Electrical and Thermodynamic Properties of Cs_{0.97}Rb_{0.03}H₂PO₄

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Abstract—The transport properties of $Cs_{0.97}Rb_{0.03}H_2PO_4$ have been studied using polycrystalline samples and single crystals. The mixed salt is isostructural with cesium dihydrogen phosphate and has slightly smaller unit-cell parameters. The cation substitution increases the low-temperature ionic conductivity of the material by about two orders of magnitude but has an insignificant effect on the conductivity of the high-temperature phase. The low-temperature conductivity of single-crystal samples exhibits significant anisotropy, with $\sigma_a < \sigma_{b\pm c}$. The conductivity of the polycrystalline material is close to $\sigma_{b\pm c}$. The substitution reduces the temperature of the superionic phase transition by 20°C and enhances the thermal stability of the high-temperature phase at low humidity (1 mol % H₂O).

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INTRODUCTION

The high-temperature phase of CsH_2PO_4 ($t \ge 230^{\circ}C$) has almost the highest electrical conductivity among superprotonic salts. In addition, CsH_2PO_4 is potentially attractive as an electrolyte for medium-temperature fuel cells [1, 2]. The stability of this superionic material is, however, influenced by the relative humidity; preparation, storage, and experimental conditions; and trace impurities and water on its surface.

Humidity has a particularly strong effect on the properties of this material: in a dry atmosphere, the superionic phase transition is accompanied by dehydration, and the conductivity of the high-temperature phase of CsH_2PO_4 drops sharply by orders of magnitude. At the same time, at an increased water vapor content in the ambient atmosphere (~30 mol %) the salt is thermodynamically stable [3, 4]. This high humidity, however, has an adverse effect on the mechanical properties of the electrolyte, and the necessity to humidify the ambient atmosphere adds complexity to the fuel cell design.

Along with fine-particle oxide additions [5–8], one possible way of extending the temperature stability range of the superionic material is by cation or anion substitution. Superionic acid salts obey the so-called chemical pressure principle: an increase in the radius of a cation or anion is equivalent to an increase in hydrostatic pressure, and vice versa. This suggests that substitution of a smaller sized cation for cesium may reduce the phase transition temperature.

Indeed, partial ammonium substitution for cesium in cesium dihydrogen phosphate, as represented by the

formula $Cs_{1-x}(NH_4)_xH_2PO_4$ ($x \le 0.1$), reduces the phase transition temperature by 10°C during heating and by 37°C during cooling [9, 10]. In addition, it stabilizes the high conductivity of the salt, but the mechanism behind this effect is not yet understood. In particular, it is unclear whether this is due to the difference in cation configuration or to the greater number of protons in the ammonium ion and the higher concentration of hydrogen bonds in the system, even though these are known not to be involved in proton transport in other acid salts. In this context, it is of interest to assess the effect of partial Rb⁺ substitution for Cs⁺ on the properties of cesium dihydrogen phosphate, because these cations differ less.

The purpose of this work was to study the transport properties of $Cs_{0.97}Rb_{0.03}H_2PO_4$ and the thermodynamic stability of its high-temperature phase.

EXPERIMENTAL

CsH₂PO₄ and Cs_{0.97}Rb_{0.03}H₂PO₄ single crystals were grown from aqueous solutions containing appropriate ratios of phosphoric acid, cesium carbonate, and rubidium carbonate by isothermal evaporation. The crystals were washed with acetone and heated at 150°C for 2 h to remove the residual water. The cation composition of the crystals was determined by a combination of atomic absorption and emission flame photometry ($\lambda = 852.1$ nm) [11]. H₂PO₄⁻ was determined by differential colorimetry as the yellow vanadomolybdate complex [12]. From the X-ray diffraction (XRD), colorimetry, and chemical



Fig. 1. XRD patterns of (1) $Cs_{0.97}Rb_{0.03}H_2PO_4$ and (2) CsH_2PO_4 at 25°C.

analysis data, the accuracy in the compositions obtained was estimated at 2%.

XRD patterns were collected on a Bruker powder diffractometer (Cu $K_{\alpha 1}$ radiation, continuous scan rate of 2°/min) at room temperature. The crystal structures of the salts at 235°C were determined at the Difrakt-sionnoe Kino Station at the Siberian Synchrotron Radiation Centre. The diffracted radiation ($\lambda = 1.525$ Å) was detected by an OD-3 linear array detector [13] in the angular range 2 θ = 23°–54°. The samples were heated at a rate of 10°C/min in an Anton Paar XRK900 chamber.

Electrical conductivity was measured by a twoprobe ac method at frequencies from 12 Hz to 200 kHz using an Instek LCR-821 impedance meter. For anisotropic conductivity measurements, the crystals were lapped in various crystallographic directions. The crystals measured ~ $0.2 \times 0.3 \times 0.4$ cm, and the crystal size depended on the crystallographic direction (the (100) face had the largest area). The conductivity of polycrystalline material was measured using samples 6 mm in diameter and 1–2 mm in thickness with a relative density of ~95%. Electrical contacts were made with fineparticle palladium paste or pressed fine-particle silver. The measurements were performed isothermally or during cooling at a rate of 0.1–0.2°C/min in air at ~15% relative humidity.

