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High-temperature thermal behaviors of XH_2PO_4 (X = Cs, Rb, K, Na) and LiH_2PO_3

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ABSTRACT

XH_2PO_4 ionic compounds have emerged as a viable electrolyte for intermediate temperature fuel cells, and here have been subjected to thermal analysis to clarify their high-temperature properties. Thermoanalytical peaks were identified at 231.5, 239 and 349 °C for CsH_2PO_4; 127, 250 and 354 °C for RbH_2PO_4; 232, 270 and 319 °C for KH_2PO_4; 223, 330 and 352 °C for NaH_2PO_4; also, 195 and 220 °C for LiH_2PO_3 (peak temperature values as measured at the same heating rate of 10 K/min). The thermal events at 231.5 °C in CsH_2PO_4 and 127 °C in RbH_2PO_4 were previously interpreted as thermal decomposition by numerous researchers, but we confirm their origin in structural phase transition. The high-temperature variations in KH_2PO_4 and NaH_2PO_4 are entirely due to thermal dehydration rather than phase transition. We have also examined LiH_2PO_3, and found, for the first time, an endothermic peak at 195 °C, and attributed it to structural phase transition.

1. Introduction

The XH_2PO_4-type compounds are comprised of hydrogen-bonded tetrahedral oxy-anion (PO_4) and monovalent cations (e.g. X = alkali metal or NH_4). These solid acid materials exhibit an ordered arrangement of hydrogen bonds at room temperature but, upon heating, undergo a structural transition to a disordered state. Accompanying this so-called "superprotonic transition" is an increase in its proton conductivity by several orders of magnitude [1–5]. Its high conductivity, along with the fact that the proton transport does not rely on the presence of water, makes it an excellent candidate for the electrolyte in next generation fuel cells. Such an application was first reported by Haile et al. [6], who used the electrolyte $CsHSO_4$. Later, they presented such fuel cells based on CsH_2PO_4 as electrolyte and found that it can perform stably for over one hundred hours of continuous operation [7]. Comparing with the traditional polymer electrolyte fuel cells, solid acid fuel cells with XH_2PO_4-type compounds as electrolyte offer several advantages: anhydrous proton transport eliminates the need for auxiliary humidification equipment; complete impermeability of the solid acid materials to H_2 and O_2 results in measurably higher open circuit voltages; complete impermeability to methanol makes possible the operation of high efficiency direct methanol fuel cells and so on. Several challenges certainly remain, however, before solid acid based fuel cells can be commercially viable.

Recently, a dispute in literature as to whether or not these solid acids undergo a true, polymorphic superprotonic transition appeared, arising from the simultaneous occurrence of dehydration and phase transition in the heating process. Baranov et al. [8], Romain and Novak [9], Preisinger et al. [10], Gupta et al. [11] and Luspin et al. [12] attributed the increase in conductivity to a structural transition to a stable, high-temperature phase, whereas Lee [13,14], Ortiz et al. [15,16], Nirsha et al. [17] and Park et al. [18,19] attribute it to water loss due to thermal decomposition, in such a case, the rapid evolution of water from the compound is responsible to a transient increase in conductivity, also, they argued the thermal dehydration through the following chemical reaction: $nXH_2PO_4(s) \rightarrow X_nH_2P_nO_{3n+1}(s) + (n-1)H_2O(v)$, where n is the number of molecules present in stoichiometric equation, the letter 's' or 'v' enclosed in parenthesis denotes that the corresponding compound is in the solid or vapor state. More Recently, Boysen et al. and Otomo et al. demonstrated that a superprotonic phase transition indeed occurred at around 228 °C prior to thermal decomposition in CsH_2PO_4 crystal, through either the use of pressure or elevated water partial pressures [20–22]. In addition to CsH_2PO_4, materials including $CsHSeO_4$, NH_4HSeO_4, $Rb_3H(SeO_4)_2$, $K_3H(SO_4)_2$ and so on are all studied. Given above observation of different compounds, it is of relevance to establish whether alternative cation in XH_2PO_4 family gives rise to the same chemical behavior as many other researchers reported. In particular, we examine the compounds CsH_2PO_4, RbH_2PO_4, KH_2PO_4 and NaH_2PO_4 in this work mainly via thermal analysis and present new data supporting the position that a true structural phase transition occurs in CsH_2PO_4 and RbH_2PO_4 compounds. Also, we discussed the high-temperature thermal behavior of a new compound $LiHPO_3$. Here some ther-

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mal analysis results at ambient pressure have been shown in this paper.

