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Electrical Conductivity and Thermal Stability of $(1 - x)CsH_2PO_4/xSiP_yO_z$ ($x = 0.2–0.7$) Composites

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Abstract—The physicochemical properties of $(1 - x)CsH_2PO_4/xSiP_yO_z$ ($x = 0.2–0.7$) composites containing fine-particle silicon phosphates as heterogeneous additives have been studied at different humidities. The introduction of silicon phosphates suppresses the superionic phase transition of CsH_2PO_4 and increases the low-temperature conductivity of the materials, which depends significantly on humidity. The CsH_2PO_4–SiP_yO_z materials offer high conductivity (~3×10^{-3} to 10^{-2} S/cm at ~110–230°C) at low water vapor pressures (3 mol % H_2O). Amorphization of the CsH_2PO_4 in the composites markedly changes its thermodynamic properties. The effect of long-term isothermal holding (210°C, 3 mol % H_2O) on the conductivity of the composites has been studied.

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INTRODUCTION

CsH_2PO_4 belongs to the family of proton conductors having a dynamically disordered hydrogen-bond network in a superionic phase [1–4]. In this family, CsH_2PO_4 is one of the best conductors, with a conductivity ($\sigma > 2 \times 10^{-2}$ S/cm at $t \geq 230$°C) comparable to that of melts. In addition, it has a high melting point (t_m ~345°C). Below the phase transition, its conductivity is low ($\sigma < 10^{-6}$ S/cm) [1]. In a dry atmosphere, the superionic phase transition is accompanied by dehydration, and the conductivity of CsH_2PO_4 drops by several orders of magnitude. At an increased water vapor pressure, the salt is thermodynamically stable [5]. However, at high humidity its mechanical properties are not good enough for practical application.

The ability to modify the properties of CsH_2PO_4 and to synthesize proton-conducting electrolytes with enhanced mechanical strength and high conductivity at medium temperatures (up to the phase transition) is not only of scientific interest but also of technological importance because CsH_2PO_4 is a potential membrane material for medium-temperature fuel cells [6].

It is well known that heterogeneous doping of a number of acid salts with fine nonconducting oxide particles offers the possibility of producing, in a wide temperature range, high-conductivity materials with enhanced thermal stability and improved mechanical performance owing to the properties of the oxide matrix [7–9]. The salts forming on the surface of the oxide nanoparticles are defect-rich and differ in properties from bulk materials. At a sufficiently high doping level and large specific surface of the dopant, the volume fraction of the high-conductivity layer is close to unity, and it determines the physicochemical properties of the material. This leads to the development of metastable states, including partial or complete amorphization of the salt [8, 9].

In recent years, considerable research effort has been focused on medium-temperature composites of CsH_2PO_4 and various additives, such as SiO_2 and SiP_2O_7 [7, 10–13]. Otomo et al. [7] used hydrophilic and hydrophobic silicas with different specific surface areas as heterogeneous additives. According to their results, the highest conductivity is offered by systems containing hydrophilic silica in a 30 mol % H_2O + argon atmosphere. Their low-temperature conductivity, however, exceeds that of the salt by an order of magnitude, and their thermal stability is not high enough for practical application. At the same time, recent work [10] has shown that, in $(1 - x)CsH_2PO_4/xSiO_2$ composites containing silica particles with different morphologies and specific surface areas, there is strong surface interaction with the matrix even at $x = 0.4–0.5$, which leads to partial dehydration of the salt, the formation of a mixture of cesium hydrogen and cesium dihydrogen pyrophosphates, and, as a consequence, low conductivity.

Acid centers on the oxide surface were shown to play an important role in the formation of high-conductivity composite systems [10, 11]. Indeed, modifying the silica surface with phosphoric acid enabled the fabrication of composites with a proton conductivity of ~10^{-3} to 10^{-2} S/cm in the range ~130–230°C ($x = 0.3$) at lower water vapor partial pressures in comparison with the pure salt (~4–5 mol % H_2O) [10, 11].