Thermal analysis (TG + DTA) was carried out with a Netzsch STA 449C system in the temperature range 20–400°C at a heating rate of 10°C/min (argon, flow rate of 30 ml/min).

IR absorption spectra of powder samples preheated at ~140–150°C for 10 h were measured in the range 580–4000 cm⁻¹ on a Digilab Excalibur 3100 (ZnSe) spectrometer.

RESULTS AND DISCUSSION

According to our XRD data, the low-temperature phase of the synthesized CsH₂PO₄ has a monoclinic structure (sp. gr. $P2_1/m$) with unit-cell parameters a = 7.9120 Å, b = 6.3830 Å, c = 4.8802 Å, and $\beta = 107.73^\circ$, V = 234.75 Å³, in agreement with previous data [14] (Fig. 1). In the XRD pattern of Cs_{0.97}Rb_{0.03}H₂PO₄, the reflections are shifted to larger angles, attesting to the formation of a CsH₂PO₄-based solid solution with a reduced unit cell. Its lattice parameters determined by a fit among the 11 strongest reflections (IK software) are a = 7.9052 Å, b = 6.3742 Å, c = 4.8757 Å, $\beta = 107.8280^\circ$, and V = 233.89 Å³ (ΔV within 0.4%).

XRD results show that, above 225°C, CsH_2PO_4 transforms into a cubic phase (sp. gr. *Pm3m*) with a = 4.961 Å (Fig. 2), in accordance with previous results [15]. In the XRD pattern of the mixed salt, reflections from the cubic phase emerge below 220°C. The observed shift of the reflections indicates that the high-



Fig. 2. XRD patterns of the high-temperature phase of (1) $Cs_{0.97}Rb_{0.03}H_2PO_4$ and (2) CsH_2PO_4 .



Fig. 3. Arrhenius plots of conductivity for (1) polycrystalline and (2, 3) single-crystal $Cs_{0.97}Rb_{0.03}H_2PO_4$ in comparison with (4) CsH_2PO_4 ; (2) σ_a , (3) $\sigma_{b \pm c}$. Polycrystalline $Cs_{0.97}Rb_{0.03}H_2PO_4$ was cooled at 0.1–0.2°C/min; the other measurements were made at a cooling rate of 1–2°C/min in air.

temperature phase also has a reduced unit-cell parameter: a = 4.940 Å (ΔV also within ~0.4%).

Figure 3 shows the Arrhenius plots of conductivity in different crystallographic directions for $Cs_{0.97}Rb_{0.03}H_2PO_4$ in comparison with CsH_2PO_4 . The proton conductivity of the mixed salt in the superionic state is seen to be close to that of CsH_2PO_4 , whereas its low-temperature proton conductivity is about two and half orders of magnitude higher. Over the entire temperature range studied, the activation energy for conduction in the mixed salt is lower, which seems to be due to a higher degree of structural disordering.

The conductivity of single-crystal Cs_{0.97}Rb_{0.03}H₂PO₄ depends on crystallographic orientation (Fig. 3). Note that a correlation of conductivity anisotropy with the crystal structure and hydrogen-bond configuration was reported previously for a variety of salts. For example, in the low-temperature phase of CsHSO₄, where the hydrogen bonds have the form of zigzag chains in the [010] direction, the values of $\sigma_{[010]}$ and $\sigma_{[001]}$ differ by two orders of magnitude [16]. The conductivity of $Cs_5H_3(SO_4)_4\cdot H_2O$ and $Cs_5H_3(SeO_4)_4\cdot H_2O$ in the hexagonal or pseudohexagonal plane is one to two orders of magnitude higher than that along the normal to this plane [17], which is consistent with the two-dimensional geometry of the dynamically disordered hydrogen bond network [18]. The compound $CsH_5(PO_4)_2$ also has the lowest conductivity in the [100] direction, normal to the layers of hydrogen-bonded phosphate tetrahedra [19].

The low-temperature phase of CsH₂PO₄ has hydrogen bonds of different lengths: disordered hydrogen bonds 2.48 Å in length and more ordered bonds 2.52 Å in length [14]. As would be expected on structural grounds, $\sigma_{b\pm c}$ (in the plane of the disordered hydrogen bonds) is an order of magnitude higher than σ_a . The observed reduction in phase transition temperature (~20°C) upon partial rubidium substitution for cesium is less significant than that upon ammonium substitution [10], which correlates with the ionic radii of Cs⁺, Rb^+ , and NH_4^+ : 1.81, 1.66, and 1.42 Å, respectively. The lower activation energy for conduction in ammoniasubstituted cesium dihydrogen phosphate was attributed to the lower N–O–H hydrogen bond strength, the activation energy being lower at higher ammonium contents. At the same time, partial rubidium substitution produces no additional hydrogen bonds but reduces the hydrogen bond strength. Conductivity measurements at different cooling rates (0.1-0.2 and 2°C/min) demonstrate that partial Rb⁺ substitution for Cs⁺ hinders the kinetics of the transition from the superionic to the low-temperature, ordered phase.

