Weight change at different stages with the heating-rate of 10 °C/min under flowing 50 ml/min dry N<sub>2</sub> gas.

events of RbH<sub>2</sub>PO<sub>4</sub> with increasing temperature and the maximum rate of dehydration is initially reached at  ${\sim}250\ {}^\circ\text{C}.$  The detailed dehydration process and the second possible phase transition at  $T'_p$ (~276 °C) will be discussed in later section. As an example of heating-rate independent thermal behavior of solid acids, especially for the phase transition of  $RbH_2PO_4$  at  $T_p$ , a plot of DSC traces obtained at several different heating-rates is shown in Fig. 2(b). It can be noted that the onset temperature  $T_o$  corresponding to different DSC signals almost keeps unchanged although the endothermic peaks have a slight shift, i.e.,  $T_0$  is likely independent of the heating-rate  $\Phi$ . In order to further determine the exact value of  $T_o$ , the peak temperatures  $T_{peak}$  are plotted as a function of heating-rate, as the inset shows. A linear relationship between  $T_{peak}$  and  $\Phi^{1/2}$  is indeed evident. Therefore, the true or equilibrium onset temperature, determined by extrapolation of the fitting line to zero heating-rate, is  $T_o = 109$  °C, which is denoted as the phase transition temperature  $T_p$ . For RbH<sub>2</sub>PO<sub>4</sub> crystals, the phase transition at  $T_p$ , in fact, will not depend on the heating-rate.

#### 3.2. XRD analysis of dehydrated products

In order to determine the nature of dehydrated products as well as to further elucidate the reaction pathway, HT powder XRD studies were made from 235 to 450 °C, and the results are shown in Fig. 3. The last pattern, labeled as (5) in Fig. 3(a), corresponds to that of fully dehydrated product, in which the dehydration was carried out under flowing dry N<sub>2</sub> gas at 450 °C. The total weight loss of this sample was 9.9% indicated in Fig. 3(b), corresponding very well to that for the formation of RbPO<sub>3</sub> as follow ( $n \gg 1$ ):

$$RbH_2PO_4 \rightarrow RbPO_3 + H_2O \tag{2}$$

Accordingly, we take this be the reference pattern of rubidium metaphosphate (RbPO<sub>3</sub>). On the contrary, the first pattern, labeled as (1) in Fig. 3(a), was obtained before the onset of dehydration at 235 °C. It can be clearly seen that the pattern presents a single phase: monoclinic phase of RbH<sub>2</sub>PO<sub>4</sub> with space group  $P2_1/a$  [26]. Subsequently, the sample was heat-treated 1 min at 265 °C, some new and small signals other than the ones from monoclinic phase start to appear in the pattern (2). With increasing the heat-treat time to 10 h at the same temperature for comparison, a drastic reduction in intensity is observed for most diffraction peaks, however, these new peaks becomes stronger. In fact, these fresh peaks belong to the dimer Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [27]. From the TGA measurements in Fig. 3(b), we have found that a weight loss of

4.9% can be reached only if the sample was heated up to  $\sim$ 320 °C, corresponding to the complete formation of Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> according to reaction below (*n* = 2):

$$2RbH_2PO_4 \rightarrow Rb_2H_2P_2O_7 + H_2O \tag{3}$$

Therefore, it can be confirmed that the pattern (2) represents the superposition of two different single phases: monomer RbH<sub>2</sub>PO<sub>4</sub> (marked with black triangle) and dimer Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (marked with black circle). The intensity of RbH<sub>2</sub>PO<sub>4</sub> peaks has been reduced because part of RbH<sub>2</sub>PO<sub>4</sub> dehydrated and transformed into Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. Also, the appearance of Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase suggests that the dehydration will occur by a multi-step process. To reaction (1), in other words, the material first forms  $Rb_2H_2P_2O_7$ (n = 2), rubidium pyrophosphate, and finally dehydrates to form RbPO<sub>3</sub> ( $n \gg 1$ ), rubidium metaphosphate. It is noteworthy that these behaviors indeed occur despite the absence of obvious evidence for a change in the rate of weight loss. The diffraction data and weight change thus suggest that the multiple steps of dehydration are highly overlapping, consistent with the transient nature of Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. On the other hand, an additional X-ray study of the sample at 285 °C, pattern (4) in Fig. 3(a), shows a different diffraction pattern from that plotted in pattern (2). Clearly, some diffraction peaks become extremely weak even disappear. This phenomenon, combining with the strong endothermic peak at 276 °C in Fig. 2(a), demonstrates that a true structural phase transition takes place between 275 and 285 °C. As has been reported earlier, a second structural transition from phase II to I exists at ~280 °C [13-15], but the new phase I was not identified as yet. Here, the difference between pattern (2) and (4) thus further confirms this phase transition at  $T'_{p}$ .

