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Phase transitions and proton conductivity in hafnium hydrogen phosphate with the NASICON structure

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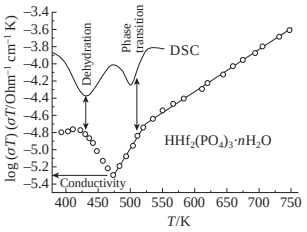
Triclinic NASICON-type hafnium hydrogen phosphate $HHf_2(PO_4)_3·0.5H_2O$ was obtained by ion exchange from $LiHf_2(PO_4)_3$. The dehydration of $HHf_2(PO_4)_3·0.5H_2O$ (~400 K) followed by a triclinic-rhombohedral phase transition (~470 K) was observed, and the resulting $HHf_2(PO_4)_3$ was stable up to 870 K. The proton conductivity of the sample was $4.7×10^{-7}$ Ohm^{-1} cm^{-1} at 773 K.



Double phosphates with the NASICON structure belong to a class of compounds with the general formula $A_xB_2(PO_4)_3$, where A = H, Li, Na, K, Cu(0.5), H_3O, NH_4, and B = In, Sc, Fe, Zr, Ti, Hf, Sn, Ge, *etc*.[1] The alternation of the two types of cavities along conductive channels gives a three-dimensional network for fast ion transport. Furthermore, these compounds are characterized by high hydrolytic and thermal stability.[1–5]

Hydrogen phosphates of polyvalent elements are promising materials for applications at elevated temperatures in processes where organic proton-exchange membranes cannot be employed because of their degradability.[6,7] High-temperature proton fuel cells have received substantial attention due to their high carbon monoxide tolerance allowing to use cheap hydrogen produced by conversion of hydrocarbons and simplified water management.[8,9] Previously, it was shown that the double hydrogen phosphates with the NASICON structure $HZr_2(PO_4)_3·nH_2O$, $H_{1±x}Zr_{2-x}M_x(PO_4)_3·H_2O$ (M = Nb, Y) and $H_{3-2x}M^{III}_{2-x}Nb_x(PO_4)_3·nH_2O$ (M^{III} = In, Fe) are characterized by high thermal stability and high proton conductivity at high temperatures.[10–16] At the same time, there are no data on the properties of hafnium hydrogen phosphate with the NASICON structure. Therefore, the synthesis and proton mobility of $HHf_2(PO_4)_3$ are of theoretical interest. Previously, high ion conductivity of rhombohedral NASICON-type $LiHf_2(PO_4)_3$ was reported.[17–19]

Here, we synthesized hafnium hydrogen phosphate with the NASICON structure for the first time and characterized its composition, thermal stability and proton mobility.

Hafnium hydrogen phosphate was obtained by ion exchange in hot nitric acid for 30 days from $LiHf_2(PO_4)_3$ with the NASICON structure previously synthesized by a solid state method.[19]

According to SEM data, the initial $LiHf_2(PO_4)_3$ with the NASICON structure is characterized by a broad particle size distribution (1–20 μm) with an average particle size of about 5 μm.[19] The hydrogen form that was obtained as a result of ion exchange is characterized by smaller and more uniform particles with an average size of about 3 μm.

The initial $LiHf_2(PO_4)_3$ possesses rhombohedral symmetry.[19] The XRD patterns of prepared sample have revealed that the NASICON structure is kept after ion exchange, but a decrease in the lattice symmetry is observed. The X-ray diffraction pattern of the sample can be indexed in the triclinic system. The unit cell parameters are as follows: a = 15.46±0.03, b = 8.85±0.01 and c = = 9.32±0.02 Å, α = 89.8±0.1°, β = 123.5±0.1° and γ = 88.75±0.1°.

Two steps of weight loss are observed in the TGA curve of hydrogen hafnium phosphate. The first one corresponds to the loss of crystalline water. The hydration degree calculated from the first step of weight loss is 0.5 molecules of H_2O per formula unit of $HHf_2(PO_4)_3$. The second step (870–1170 K) corresponds to anhydrous hydrogen phosphate decomposition with split out of structural water followed by hafnium oxide and hafnium pyrophosphate formation [equation (1)]. The decomposition of $HHf_2(PO_4)_3·0.5H_2O$ is similar to that of $HZr_2(PO_4)_3·nH_2O$ reported elsewhere.[10]

$$HHf_2(PO_4)_3·0.5H_2O \rightarrow HHf_2(PO_4)_3 + 0.5\,H_2O\uparrow \rightarrow 3/2\,HfP_2O_7 + 1/2\,HfO_2 + 1/2\,H_2O\uparrow. \quad (1)$$

The observed weight loss corresponds to 100% lithium ion exchange.