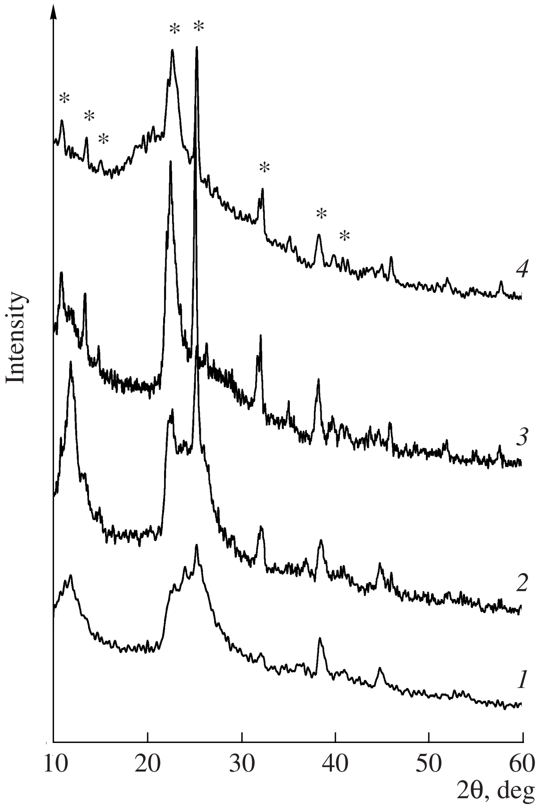

Fig. 1. XRD patterns of the compound obtained by reacting silica with phosphoric acid at (*1*) 200, (*2*) 300, (3) 450, and (*4*) 700°C for (*1*) 3 and (*2–4*) 2 h.

Heating H_3PO_4-treated silica leads to the formation of SiP_2O_7-type matrices. Matsui et al. [12, 13] investigated $(1 - x)CsH_2PO_4/xSiP_2O_7$ composites containing different amounts of the heterogeneous additive (x = 0.33–0.83). They observed a rise in conductivity and disappearance of the phase transition in these systems. At temperatures from 100 to 270°C, the composites had high conductivity (σ_{max} = ~6.6×10^{-2} S/cm (x = 0.3–0.5) at 270°C and 30 mol % H_2O in argon), exceeding that of CsH_2PO_4. According to Matsui et al. [12, 13], the high conductivity of the composites is due to the formation of interfacial $CsH_5(PO_4)_2$ through the reaction between the salt and SiP_2O_7 at temperatures above 220°C [13]. It is, however, known that, under normal conditions, the conductivity of $CsH_5(PO_4)_2$ crystals is well below the above values, no higher than ~10^{-3} S/cm at 135°C. At temperatures above t_m ~ 151°C, $CsH_5(PO_4)_2$ decomposes rather slowly [14]. It seems likely that the formation of $CsH_5(PO_4)_2$ in the composites in question may lead to slow degradation of the electrolyte at high working temperatures (~270°C), in particular at increased humidity. The formation mechanism and state of $CsH_5(PO_4)_2$ in composites and the influence of humidity on their transport properties and thermal stability are still not thoroughly understood.

The purpose of this work was to study the effect of humidity on the physicochemical properties of $(1 - x)CsH_2PO_4/xSiP_yO_z$ (x = 0.2–0.7) composites containing fine-particle silicon phosphates as heterogeneous additives.

EXPERIMENTAL

CsH_2PO_4 was synthesized in a dilute aqueous solution containing cesium carbonate and phosphoric acid in the ratio 1 : 2. The crystals were washed with acetone and then calcined at 150°C for 2 h to remove the residual water. The x-ray diffraction (XRD) data for the synthesized salt were in good agreement with earlier results [3, 15].

The fine-particle component based on silicon phosphate was prepared by heat-treating silica (specific surface S ~98 m^2/g) with phosphoric acid in several steps. A 1 : 1 mixture of SiO_2 and H_3PO_4 was first calcined at 120–220°C for two days and then heat-treated for 2 h at 300, 450, and 700°C. The phase composition of the reaction products was monitored using XRD. The specific surface area of the silicon phosphate was determined by temperature-programmed argon desorption measurements (S = 11.3 m^2/g).

Composites were synthesized from appropriate starting mixtures thoroughly ground in a ceramic mortar and pressed into pellets (d = 0.6 cm, l = 0.15–0.3 cm) at 300–500 MPa. The pellets were calcined in air or in a closed space between 220 and 250°C at a controlled content of water vapor generated by bubbling air through a water layer. The density of the $(1 - x)CsH_2PO_4/xSiP_yO_z$ samples with x = 0.2–0.67 was 2.5–2.8 g/cm^3. In evaluating the mole fraction, the molecular weight of the forming SiP_yO_z mixture was taken to be 192 (SiP_2O_7).