2. Experimental

2.1. Materials

The compounds under study were prepared from aqueous solutions by mixing stoichiometric amounts of corresponding carbonate (X_2CO_3) and phosphorous acid (H_3PO_4) in which the X:PO_4 molar ratio was fixed at 1:1 according to $X_2CO_3 + 2H_3PO_4 \rightarrow 2XH_2PO_4 + CO_2 + H_2O$. Rapid precipitation of products was then induced by the introduction of methanol, and the precipitates were filtered out. An alternative route of synthesis proceeds via the reaction $XOH + H_3PO_4 \rightarrow XH_2PO_4 + H_2O$, with pH kept at 4.0, where the acidity facilitated good morphology of the eventual crystals, after the resultant solution was heated to 80 °C to evaporate the water and induce crystallization [19]. The powders by either method were dried in an oven at 80 °C for at least 6 h, both after preparation and prior to all measurements, in view of their hygroscopicity.

2.2. Equipment

Prior to the detailed analysis of thermal behaviors of various compounds, powder X-ray diffraction (XRD) patterns of the powders were recorded with a Rigaku Rotaflex RU-200B diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å), to confirm their identities and chemical purities. In all cases no discernible diffraction peaks from impurities have been detected, indicating that pure materials have been obtained.

Differential scanning calorimetry (DSC) was performed in a PerkinElmer Diamond DSC thermal analyzer, and thermogravimetric analysis (TGA) in a PerkinElmer Pyris-6 instrument. In both cases the sample sat in a platinum pan, to be heated at the same rate of 10 K/min, to 500 °C, in a dynamic atmosphere of dried N_2 flowing at 50 ml/min, and the corresponding scan-time was controlled to about 1 h in the TG and DSC measurements. From a lot of iterative measurements, the repeatable thermoanalytical results can be confirmed.

3. Results and discussion

3.1. CsH_2PO_4

3.1.1. The literature debate and recent progress

In previous research of CsH_2PO_4, several high-temperature phase transitions have been reported, especially, the variations at 149 and 230 °C have attracted the great interest of numerous researchers. The earliest report on the topic of the thermal behavior of CsH_2PO_4 by Rashkovich et al. [23] suggested that these two phase transitions occur prior to thermal decomposition, whereas a latter paper [24] by the same author concluded that these thermal events are entirely owing to decomposition, which gradually developed into the seed of drastic discussion referring to the high-temperature behavior of CsH_2PO_4. Rapoport et al. [25] reported two polymorphic transition temperatures as follows: a quasi-irreversible transition at 149 °C, a fully reversible transition at 230 °C which later would be called “superprotonic transition” by Baranov et al. [26], but it was associated with a slight weight loss for powdered samples examined under ambient conditions. Subsequently, Wada et al. [27] reported that the transition at 230 °C was observed by dilatometry measurements of single crystal samples, but the one at 149 °C was not. Simultaneously, Gupta et al. [11] reported a polymorphic transition at 235 °C prior to the maximum of thermal decomposition, and the initiation of weight loss is also at around 235 °C. However, Nirsha et al. [17] confirmed that thermal events at 233 °C and higher in CsH_2PO_4 are entirely owing to thermal decomposition. Baranov et al. [4,8,26] reported a sudden ionic conductivity jump at 230 °C for CsH_2PO_4 single crystal in which dehydration is very slow compared to powdered sample, and suggested that the high-temperature cubic phase above 230 °C was a superionic conduction phase and CsH_2PO_4 is a superprotonic conductor. Through DTA measurements, Rashkovich et al. [23,24] reported two peaks below 300 °C and concluded that CsH_2PO_4 crystal undergoes polymorphic transformation at 230 and 256 °C when it is heated, in the latter report, two maxima were observed in the dielectric constant for CsH_2PO_4 crystal at 230 and 265 °C, confirming the initial DTA results. Besides, Bronowska et al. [28] reported that the lattice parameter of the crystal changes on heating above 149 °C, but the space group above 149 °C up to 230 °C does not change. From the temperature dependence of XRD pattern, they also observed the structure changes connected with the phase transition at 230 °C, as well as the changes which were related to the decomposition of the compound. According to the heat capacity measurements on CsH_2PO_4, Vargas and Torijano [29] explained that a gradual change of the excited phonon modes leads to the lattice parameter changes observed at 149 °C by Bronowska and Pietraszko [28]. Also, Luspin et al. [12] reported two polymorphic transitions on heating above room temperature: a first transition at 120 °C and the second one at 230 °C. Nevertheless, a report by Lee [13,17] indicated that the observed conductivity effects and the high-temperature events occurring at around 230 °C were entirely due to thermal dehydration, and they suggested that the term *high-temperature phase transition* should be replaced by the term *onset of partial polymerization at reaction sites on the surface*. Subsequently, Ortiz et al. [14,15] and Park et al. [18,19] published a series of papers also taking the view that only thermal decomposition occurs at the supposed superprotonic transition points. In parallel to the studies refuting a superprotonic transition in CsH_2PO_4, several research groups still support its existence [7,20,21,30].

