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Phase transition through intermediate formation?

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The ionic conductivity and phase transitions of $HZr_2(PO_4)_3{\cdot}H_2O$ and $H_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3{\cdot}H_2O$ were studied using impedance spectroscopy and high temperature X-ray powder diffraction.

Phase transitions determine the properties of inorganic compounds, including solid-state ionic conductors. In these materials, high ionic mobility appears only after a superionic phase transition, which goes with sharp changes in the ordering of a cationic or anionic sublattice.[1] In other compounds, on the contrary, a gradual growth of ion mobility with temperature leads to second-order phase transitions, accompanying by changes in the symmetry and properties of crystals. Materials with the NASICON structure [$M_yA_2(XO_4)_2$, where M is a monovalent cation, A is a polyvalent cation and X is P, Si or As] are typical examples of such compounds.[1,2] This family exhibits a complex polymorphism.[3,4] Materials with the highest ion mobility are usually rhombohedral. However, they can transform to triclinic at low temperatures.[5,6] Sodium- and lithium-based NASICON-type compounds have been thoroughly investigated.[1,2] Much less is known about hydrogen analogues. Data on the conductivity of $HZr_2(PO_4)_3{\cdot}nH_2O$ were reported.[7,8]

The aim of this work was to study phase transitions in the proton forms of materials with the NASICON structure, $HZr_2(PO_4)_3{\cdot}H_2O$ and $H_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3{\cdot}H_2O$.

$LiZr_2(PO_4)_3$ and $Li_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3$ were synthesised using a standard procedure.[6] $HZr_2(PO_4)_3{\cdot}H_2O$ and $H_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3{\cdot}H_2O$ were prepared by refluxing the lithium forms in nitric acid for 20 days. Thermogravimetric analysis was used to monitor the degree of ion exchange. High-temperature X-ray diffraction (XRD) patterns were obtained on a Philips X'pert

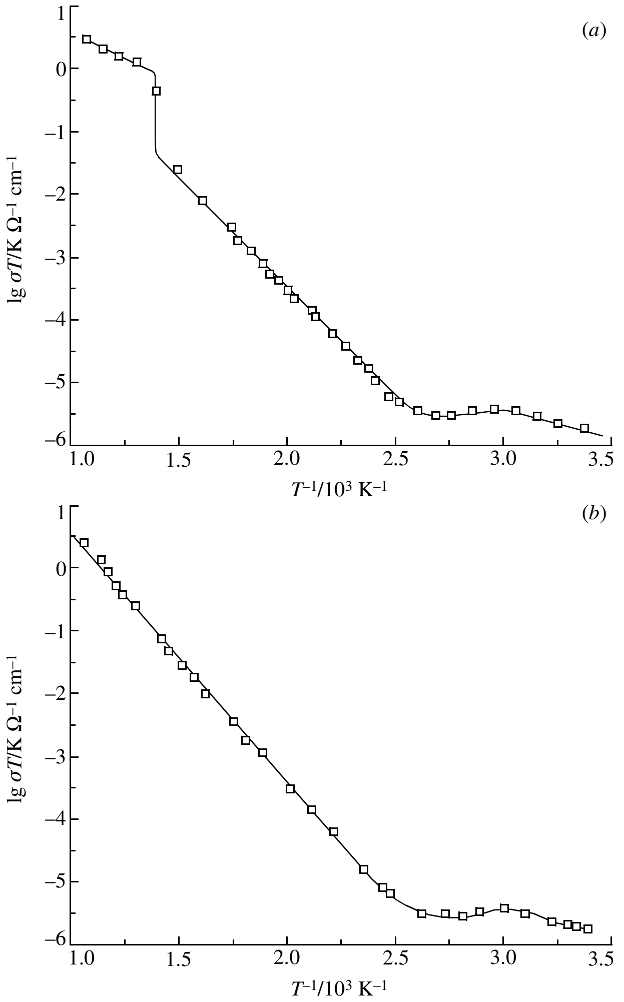

Figure 1 Dependence of conductivity on inverse temperature for $H_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3{\cdot}H_2O$ obtained with (*a*) silver and (*b*) platinum electrodes.

powder diffractometer. The heating rate was 5 K min^{-1} with delays at a constant temperature for XRD data collection. Conductivity measurements were performed using an IPU-p.62 impedance analyzer in the frequency range 10 Hz–2 MHz. Electrodes (silver or platinum fine powder) were applied on both faces of the right-angled pellets (5×7×4 mm, 3×10^9 Pa).