To account for the experimental facts above related with the HT phenomena in RbH<sub>2</sub>PO<sub>4</sub>, we support the standpoint that the dehydration reaction (1) takes place at reaction sites on the external surface of RbH<sub>2</sub>PO<sub>4</sub> particles firstly [7]. From the theory concerning the formation and growth of nuclei of product in the decomposition of solids, the kinetic course in general is dominated by the initiation of localized reaction of particular localities and the subsequent advancement of a reactive interface into the undecomposed reactant [28,7]. The corresponding schematic diagrams have been presented in Fig. 4. The initial decomposition occurs at the external crystal surface at sites where crystallographic disorder exists, and these sites are the intersection with the surface of edge and screw dislocations. Also, the surface is assumed to contain the potential growth nuclei



Fig. 4. Formation and growth of nuclei of product in the decomposition of solids: (a) nucleation sites; (b) first nuclei formed; (c) growth and further nucleation; (d) overlap and continued growth of nuclei.

forming sites of enhanced reactivity, and the active growth nuclei will increase its size and form crystal as soon as they receive a critical quantity of energy. Thus kinetics can be described in terms of the rate of nucleus formation and growth [28,7]. Based on the discussion of XRD results and thermal analysis, we speculate a possible evolution mechanism of RbH<sub>2</sub>PO<sub>4</sub> crystal in the heating process, especially within the range from 235 to 285 °C in Fig. 5. In the first stage, the monomer RbH<sub>2</sub>PO<sub>4</sub> is monoclinic structure (phase II) before the onset of dehydration. As the temperature increases above 250 °C, the first layer of dimer Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> has formed on the surface of crystal particles. This solid dimer crust can hinder the partial dehydration event and decelerate the dehydration process, which is in close agreement with the results in TGA experiment. However, in the center of crystal particles is still the monomer RbH<sub>2</sub>PO<sub>4</sub> in phase II. Upon heating above  $\sim$ 276 °C, a structural transition of RbH<sub>2</sub>PO<sub>4</sub> from phase II to I takes place at the center while more monomers take part in the thermal dehydration at the surface, leading to a strong endothermic signal at  $T'_{v}$ . In this way, the red zone (dimer Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) in Fig. 5 will



extend from the surface to interior of the crystal particles until complete dehydration in which RbPO<sub>3</sub> forms with a weight loss of 9.87% described by reaction (2).

#### 3.3. Electrochemical analysis

The ac impedance measurements of  $\text{RbH}_2\text{PO}_4$  pellets were carried out in a highly humidified N<sub>2</sub> atmosphere  $P_{\text{H}_2\text{O}} \approx 0.56$  atm



Fig. 5. Evolution schematic diagrams of the  $RbH_2PO_4$  crystal particles with increasing temperature from 235 to 285  $^\circ C.$ 

**Fig. 6.** Cole–Cole plots of impedance data obtained from polycrystalline RbH<sub>2</sub>PO<sub>4</sub> under high humid condition  $P_{H_2O} \approx 0.56$  atm at (a) 200 °C; (b) 270 °C; and (c) 283 °C.