3.1.2. Thermal analysis results

The temperature dependence of weight loss for a freshly prepared CsH_2PO_4 powered sample is plotted in Fig. 1, and the whole temperature range is from 100 to 450 °C. From the TGA pattern one can observe that when the crystal is heated at a constant heating rate, a weight loss of about 7.8% was observed in the whole process. According to the dehydration reaction of CsH_2PO_4 crystal: $CsH_2PO_4 \rightarrow CsPO_3 + H_2O$, a weight loss of 7.83% is expected theoretically, and this value is in good agreement with the one from our experiments, which indicates that the weight loss is entirely due to dehydration. Two major variations in the water loss occur and the maximum rate of dehydration is reached at 239 and 349 °C, respectively, as the DTG pattern shows. On the basis of additional DSC measurement on CsH_2PO_4 crystal from the same batch used for the TGA measurement, we can also observe that two endothermic peaks at around 239 and 349 °C correspond well to the DTG signal peaks. Especially notable, a strongest peak at 231.5 °C has no corresponding signal in the DTG plot, that is, in no case has the thermal behavior at 231.5 °C stemmed from the dehydration event, presumably, which is the so-called high-temperature phase transition, as many researchers reported. Haile [31] observed that the conductivity of CsH_2PO_4 immediately decreased after the transition at around 230 °C, which is due to dehydration if the superprotonic phase did exist. Here, the observed DSC peak at 231.5 °C followed by a dehydration event at 239.8 °C seems to correspond very well to this case. Wada et al. [27] showed that the transition at 230 °C was confirmed but the one at 149 °C was not. We also could not detect any variation at around 149 °C. The present investigation of CsH_2PO_4 crystal seems to agree with Haile et al. and Wada et al., and

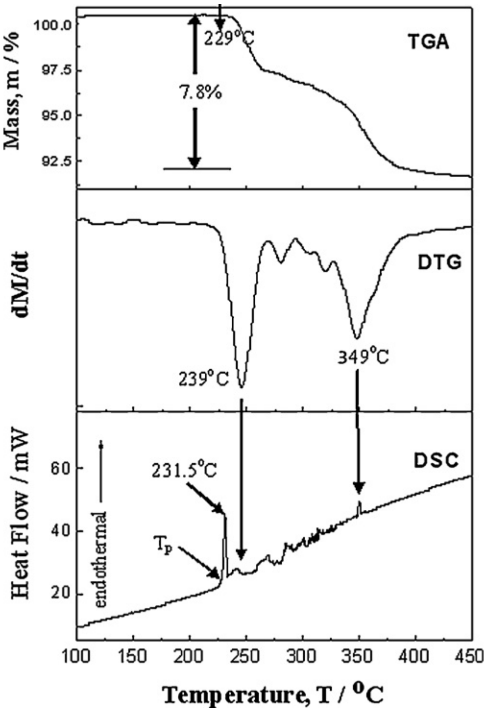

Fig. 1. TGA and corresponding DTG curves, DSC thermogram of CsH_2PO_4 heated at 10 K/min under flowing 50 ml/min dry N_2 gas.