The initial lithium form $LiZr_2(PO_4)_3$ is triclinic; however, its monohydrated proton analogue is rhombohedral even at room temperature. Its X-ray diffraction pattern is similar to that reported by Rudolf *et al.*[9] The temperature dependence of ionic conductivity is usually given by the Frenkel equation

$$\sigma T = A\exp(-E_\sigma/RT), \qquad (1)$$

where σ is the conductivity, T is the absolute temperature, A is the pre-exponential factor, E_σ is the activation energy and R is the gas constant. The plot of $\log \sigma T$ *vs.* $1/T$ for $H_{0.98}Zr_{1.98}Nb_{0.02}(PO_4)_3{\cdot}H_2O$ with silver electrodes is shown in Figure 1(*a*). This plot exhibits several distinct regions and two important features: an inflection at 400 K and a sharp increase in conductivity by more than one order of magnitude at 700 K. At the inflection point, the activation energy increases from 17±2 to 69±2 kJ mol^{-1} for 293–333 K and 400–700 K, respectively, whereas above 700 K the activation energy decreases again to 33±3 kJ mol^{-1}. A similar dependence was found for $HZr_2(PO_4)_3$.

Typically an inflection or change in the slope of conductivity results from a changeover from extrinsic to intrinsic defect generation, where extrinsic defects are controlled by the dopant concentration and intrinsic defects, by a thermal disorder. It is also typical to attribute a sharp jump in conductivity to a superprotonic phase transition accompanied by a significant change in the crystal structure. However, in our case, the situation is much more complicated. Portions of XRD patterns for $HZr_2(PO_4)_3$ at different temperatures are shown in Figure 2. At 420–470 K, a part of reflections shifted, and lattice parameters changed sharply from $a = 8.746(1)$ and $c = 23.790(3)$ Å at 400 K to $a = 8.884(1)$ and $c = 22.804(5)$ Å at 470 K (parameters are given for the hexagonal unit cell) (Figure 3). The observed changes are not typical of usual phase transitions. In the region 2θ of about 13.8°, only one reflection (012) can be observed for the rhombohedral modification, which remains unaltered even after a phase transition. However, the XRD patterns obtained at 420–470 K contained sharp satellites, which disappeared again at 490 K [Figure 2(*a*)]. These satellites cannot be attributed to either high- or low-temperature rhombohedral phases. Their presence can be explained assuming that a new low-symmetry intermediate phase can be formed in this temperature range. Intermediate formation is typical of chemical reactions rather than phase transitions.

The TGA of $HZr_2(PO_4)_3{\cdot}H_2O$ showed a weight loss in the temperature range 350–490 K, which is apparently due to the loss of crystalline water. A slight decrease in the conductivity was observed at the beginning of this temperature range due to the loss of H_2O, which decreases proton transport.[10] Thus, the removal of crystalline water leads to a decrease in the cationic disordering of the crystal and causes a phase transition to a low-symmetry triclinic phase. Three and four new reflections of this new phase appeared in the fragments of XRD patterns at 2θ of 13–14° and 18–21°, respectively (Figure 2).

Further heating results in an increase in structural disorder and proton mobility. As a result, at temperatures higher than 470 K, the triclinic structure becomes unstable, and another transition to a rhombohedral phase takes place. Water loss causes the observed change in the lattice parameters of a rhombohedral phase. Thus, the triclinic modification of $HZr_2(PO_4)_3$ can be observed only in a narrow temperature range. However, on cooling this material, rehydration processes slow down because

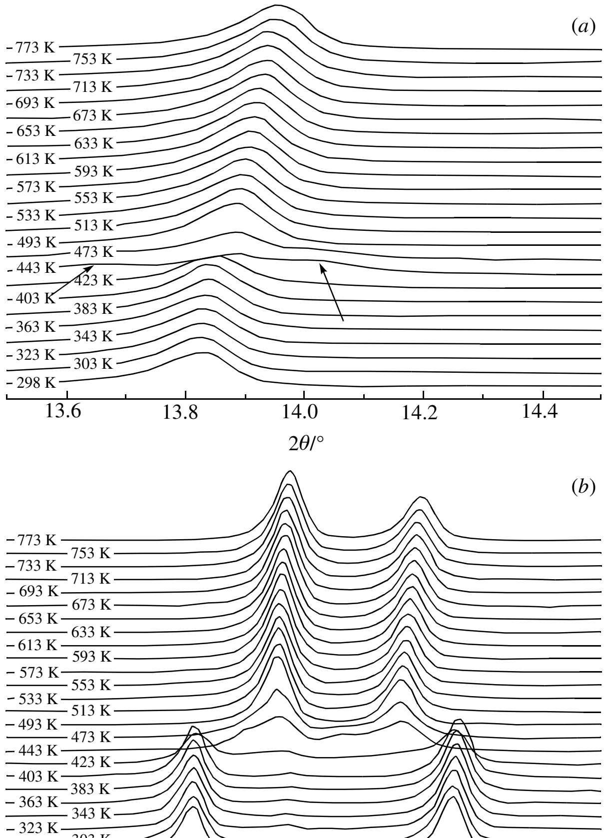

Figure 2 Fragments of XRD patterns at 2θ of 13–14° (*a*) and 18–21° (*b*) for $HZr_2(PO_4)_3{\cdot}H_2O$ at different temperatures.