The ac conductivity of samples sandwiched between silver or platinum electrodes was measured with an Instek LCR-821 precision LCR meter and Elins Z-350 impedance meter at frequencies from 5 Hz to 500 kHz. The measurements were made during cooling at a rate of 2–3°C/min at temperatures from 20 to 250°C and different humidities.

XRD patterns were collected on a DRON-3 powder diffractometer ($CuK_{\alpha1}$ radiation, continuous scan rate of 2°/min) at room temperature. The materials were also characterized by differential scanning calorimetry (DSC) in argon between 20 and 400°C at a heating rate of 10°C/min, using a Netzsch Jupiter STA 449C high-resolution system.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the compounds obtained by reacting silica with phosphoric acid at dif-

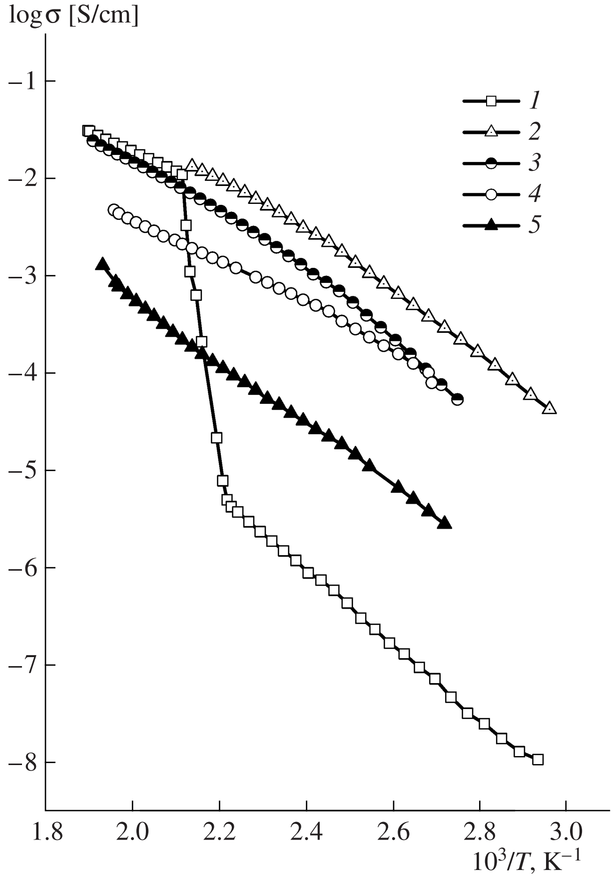

Fig. 2. Arrhenius plots of conductivity for (*1*) CsH_2PO_4 and (*2–5*) (1 – *x*)$CsH_2PO_4/xSiP_yO_z$ composites: *x* = (*2*) 0.2, (*3*) 0.33, (*4*) 0.5, (*5*) 0.67; cooling in air at 2°C/min.

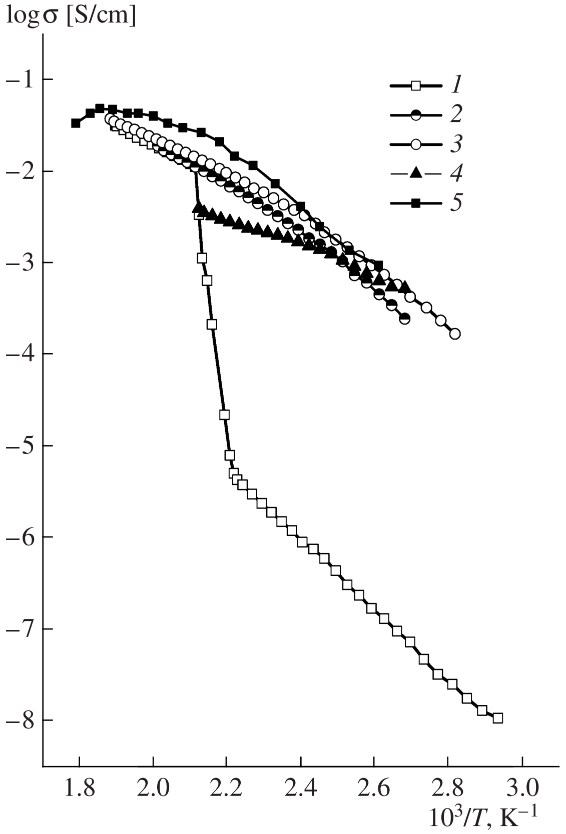

Fig. 3. Arrhenius plots of conductivity for (1 – *x*)$CsH_2PO_4/xSiP_yO_z$ composites with *x* = (*1*) 0, (*2*) 0.33, (*3*) 0.5, and (*4*, *5*) 0.67; (*5*) data from [13]; cooling rate, 2°C/min; 3 mol % water vapor in air.