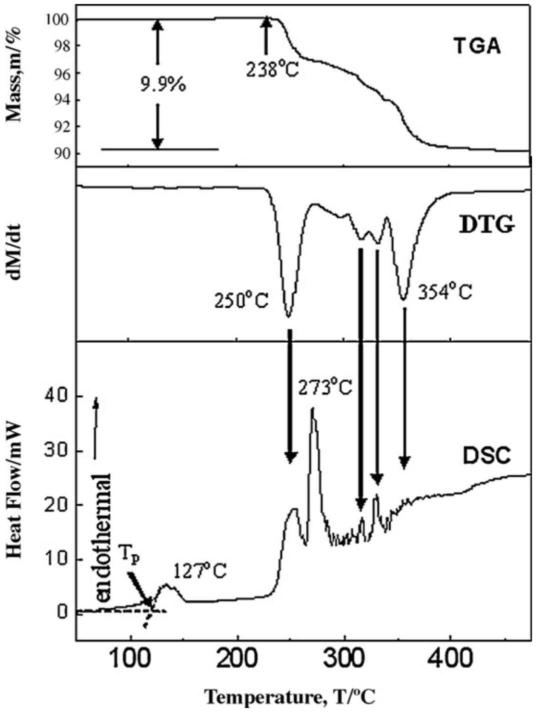

Fig. 2. TGA and corresponding DTG curves, DSC thermogram of RbH_2PO_4 heated at 10 K/min under flowing 50 ml/min dry N_2 gas.

disagree with Ortiz, Lee and Park et al. In addition, Boysen et al. [7] gave out the reasons to explain the literature discrepancies in temperatures reported above, they suggested that surface area plays a significant role in the thermal decomposition or dehydration of CsH_2PO_4, such as, the fine powder crystal can carry out dehydration at relatively low temperature, whereas for single crystal the same weight loss will not be observed until higher temperature. Especially, regardless of sample surface area, in all case a polymorphic transition independent of decomposition is clearly evident at $T_p \approx 230\,^\circ C$. Thus for CsH_2PO_4 our results support Haile and Boysen's suggestion.

3.2. RbH_2PO_4

3.2.1. The literature debate and recent progress

In recent decades, the behavior of RbH_2PO_4 crystal on heating above room temperature has also been studied and a high-temperature event near T_p has been reported by a number of workers [8,25,29,32–39]. However, there are considerable differences in the published reports concerning the behavior at T_p. Based on the dielectric constant, thermal analysis, thermo-microscopy data, X-ray and so on, Park and Lee [13,40–44], Ortiz et al. [35–37] have argued that RbH_2PO_4 compound does not undergo a polymorphic phase transition prior to thermal decomposition or polymerization, and claimed that this variation at T_p is due to thermal decomposition process involving phosphate condensation and polymerization. Whereas others, including Blinc et al. [32] and Baranov et al. [8], attributed it to a high-temperature structural phase transition, primarily on the base of optical observations, Raman scattering, nuclear magnetic resonance (NMR). In addition, Metcalfe and Clark [45] reported the variation temperature T_p is scattered widely over the range between 80 and 120 °C, strongly depending on the details of the sample preparation and experimental conditions. Furthermore, another variation from monoclinic phase to an as-of-yet unidentified phase has also been reported at $T_p' \approx 281\,^\circ C$ [13]. In parallel to the controversy regarding whether it is the existence of a structural phase transition or thermal decomposition that give rise to the high-temperature variation at T_p, a recent paper supported neither side. Boysen et al. [7] reported the initial dehydration event in RbH_2PO_4 compound occurs at 257 °C, without indication of either solid-solid or solid-liquid transition prior to weight loss.