to suppress its dehydration which has been confirmed, and the sample in heating/cooling cycle was kept for about 30 min at each temperature so as to be in equilibrium before measurement. Fig. 6 shows the results of the frequency-dependent complex impedance at several selected temperatures. It was clearly seen that at relatively low-temperature (LT) (top panel), a well-resolved semicircle was obtained. The real resistance can be determined by fitting to an equivalent circuit model composed of a resistor. R. and constant phase element, Q, in parallel with each other. Its impedance was generally given by  $Z_0 = [Y(i\omega)^n]^{-1}$ , where Y and n (0 < n < 1) are frequency-independence constants, *i* and  $\omega$  denote imaginary unit and angular frequency, respectively [23]. As the temperature increases to 270 °C, the spectrum in the complex plane mainly consists of two parts (middle panel): a highfrequency region due to the ionic conduction of RbH<sub>2</sub>PO<sub>4</sub> pellet and a low-frequency region characterized by a straight line due to a surface layer effect. Moreover, the surface impedance is found to be more and more dominant with further increasing temperature. The semicircle, however, was not observed finally (bottom panel) because the ionic conduction process was too fast to be tested under the given testing conditions. In this case, only the surface response was detected and the intercept with the real axis (Z') is the estimated resistance of RbH<sub>2</sub>PO<sub>4</sub> pellet. The Cole-Cole plot expressed the RbH<sub>2</sub>PO<sub>4</sub> pellet resistance which reduced with the increase in working temperature.

The conductivity,  $\sigma$ , of RbH<sub>2</sub>PO<sub>4</sub> pellet obtained from the impedance measurements discussed above is presented in Arrhenius plot in Fig. 7. According to the previous analysis, the HT behavior of RbH<sub>2</sub>PO<sub>4</sub> is extremely explicit: upon heating the sample above  $T_p \approx 109 \ ^\circ\text{C}$  and  $T'_p \approx 276 \ ^\circ\text{C}$ , the III-II and II-I phase transition are expected, respectively. From the Arrhenius curve in the humidity atmosphere  $P_{\rm H_2O} \approx 0.56$  atm, an obvious increase in conductivity was first observed at  $T_p$  in the heating cycle. In response to further heating, a second sharp increase by about two orders of magnitude in conductivity occurred at  $T'_p$ , beyond which Arrhenius behavior was exhibited up to melting. Upon cooling, however, the transition (II–I) exhibited some hysteresis ( $\sim$ 10 °C), with the conductivity dropping by the same order of magnitude as in the heating cycle. The reversible behavior in the heating/cooling cycle around  $T'_n$  indicates that a superprotonic phase transition indeed occurs. Furthermore, the reproducible Arrhenius behavior of the superprotonic phase I was also observed. The one of RbH<sub>2</sub>PO<sub>4</sub> in phase II, however, was somewhat irreproducible although it is much Arrhenius in nature. Therefore, the magnitude of conductivity at HT was highly



Fig. 7. Temperature dependence of the conductivity ( $\sigma$ ) of polycrystalline RbH<sub>2</sub>PO<sub>4</sub> from ac impedance measurements performed in dry and highly humidified N2 atmosphere.



Fig. 8. Time dependence of the conductivity ( $\sigma$ ) of polycrystalline RbH<sub>2</sub>PO<sub>4</sub> at 280 °C under various humidity conditions.

reproducible, whereas that at relatively LT was generally not. For the transformation at  $T_p$ , the conductivity changed reversibly without hysteresis during the heating/cooling cycles, also, indicative of another superprotonic phase transition from III to II.

Also. the Arrhenius curve under the condition of dry N<sub>2</sub> flow was presented for comparison. Upon heating the sample to  $\sim$ 246 °C, a sharp drop in conductivity takes place. From the thermal analysis, an endothermic peak at  $\sim$ 250 °C is only the consequence of chemical dehydration rather than any structural phase transition. We thus deduce the decrease in conductivity is due to dehydration behavior in RbH<sub>2</sub>PO<sub>4</sub>. For the purpose of suppressing the dehydration and further making clear the role of humidity and thermal stability of conductivity, time dependence of the conductivity at 280 °C was investigated under various humidified N<sub>2</sub> flow conditions, as shown in Fig. 8. When the sample was kept in dry N<sub>2</sub> atmosphere, its conductivity is very low and decreases faster with an elapse of time. In contrast, a relatively high and stable conductivity can be obtained in higher humidity atmosphere, which indicates that the dehydration over the surface of RbH<sub>2</sub>PO<sub>4</sub> crystal particles has been suppressed successfully by maintaining the water partial pressure at  $\sim$ 0.56 atm. In such highly humidified N<sub>2</sub> flow, the complete measurement of conductivity can be carried out.