ferent temperatures. It can be seen that raising the temperature to 700°C changes the phase composition of the mixture and improves its crystallinity. Note that, at lower reaction temperatures (300°C), the XRD pattern is more similar to that of SiP_2O_7 [16]. At higher temperatures (700°C), the phase composition of the matrix corresponds to a mixture of silicon phosphates ($Si_3(PO_4)_4$ and $Si_5P_6O_{25}$) and SiO_2 (cristobalite) [16–18] (the new reflections in Fig. 1 are marked by asterisks). During storage, the matrix structure experiences partial amorphization, probably because of the adsorption of atmospheric moisture. The transport properties of the composites with this matrix were studied at different humidities.

Figure 2 shows the Arrhenius plots of conductivity for (1 – *x*)$CsH_2PO_4/xSiP_yO_z$ (*x* = 0.2–0.67) composites and the parent salt at a relative air humidity of 30% (0.6 mol % H_2O). The high-temperature conductivity of CsH_2PO_4 reaches $\sigma \sim 3 \times 10^{-2}$ S/cm, with an activation energy $E_a \sim 0.4$ eV. The transition to the low-temperature phase ($E_a \sim 0.8$ eV) is accompanied by a drop in conductivity by more than three orders of magnitude, in agreement with earlier results [1, 5, 10]. The addition of silicon phosphates (*x* = 0.2) increases the proton conductivity in the temperature range 20–230°C by three orders of magnitude and suppresses the phase transition. The high-temperature conductivity of the *x* = 0.33 composite is close to that of the parent salt. Increasing the additive content to *x* = 0.5 reduces the high-temperature conductivity by a factor of 3 and the low-temperature conductivity by about a factor of 0.25 in comparison with *x* = 0.33, but the conductivity remains higher than that of the parent salt. Increasing *x* to 0.67 reduces the conductivity of the composite by one order of magnitude.

Measurements in the presence of water vapor (Fig. 3) demonstrate that the conductivity of the composites depends significantly on humidity. At 3 mol % water vapor, the conductivity of the composites increases significantly with temperature up to 230°C and exceeds the σ of the parent salt by three to four orders of magnitude. The high-temperature conductivity is close to that of cesium dihydrogen phosphate. The conductivity of the composites richer in pyrophosphates (*x* = 0.67) is more sensitive to humidity. Systems differing in composition become comparable in conductivity and its temperature variation: the composites with *x* = 0.3 and 0.5 are close