3.2.2. Thermal analysis results

The temperature dependence of weight loss for RbH_2PO_4 powdered sample is plotted at the top of Fig. 2, which shows a weight drop of about 9.9% in the whole heating process with onset at around 238 °C. From the dehydration reaction of RbH_2PO_4 crystal: $RbH_2PO_4 \rightarrow RbPO_3 + H_2O$ [46], a weight loss of 9.87% in total is expected theoretically, and the residue was $RbPO_3$ as identified by powder X-ray diffraction after thermal analysis, which indicates that the weight loss is due entirely to dehydration. DTG pattern reveals two maxima in dehydration rate at 250 and 354 °C, respectively. The other two small variations are also observed within the temperature range from 300 to 340 °C, which is indicative of a multistep dehydration process. The abovementioned variations all agree well with heat absorption as measured with DSC in another sample from the same batch. On the other hand, two strong endothermic peaks at 127 and 273 °C are not accompanied by any weight change, and therefore not attributable to any form of decomposition, which may be the so-called high-temperature structural phase transition, as lots of researchers reported. Metcalfe and Clark [45] reported that RbH_2PO_4 transforms quasi-irreversibly to a monoclinic phase at a temperature somewhere between 80 and 120 °C. In addition, Pereverzeva et al. [47], Shapira et al. [38] and Blinc et al. [32] also gave out the similar reports except for some tiny discrepancies in the temperature value. In our research, the observed endothermicity at 127 °C seems to agree very well with this case, and further confirmed the physical change like structural phase transition rather than the chemical change caused by thermal decomposition at the controversial temperature T_p between 80 and 120 °C.

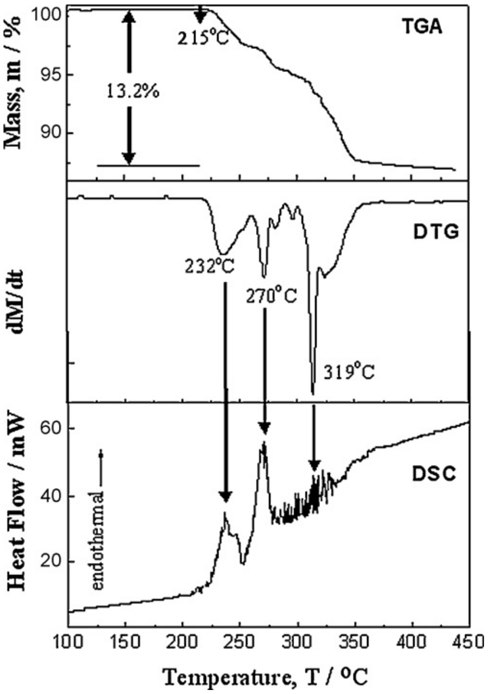

Fig. 3. TGA and corresponding DTG curves, DSC thermogram of KH_2PO_4 heated at 10 K/min under flowing 50 ml/min dry N_2 gas.

3.3. KH_2PO_4

3.3.1. The literature debate and recent progress

Early studies of KH_2PO_4 by Blinc et al. [48] indicated that the endothermic DTA variation at 171 °C is not associated with thermal decomposition, instead it is related with structural changes. Later, Rapoport [49] and Grunberg et al. [50] reported two polymorphic transitions, one at 180 °C and the second at 233 °C. Itoh et al. [51] reported that on heating through 187 °C, a structural phase transition from tetragonal to monoclinic symmetry takes place. Also, Vargas et al. [52] reported that below the translation temperature, the monoclinic phase of KH_2PO_4 is metastable and it reverts to the stable tetragonal phase after being kept some days in air at room temperature. More Recently, on the basis of dielectric constant, thermal analysis and thermo-microscopy data, Lee and Park [13,41–44] reported that these high-temperature phenomena is not a structural phase transition but an effect of thermal decomposition at surface in KH_2PO_4. Ortiz et al. also supported their position [35–37]. Both sets of authors concluded that all the variations in high-temperature properties can be attributed to chemical change, not to physical change. Indeed, at ambient pressure, the dehydration readily masks certain phase transition in KH_2PO_4, Boysen and Haile [53] used high pressure electrical measurements, free from the ambiguities introduced by dehydration, to investigate the high-temperature phase behavior of KH_2PO_4, and concluded that under a dry atmosphere and ambient pressure, dehydration dominates the high-temperature behavior and at 1 GPa pressure, KH_2PO_4 crystal does not exhibit a superprotonic phase transition prior to melting.