In light of the good linearity between  $log(\sigma T)$  and 1/T in each phase of RbH<sub>2</sub>PO<sub>4</sub> as shown in Fig. 7, these results can be fitting to the Arrhenius law as given below:

$$\sigma = \frac{A}{T} \exp\left(\frac{-\Delta H_{\alpha}}{k_B T}\right) \tag{4}$$

where  $\sigma$  is conductivity, *T* is temperature, *A* is a pre-exponential factor,  $\Delta H_{\alpha}$  is the activation enthalpy for charge transport, and  $k_{\rm B}$  is Boltzmann's constant. Actually, the values of  $\Delta H_{\alpha}$  are obtained from the slope of theoretical fitting of Arrhenius relation. It thus can be found that the activation enthalpy in phase II is much more than phase I and III, in close agreement with the report by Baranov et al. [16]. Compared with phase II, the drastic increase in conductivity and small activation enthalpy for proton transport in phase I further confirm that phase I is "superprotonic" in nature. In summary, RbH<sub>2</sub>PO<sub>4</sub> crystal undergoes two phase transitions above room temperature as follow [7]:

Room-temperature	In	termediate-temperatu	ire	High-temperature
Paraelectric		?		Superprotonic
Phase III	$T_p$	Phase II →	$T_p$	Phase I
Tetragonal, $I\overline{4}2d$		Monoclinic, $P2_1/a$		?

According to the proton transport model proposed by Baranov et al. [16,29,30], the most important characteristics of crystals with disordered H-bonds networks is fast proton diffusion. At low-conductivity phase, the protons can occupy only the normal sites and the motion of protons includes intrabond jumps and inter-bond jumps. Therefore, the increase of activation enthalpy  $\Delta H_{\alpha}$  at III-II phase transition in RbH<sub>2</sub>PO<sub>4</sub> crystal should be due to the rearrangement of the H-bond network and the changing of the potential barriers between normal and interstitial proton sites. At the transition to superprotonic phase I, the crystal symmetry rises and some interstitial proton sites become structurally equivalent to the normal proton sites. In other words, the number of these sites will exceed the number of protons and the protons will be dynamically disordered between sites, which lead to the high proton conductivity with low activation enthalpy in phase I [16]. In the crystals such as RbH<sub>2</sub>PO<sub>4</sub>, the proton conduction generally proceeds via structure diffusion mechanism consisting of two steps: (i) proton transfer in H-bonds from donor to acceptor and (ii) reorientation of PO<sub>4</sub> group to position in which a new Hbond can be formed [31].

#### 4. Conclusions

The HT properties of RbH<sub>2</sub>PO<sub>4</sub> have been investigated with the help of DSC, XRD and impedance measurements. Key conclusions are as follows:

- (1) RbH<sub>2</sub>PO<sub>4</sub> crystal undergoes the first structural transition from tetragonal to monoclinic phase at  $T_p \approx 109~^\circ\text{C}$  which is independent of heating-rate, and the second potential transition from monoclinic to an unidentified phase at  $T'_n \approx 276 \,^{\circ}$ C.
- (2) Under ambient conditions, the HT phase of  $RbH_2PO_4$  exhibits thermal instability due to dehydration. Its initial dehydration at ~250 °C results in a mixture of two single phases: monomer RbH<sub>2</sub>PO<sub>4</sub> and dimer Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. A multi-step dehydration mechanism, i.e., that Rb<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> first formed on the surface of crystal particles, is appropriate for describing the evolution process of RbH<sub>2</sub>PO<sub>4</sub> in the heating process.
- (3) Highly humidified N<sub>2</sub> flow  $P_{\rm H_2O} \approx 0.56$  atm was employed to suppress its dehydration. The conductivity of RbH<sub>2</sub>PO<sub>4</sub> rises sharply at  $T_p$  and by about two orders of magnitude at

 $T'_n \approx 276 \,^{\circ}$ C, which indicated a superprotonic phase transition nature. Furthermore, the superprotonic transitions are highly reproducible in the heating/cooling cycles, which further revealed itself as a superprotonic conductor and a potential application in future fuel cells.

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