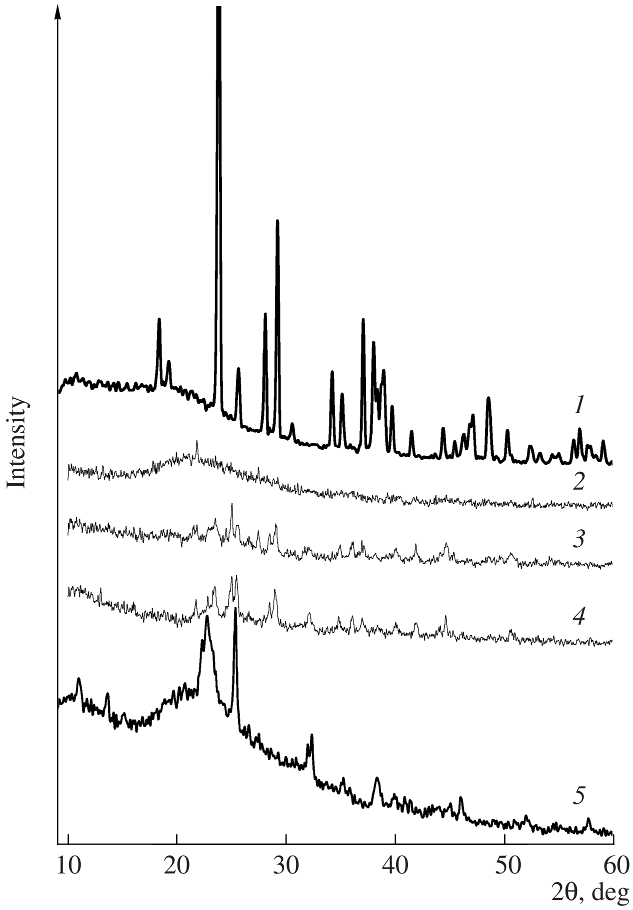

Fig. 4. XRD patterns of (*1*) CsH_2PO_4, (*2–4*) $(1 - x)$ $CsH_2PO_4/xSiP_yO_z$ composites, and (*5*) SiP_yO_z: x = (*2*) 0.33, (*3*) 0.5, (*4*) 0.67.

in conductivity and activation energy. The conductivity as a function of temperature shows non-Arrhenius behavior, and the activation energy gradually increases with decreasing temperature: from 0.4 (0.38) eV at high temperatures to 0.56 eV at low temperatures (x = 0.3 and 0.5, respectively). The most likely reason for this behavior of the system is that conduction occurs predominantly along the interfaces between the salt and heterogeneous component, and that the proton transport involves the acid centers produced by water adsorption on the grain boundaries of the silicon phosphates and on the interfaces with the salt.

For comparison, Figure 3 presents the conductivity data for CsH_2PO_4/SiP_2O_7 in argon containing 30 mol % water vapor [13]. The conductivity of our composites at 3 mol % water vapor is seen to be slightly lower than but comparable to that at high humidity. This result is of practical importance because the mechanical properties of the systems under consideration are considerably more suitable for technological applications.

The XRD patterns of our composites (Fig. 4) attest to the formation of an amorphous phase at $x = 0.33$. At higher additive contents, the XRD patterns show reflections characteristic of silicon phosphates with a higher degree of crystallinity. The reflections from unreacted materials indicate that no reaction occurs between the salt and matrix under the conditions of this study; $CsH_5(PO_4)_2$ was not detected.

Figure 5 presents the DSC data for the composites, CsH_2PO_4, and the silicon phosphate matrix. The curve for CsH_2PO_4 shows endothermic peaks at 230, 275, and 318°C, corresponding to the superionic phase transition and the formation of di-, tri, or polymers upon partial dehydration, and the melting endotherm at 345°C. The total weight loss on heating to 400°C is 7.6%, which is close to the theoretical one (removal of one water molecule per formula unit). In the DSC curves of the composites with x = 0.33 and 0.5, the endothermic peaks due to the phase transition are almost indiscernible, which is associated with the amorphization of the salt in the composites and correlates with the above XRD data. The curve of the $x = 0.67$ composite shows a weak endothermic peak at 131.3°C, presumably due to the presence of a small amount of $CsH_5(PO_4)_2$. The silicon phosphate matrix shows major weight changes at temperatures below ~210°C. The present DSC and TG data attest to significant changes in the thermodynamic properties of CsH_2PO_4, amorphization of the salt in the composites, and a slightly higher thermal stability of the composites in comparison with the parent salt and matrix at medium temperatures. The composites with x = 0.3 and 0.5 are more thermally stable than the x = 0.67 material.

It is of interest to assess how the thermal stability of the composites and their conductivity at elevated temperatures respond to long-term exposures under different conditions. Heat treatment of the $(1 - x)CsH_2PO_4/xSiP_yO_z$ (x = 0.3) composite at 210°C (3 mol % H_2O in air) for 6 h was found to have no effect on its conductivity and to produce little or no weight change, as determined by TG in flowing argon.

Thus, detailed studies of the CsH_2PO_4-based composites demonstrate that their physicochemical properties depend significantly on the nature of the heterogeneous additive, the acidic properties of its surface, and air humidity. The high conductivity of the CsH_2PO_4–SiP_yO_z composites is due to the presence of water adsorbed on the surface of the silicon phosphates. Systems of this type have high conductivity only after exposure to a humid atmosphere.