Phase transformations that occur on heating $HHf_2(PO_4)_3·0.5H_2O$ were investigated by high-temperature XRD analysis. The phase transition from triclinic to rhombohedral symmetry was observed in a temperature range of 470–570 K. The unit cell parameters of rhombohedral $HHf_2(PO_4)_3$ at 570 K are a = 8.844±0.003 and c = 22.893±0.001 Å (space group $R\bar{3}c$). The sample returns to the triclinic symmetry after cooling.

According to calorimetric data, two broad endothermic peaks at 440 and 505 K appeared on heating (Figure 1, curve *1*). Only one peak was observed in the DTG curve (at 440 K) (Figure 1, curve *3*) due to the dehydration of the sample. The second peak in the DSC curve (at 505 K) corresponds to the phase transition. The heat effects of these endothermic processes are 8.3 and

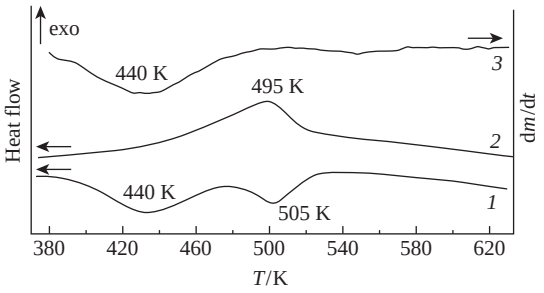


Figure 1 DSC curves obtained upon (*1*) heating and (*2*) cooling and (*3*) differential mass loss curve for $HHf_2(PO_4)_3 \cdot nH_2O$ heating.

3.4 kJ mol^{-1}, respectively. Only one exothermic peak at 495 K was detected on cooling $HHf_2(PO_4)_3$ (Figure 1, curve *2*). The mass changes were not revealed during cooling. The results indicate the reversibility of the phase transition. This fact is also confirmed by XRD analysis. The anhydrous hydrogen–hafnium phosphate reverts to a triclinic modification after cooling to room temperature.

Figure 2 shows a plot of conductivity *vs.* 1000/*T* for $HHf_2(PO_4)_3 \cdot 0.5H_2O$. Impedance measurements were performed at usual relative humidity in cylindrical pellets with platinum electrodes (platinum black) by a two-probe method using an IPU-62 alternating current bridge in a frequency range from 10 Hz to 2 MHz in a temperature range of 298–873 K with a step of 10–20 K and a heating rate of 2 K min^{-1}. Bulk conductivity was calculated by the extrapolation of the semicircle to the resistance axis. The proton conductivity of $HHf_2(PO_4)_3 \cdot 0.5H_2O$ is 5.5×10^{-8} Ohm^{-1} cm^{-1} at room temperature. At low temperatures, conductivity is most likely determined by the proton diffusion in water sorbed on $HHf_2(PO_4)_3$ particles. At 298–470 K, the conductivity decreases due to a water loss. This correlates with the first step of mass loss according to the TGA data. Above 470 K, the conductivity increases due to the thermal activation of proton transfer in $HHf_2(PO_4)_3$ with an activation energy of 40±1 kJ mol^{-1}. At the same time, a change in the slope of the Arrhenius plots owing to the phase transformation of $HHf_2(PO_4)_3$ is observed at 520 K (Figure 2).

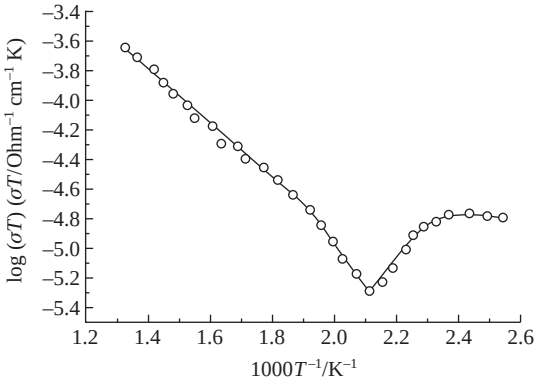


Figure 2 Temperature dependence of $HHf_2(PO_4)_3 \cdot 0.5H_2O$ proton conductivity obtained upon heating.

Note that the conductivity of $HHf_2(PO_4)_3$ is lower than that of hydrogen–zirconium phosphates with the NASICON structure[11,14,15] and $H_{3-2x}M^{III}_{2-x}Nb_x(PO_4)_3 \cdot nH_2O$ (M^{III} = In, Fe)[16] obtained at usual relative humidity even after $HHf_2(PO_4)_3$ triclinic–rhombohedral phase transition in a high-temperature range (470–750 K).

Thus, the triclinic hafnium hydrogen phosphate $HHf_2(PO_4)_3 \cdot 0.5H_2O$ with the NASICON structure was obtained for the first time and characterized in a wide temperature range. This compound possesses high thermal stability and exhibits proton conductive properties. Hydrogen phosphates with the NASICON structure can be considered as promising proton conducting thermostable electrolytes for fuel cells operated at medium temperatures (473–773 K).

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