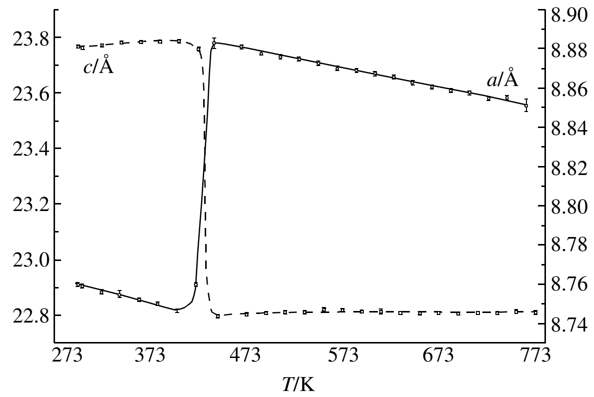

Figure 3 The temperature dependence of the lattice parameters *a* and *c* for $HZr_2(PO_4)_3 \cdot H_2O$.

of difficulties for water molecules to move through the narrow bottlenecks. Thus, at low temperatures, $HZr_2(PO_4)_3 \cdot H_2O$ does not form in air. The cooling of $HZr_2(PO_4)_3$ yielded a triclinic phase, which is stable at room temperature.

XRD data indicated that there is no phase transformation at about 700 K, where a sharp increase in conductivity was observed. In this temperature range, only a slight shift of reflections can be seen, due to the dependence of lattice parameters on temperature. Indeed, when the conductivity of $HZr_2(PO_4)_3 \cdot H_2O$ was measured with the use of platinum electrodes, no conductivity increase was observed in this temperature range [Figure 1(*b*)]. We conclude, therefore, that when silver electrodes were applied, the sharp conductivity increase at 700 K was caused by a solid state reaction between the electrode material and the sample despite the fact that in aqueous solutions the standard redox potential of the Ag^+/Ag pair is much larger than that of H^+/H_2. In the NASICON structure, all oxygen atoms form two strong bonds with polyvalent zirconium and phosphorus ions. According to this, bonds between the anion and the proton are rather weak. Furthermore, the cavities in the structure are well suited for large cations like sodium, silver and potassium. But they are too large for small hydrogen ions. That is the reason why at about 700 K a solid-state reaction between silver and $HZr_2(PO_4)_3$ took place, and the black colour of silver powder disappeared from the pellet faces. A portion of the hydrogen ions changed on silver ions, which are more mobile in the NASICON structure:

$$HZr_2(PO_4)_3 + yAg \rightarrow Ag_yH_{1-y}Zr_2(PO_4)_3 + 0.5yH_2 \qquad (2)$$

This causes in an increase in conductivity and a decrease in its activation energy in the case of impedance measurements with silver electrodes.

Another interesting feature of these compounds is an unusual change of lattice parameters with temperature. During heating $HZr_2(PO_4)_3$ above the temperature of phase transition, the parameter *c* of a rhombohedral phase stays almost unchanged (Figure 3). At the same time, the parameter *a* decreases significantly as the temperature increased (from 8.883±0.003 Å at 423 K to 8.850±0.003 Å at 773 K) (Figure 3).

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References

1 A. K. Ivanov-Shitz and I. V. Murin, *Ionika tverdogo tela (Solid State Ionics)*, Izd. S-P. Univ., St. Petersburg, 2000, vol. 1.

2 A. D. Robertson, A. R. West and A. G. Ritchie, *Solid State Ionics*, 1997, **104**, 1.

3 M. Catti, S. Stramare and R. Ibberson, *Solid State Ionics*, 1999, **123**, 173.

4 M. Catti and S. Stramare, *Solid State Ionics*, 2000, **136–137**, 489.

5 F. Sudreau, D. Petit and J. P. Boilot, *Solid State Ionics*, 1989, **83**, 78.

6 I. A. Stenina, E. V. Antipov, A. I. Rebrov, R. V. Shpanchenko and A. B. Yaroslavtsev, *Dokl. Ross. Akad. Nauk*, 2002, **382**, 790 (*Dokl. Chem.*, 2002, **382**, 46).

7 M. A. Subramanian, B. D. Roberts and A. Clearfield, *Mater. Res. Bull.*, 1984, **19**, 1471.

8 M. Ohta, F. P. Okamura, K. Hirota and A. Ono, *J. Mater. Sci. Lett.*, 1987, **6**, 583.

9 P. R. Rudolf, M. A. Subramanian, A. Clearfield and J. D. Jorgensen, *Solid State Ionics*, 1985, **17**, 337.

10 A. B. Yaroslavtsev and V. Yu. Kotov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 515 (*Russ. Chem. Bull., Int. Ed.,* 2002, **51**, 555).

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