3.3.2. Thermal analysis results

The DSC and TGA experiments were preformed with a constant heating rate, the results obtained upon heating powder of KH_2PO_4 to 450 °C are presented in Fig. 3. The DTG results show multiple dehydration events, with three major events occurring at 232, 270 and 319 °C, respectively. A rather broad endothermic peak observed from the DSC measurement at around 232 °C is perhaps the result of the multiple overlapping dehydration events, and another sharp endothermic peak at around 270 °C is in good agreement with the DTG measurement. Besides, in the DSC thermogram, several rather weak peaks at around 319 °C correspond to a narrow peak observed in DTG pattern, which may be also due to the overlapping dehydration events. In our research, the TGA measurement gives same results as already reported by Blinc et al. [48], Boysen and Haile [53], onset of weight loss at around 215 °C, a somewhat higher temperature than others reported, is taken to indicate the beginning of thermal decomposition. On heating further, the thermal events will happen frequently at different temperatures. These high-temperature behaviors are caused by thermal dehydration and occurred via the formation of polyphosphate intermediates. Nevertheless, the overall dehydration can be described by the reaction: $KH_2PO_4 \rightarrow KPO_3 + H_2O$, this reaction results in a 13.2% loss of weight and a constant weight was reached at around 350 °C. Earlier studies of KH_2PO_4 at ambient pressure indicated two polymorphic transitions, one at 180 °C and the other one at 233 °C, however, in our investigation, no any change at around 180 °C is detected before dehydration. The present experimental results keep consistent with the ones already reported by Lee and Park, Ortiz et al., Boysen and Haile [53], and further demonstrate that all the high-temperature events in KH_2PO_4 are entirely due to dehydration.

3.4. NaH_2PO_4

3.4.1. Brief introduction and recent progress

As one member of XH_2PO_4 family, NaH_2PO_4 did not get widely attention in the tentative application of fuel cells like other members such as CsH_2PO_4, RbH_2PO_4 and KH_2PO_4 due to its low melting point and inexistence of superprotonic phase transition. Ghule et al. [54] adopted thermo-Raman spectroscopy in the temperature range from 25 to 600 °C to study its thermal properties and reported that it experienced dehydration, condensation and phase transformations as the temperature was increasing.

3.4.2. Thermal analysis results

The typical thermal analysis results of NaH_2PO_4 powered sample are presented in Fig. 4. The TGA pattern shows the onset of weight loss at around 210 °C. On heating further, the thermal variations mainly occurring at 223 and 352 °C give rise to the corresponding endothermic peaks in DSC measurement. Generally, such thermal variations are believed to be caused by chemical decomposition such as: $n\mathrm{NaH_2PO_4} \rightarrow \mathrm{Na}_n\mathrm{H_2P}_n\mathrm{O}_{3n+1} + (n-1)\mathrm{H_2O}$, and $n \geq 1$. The existence of multiple thermal events indicates a multistep process, occurring via the formation of intermediate products. In order to compare the experimental results with theoretical ones, the possible products are deduced. Similar to the calculation method reported by Park et al. [41–44], the ratio of the changed products (polymerization) and evolved products (water) are related to the chemical change in NaH_2PO_4 for the possible n values as follows:

(1) For $n = 2$, $2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$

$$\text{Ratio of changed product}: \frac{\mathrm{M(Na_2H_2P_2O_7)}}{\mathrm{M(2NaH_2PO_4)}} = 92.5\%$$

$$\text{Ratio of escaped product}: \frac{\mathrm{M(H_2O)}}{\mathrm{M(2NaH_2PO_4)}} = 7.5\%$$

(2) For $n = 4$, $4NaH_2PO_4 \rightarrow Na_4H_2P_4O_{13} + 3H_2O$

$$\text{Ratio of changed product}: \frac{\mathrm{M(Na_4H_2P_4O_{13})}}{\mathrm{M(4NaH_2PO_4)}} = 88.75\%$$

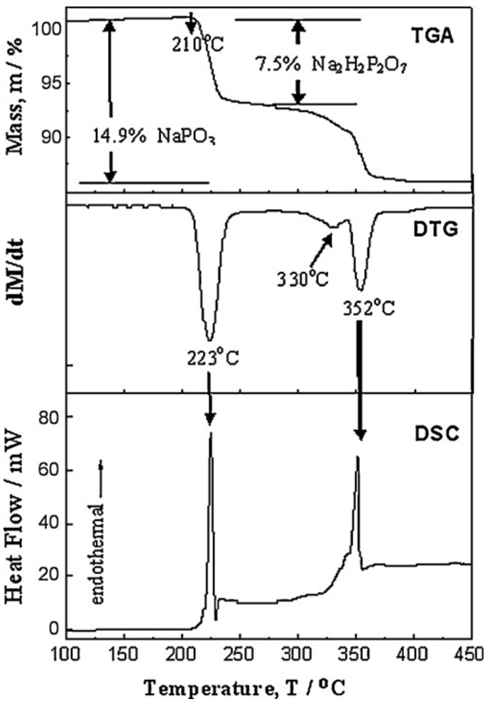

Fig. 4. TGA and corresponding DTG curves, DSC thermogram of NaH_2PO_4 heated at 10 K/min under flowing 50 ml/min dry N_2 gas.