The mechanical properties of the composites depend significantly on their composites and air humidity. For example, at 30 mol % H_2O in air, composites based on acid salts are easy to deform, whereas at 3 mol % H_2O such composites retain their strength. Note that the x = 0.67 composite has poor performance even at 3 mol % H_2O. Therefore, the compositions of composites based

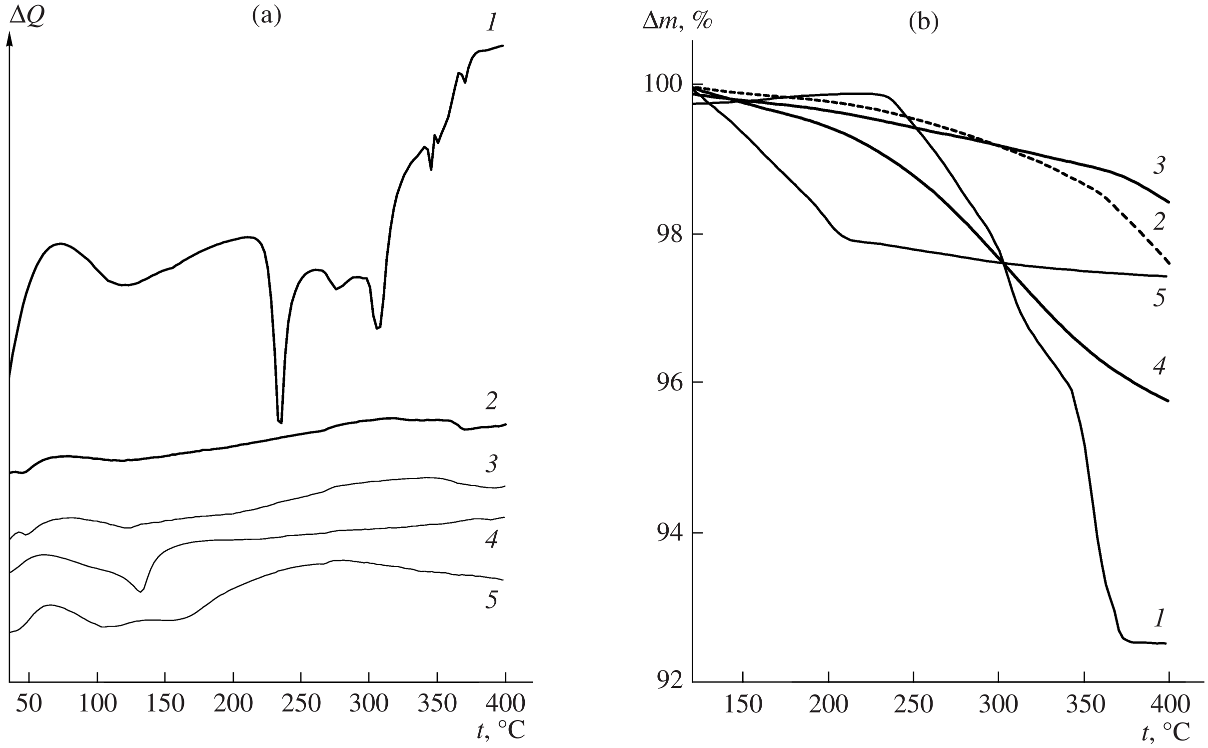

Fig. 5. (a) DSC and (b) TG data for (*1*) CsH_2PO_4, (*2–4*) $(1 - x)CsH_2PO_4/xSiP_yO_z$ composites, and (*5*) SiP_yO_z: x = (*2*) 0.33, (*3*) 0.5, (*4*) 0.67.

on cesium dihydrogen phosphate should be optimized so that their high proton conductivity be combined with good mechanical properties. It seems likely that, with these two factors, the $(1 - x)CsH_2PO_4/xSiP_yO_z$ composites with $x = 0.3–0.5$ are optimal.

CONCLUSIONS

We synthesized $(1 - x)CsH_2PO_4/xSiP_yO_z$ composites and investigated their physicochemical properties in air containing 0.6–3 mol % water vapor.

The results demonstrate that the chemical nature of the heterogeneous component has a significant effect on the electrical transport in the composites. Composites based on silicon phosphates of different compositions have high conductivity (~3×10^{-3} to 10^{-2} S/cm at ~110–230°C) and thermal stability (210°C) even at low water vapor partial pressures, which is of importance for improving their mechanical performance.

The thermodynamic and structural properties of the CsH_2PO_4 in the composites studied differ significantly from those of the individual salt because of the structural disordering and amorphization of the salt, but there is no chemical interaction between the salt and matrix.

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