Cesium dihydrogen phosphate contains a system of strong hydrogen bonds, which give rise to prominent IR absorption bands in the spectral range 1700–2800 cm⁻¹ [20]. The IR spectrum of the polycrystalline CsH_2PO_4 obtained in this study (Fig. 4a, spectrum 1) is very similar to that reported by Marchon and Novak [20]. The cation substitution gives rise to changes in the system of hydrogen bonds (Fig. 4a). In particular, in the spectrum of Cs_{0.97}Rb_{0.03}H₂PO₄ a broad, strong absorption band emerges in the range 3200-3400 cm⁻¹, and the 2650-cm⁻¹ band, arising from the OH stretching mode (δ_{OH}) , is shifted to higher frequencies (~2700 cm⁻¹). In addition, the substitution increases the intensity of the broad bands in the range 1600–2400 cm⁻¹ and shifts them from 2320 and 1680 to 2300 and 1660 cm^{-1} . respectively. In the spectral range of the phosphate group (600–1300 cm⁻¹), we also observe significant changes in the shape and relative intensity of absorption bands (Fig. 4b): the bands at 868, 931, and 1068 cm^{-1} become broader and shift to lower frequencies (to 852, 918, and 1055.4 cm⁻¹, respectively), the band at 1130 cm⁻¹ disappears almost completely, and the spectrum becomes more symmetric. This behavior suggests that partial rubidium substitution for cesium leads to a reduction in hydrogen bond strength and structural disordering of the phosphate tetrahedra.

The DTA curve of CsH₂PO₄ (Fig. 5) shows endothermic peaks at 230, 280, and 345°C, due to the superionic phase transition, the formation of dimers, trimers, or polymers as a result of partial dehydration, and melting, respectively. The dehydration of CsH₂PO₄ begins near $\sim 220^{\circ}$ C, and the total weight loss on heating to 400°C amounts to $\sim 7.8\%$, which corresponds to the removal of two water molecules per formula unit. The temperatures of the endotherms and the total weight loss agree with previous results [3]. The DTA curve of the mixed salt shows a broad endotherm between 138– 175°C, accompanied by a weight loss of 1.2%. This is most likely due to the presence of hydrous phases on the surface of the mixed crystals: the samples with partial Rb substitution for Cs were more hygroscopic. The substitution reduces the enthalpy of the superionic phase transition. In addition, the dehydration endotherm around 280°C shifts to higher temperatures and disappears almost completely. In the temperature range 230–310°C, the dehydration process slows down, and the total weight loss decreases, indicating a rise in the thermal stability of the high-temperature phase.

Indeed, long-term holding of $Cs_{0.97}Rb_{0.03}H_2PO_4$ at 235–240°C in air (1 mol % H₂O) showed that the stability of the cation-substituted high-temperature phase was markedly higher than that of CsH_2PO_4 (Fig. 6). The conductivity of the unsubstituted salt dropped by five



Fig. 4. IR spectra of (1) CsH_2PO_4 and (2) $Cs_{0.97}Rb_{0.03}H_2PO_4$.

orders of magnitude after 90 h, whereas that of the mixed salt dropped by no more than a factor of 1.5 after 170 h. XRD examination showed that the reflections from the low-temperature phase of cesium dihydrogen phosphate remained unchanged.

The question that now arises is what can be responsible for the considerable rise in the thermal stability of the salt in spite of the low degree of cation substitution? There are two possible answers: cation substitution may influence both the thermodynamics of the dehydration process (a reduction in the equilibrium water vapor pressure in the mixed salt) and its kinetics. Both possibilities may be associated with the formation of a more stable, disordered high-temperature phase, with partial amorphization, which would hinder cooperative processes. To shed light on this problem, further investigation of the dehydration process in CsH₂PO₄ and partially substituted analogs is needed.



Fig. 5. TG and DTA data for (1) $Cs_{0.97}Rb_{0.03}H_2PO_4$ and (2) CsH_2PO_4 ; heating in Ar at a rate of 10°C/min.



Fig. 6. Conductivity as a function of time for (1) $Cs_{0.97}Rb_{0.03}H_2PO_4$ and (2) CsH_2PO_4 during isothermal holding in air (235°C, 0.5 mol % H₂O).

CONCLUSIONS

The mixed salt $Cs_{0.97}Rb_{0.03}H_2PO_4$ was synthesized, and its structural, electrical, and thermodynamic properties were studied. The structure of the partially substituted salt $Cs_{0.97}Rb_{0.03}H_2PO_4$ corresponds to a cesium dihydrogen phosphate based solid solution with slightly reduced lattice parameters.

Rubidium substitution for 3 mol % cesium in CsH₂PO₄ increases the low-temperature electrical conductivity of the material by about two orders of magni-

tude but has an insignificant effect on the conductivity of the high-temperature phase.

The low-temperature conductivity of single-crystal samples exhibits significant anisotropy, with $\sigma_a < \sigma_{b\pm c}$. The substitution changes the enthalpy of the superionic phase transition and the enthalpy of fusion. The thermal stability of the high-temperature phase at low humidity increases, suggesting that the mixed salt is a candidate material for medium-temperature fuel cells.

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