$$\text{Ratio of escaped product}: \frac{M(3H_2O)}{M(4NaH_2PO_4)} = 11.25\%$$

(3) For $n = 6$, $6NaH_2PO_4 \rightarrow Na_6H_2P_6O_{19} + 5H_2O$

$$\text{Ratio of changed product}: \frac{M(Na_6H_2P_6O_{19})}{M(6NaH_2PO_4)} = 87.5\%$$

$$\text{Ratio of escaped product}: \frac{M(5H_2O)}{M(6NaH_2PO_4)} = 12.5\%$$

(4) For $n \gg 6$, $nNaH_2PO_4 \rightarrow Na_nH_2P_nO_{3n+1} + (n-1)H_2O \rightarrow nNaPO_3 + nH_2O$

$$\text{Ratio of changed product}: \frac{M(nNaPO_3)}{M(nNaH_2PO_4)} = 85\%$$

$$\text{Ratio of escaped product}: \frac{M(nH_2O)}{M(nNaH_2PO_4)} = 15\%$$

According to the stoichiometric calculation, one can find that the overall water loss of 15% corresponds very well to the experimental value (14.9%), which confirms the dehydration behavior in the heating process. In addition, water loss leads to the formation of various polymeric intermediates. From the TGA and DTG patterns, the first dehydration event at 223 °C leads to water loss of 7.5% which is the same as the calculated weight loss to the intermediate product of $Na_2H_2PO_7$ ($n = 2$). For the given value $n = 4$ and 6, very small weight is lost and their corresponding dehydration events should be during the temperature region from 270 to 340 °C. Also, one can find a rather broad and weak DTG signal or DSC endothermic peak at around 330 °C, which is just due to two overlapping dehydration events during the formation of intermediate products $Na_4H_2P_4O_{13}$ and $Na_6H_2P_6O_{19}$. Park et al. [41–44] has pointed out that the process of polymerization or decomposition depends on temperature, and the intermediate product is unstable. Therefore, it is commonly believed that a mixed intermediate product exists within the temperature region from 270 to 340 °C. For $n \gg 6$, the final product $NaPO_3$ is formed, which brings about an endothermal peak at 352 °C. Thus, the NaH_2PO_4 powdered sample used here is dominated by thermal decomposition in the heating process, and no structural phase transition exists, as has been shown in KH_2PO_4 crystal.

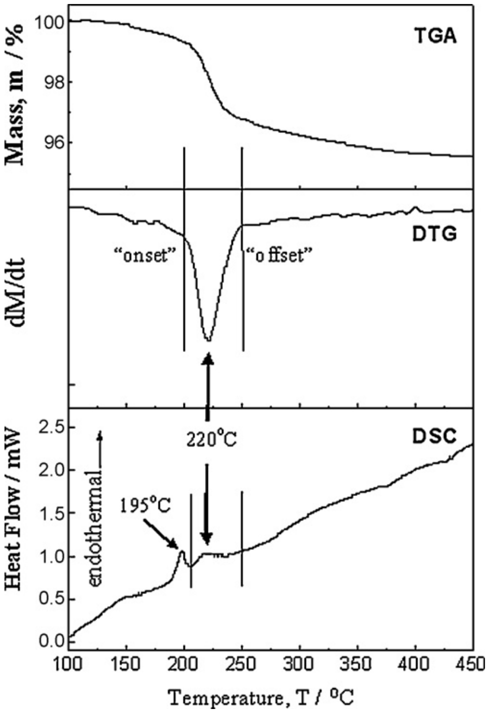

Fig. 5. TGA and corresponding DTG curves, DSC thermogram of LiH_2PO_3 heated at 10 K/min under flowing 50 ml/min dry N_2 gas.

3.5. LiH_2PO_3 or $LiH(PO_3H)$

3.5.1. Brief introduction and recent progress

Since Baranov et al. [8] reported that the conductivity of $CsHSO_4$ increases by several orders of magnitude upon transformation from monoclinic phase to a high-temperature tetragonal phase, various solid acid compounds attracted many researchers' attention to investigate them as superprotonic conductors. In fact, these compounds have a common point that all are formed of oxy-anion tetragonal groups XO_4 which are linked together by hydrogen bonds, where X = P, S or Se. Recently, the high-temperature behaviors and a superprotonic phase transition in the new compound CsH_2PO_3 or $CsH(PO_3H)$ was reported by Chiholm et al. [55], in addition, Kosterina et al. [56] reported the structure of this material, it contains the tetrahedral group PO_3H, like other typical salts of phosphorous acid. Given the chemical and structural similarity of CsH_2PO_3 and $CsHSO_4$, we gave in to curiosity and studied the similar compound LiH_2PO_3, it is of relevance to establish whether this alternative cation or anion chemistries can give rise to the same properties. The corresponding high-temperature thermal results of LiH_2PO_3 crystal are presented here.

3.5.2. Thermal analysis results

The TGA and DTG profiles in Fig. 5 for the powdered LiH_2PO_3 sample show a wide peak of weight loss with around 200 and 250 °C as "onset" and "offset" temperature, respectively, and the maximum rate of weight loss is reached at around 220 °C. From TGA pattern, one can also find that at lower temperature region, a very slight weight loss is likely due to the loss of surface absorbed H_2O, because the LiH_2PO_3 crystal is somewhat hygroscopic under normal circumstances. The bottom pattern shows the DSC thermogram, it is clearly that the DTG and DSC curves are closely correlated: "onset" and "offset" temperatures of these thermograms coincide approximately as well as the peak temperature of the endothermic effect, although the peak is only a broad and weak one and the temperature range between "onset" and "offset" reaches about 50 °C. Especially notable, LiH_2PO_3 shows an endothermic change at around 195 °C in the DSC measurement prior to the beginning of weight loss, which indicates that the high-temperature variation at 195 °C is not associated with thermal decomposition. In the narrowest sense, this temperature, presumably, corresponds to the so-called high-temperature phase transition, though no sufficient demonstration can be available. Similarly, Chisholm et al. [55] reported that the thermal decomposition of CsH_2PO_3 crystal begins at temperature just beyond the superprotonic transition, with an onset of 137 °C, to a phase of high proton conductivity, and they pointed out that the superprotonic phase transition of CsH_2PO_3 can be well resolved from thermal decomposition, unlike the case for CsH_2PO_4. In light of the same structure and similar composition of CsH_2PO_3 and LiH_2PO_3 crystals, and the convincing data in our experiments, we can presume that the high-temperature event at around 195 °C should be attributable to structural phase transition, and the other one at around 220 °C should be related to thermal decomposition. Further investigation is still in progress in our laboratory.

4. Conclusions

The high-temperature behaviors of CsH_2PO_4, RbH_2PO_4, KH_2PO_4, NaH_2PO_4 and LiH_2PO_3 have been investigated with the help of thermal analysis. Key conclusions are as follows:

(1) In CsH_2PO_4, the thermal event at 231.5 °C (at heating rate of 10 K/min) is endothermic without weight loss, and attributable to superprotonic phase transition, in agreement with Haile et al. The other two events at 239 and 349 °C are entirely due to dehydration, as evident from weight loss analysis.
(2) RbH_2PO_4 undergoes a polymorphic phase transition at T_p between 80 and 120 °C without any evidence of dehydration, as reported by Blinc et al. and Baranov et al. Other peaks at 250 and 354 °C belong to thermal dehydration.
(3) Three peaks are located at 232, 270 and 319 °C for KH_2PO_4, and 223, 330 and 352 °C for NaH_2PO_4 (at heating rate of 10 K/min). They arise from dehydration, as found by previous investigators.
(4) The newly studied substance LiH_2PO_3 displays a sharp endothermic peak at 195 °C (at heating rate of 10 K/min) prior to weight loss at 220 °C. By comparison with CsH_2PO_3, the endothermicity is associated with a structural phase change and the weight loss, with thermolysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.01.010.

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