The effect of silicon dioxide on the structural, thermal and transport properties of an organic ionic plastic crystal \((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\)

Ivan Stebnitskii ab*, Yulia Mateyshina ab*, Nikolai Uvarov ab*

a: Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia
b: Department of Natural Sciences, Novosibirsk State University, Novosibirsk 630090, Russia
* Corresponding author: i.stebnitskii@g.nsu.ru

This paper belongs to a Regular Issue.

Abstract

Composite solid electrolytes based on an organic ionic plastic crystal \((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\) with highly dispersed SiO\(_2\) with specific surface area of \(S_s = 324\pm10\) m\(^2\)/g have been studied for the first time. By methods of X-ray diffraction and differential scanning calorimetry, it was found that the introduction of SiO\(_2\) leads to amorphization of the salt. An unusual size effect was observed in the composites: the temperature of the polymorphic transition of the salt shifted from 67 °C to 60 °C, while the melting point did not change. The 0.15\((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\)–0.85SiO\(_2\) composite was found to possess the highest electrical conductivity (\(\sigma = 2\times10^{-5}\) S/cm at 150 °C), which is 1.5 orders of magnitude higher than that of the initial salt. Modelling of the concentration dependences of the electrical conductivity of composites using the mixing equation showed that the reason for the increase in electrical conductivity is the formation of an amorphous layer of salt, the electrical conductivity of which is 3 orders of magnitude higher than that of the crystalline phase \((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\). The obtained results can be used for the design of high-performance composites based on organic ionic plastic crystals for application in electrochemical devices.

Key findings

- Silicon dioxide with a high specific surface area leads to the amorphization of \((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\).
- The best conductivity of 2\(\times10^{-5}\) S/cm at 150 °C was observed for 0.15\((n\text{-C}_4\text{H}_9)_4\text{NBF}_4\)–0.85SiO\(_2\) composite.
- The increase in conductivity is caused by the formation of a highly conductive amorphous phase of the salt, the conductivity of which is 3 orders of magnitude higher than that of the crystalline salt.

© 2024, the Authors. This article is published in open access under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

For the development of electrochemical energy storage devices, researchers around the world are increasingly focusing on solid electrolytes as an alternative to traditional liquid electrolytes [1–3]. The use of such electrolytes will improve the mechanical properties and safety of the devices as well as simplify the assembly technology of electrochemical energy storage devices [4–6]. However, many solid electrolytes are characterized by poor contact with electrodes, are unstable in air and have low ionic conductivity compared to liquid electrolytes [7, 8]. In this regard, the search for promising solid electrolytes and the improvement of the physico-chemical properties of already known ones are actively carried out.

Organic ionic plastic crystals (OIPCs) represent an interesting class of materials including salts of tetraalkylammonium [9], pyrroldinium [10, 11], imidazolium [12], tetraalkylphosphonium [13], morpholinium [14] with a wide variety of anions, including quite non-trivial ones, such as bis(trifluoromethanesulfonylimide) (TFSI) [15] and carbamoylcyano(nitroso)methanide [16]. A common feature of OIPCs is high thermal and electrochemical stability, plasticity, and rather high ionic conductivity due to local orientational or rotational disorder of ions or...
their parts [17,18]. For example, diethyl(methyl)(isobutyl)phosphonium hexafluorophosphate provides an electrical conductivity of $10^{-3}$ S/cm at 120 °C in the solid phase at the highest temperature [19]. However, in most cases, OIPCs exhibit rather low electrical conductivity, $\sigma \approx 10^{-5} - 10^{-6}$ S/cm, near the melting point [20,21].

A promising way to improve the transport properties of these compounds is to create composites with inert additives. By choosing appropriate heterogeneous additive, it is possible to control the physico-chemical properties of composites, in particular, to improve transport properties. Previously, heterogeneous doping has been extensively studied for inorganic systems, and the main regularities have been revealed. A number of works have demonstrated that the introduction of oxides leads to a significant increase in electrical conductivity by several orders of magnitude [22–24].

It is known that the electrical conductivity of composites increases with decreasing oxide particle size (which is approximately equivalent to an increase in specific surface area) [25]. In early studies it was also found that the absolute value of conductivity is influenced by the chemical nature of the oxide. Thus, in most cases, the best conductivity values were achieved when using basic oxides as additives, in particular, in LiClO₄ – A composites (A = MgO [26], Al₂O₃ [27], SiO₂ [27]), the maximum conductivity was observed when MgO was used. However, in some systems, on the contrary, the best effect was observed when acidic oxides were used: for example, in the CsNO₃ – A systems (A = MgO, Al₂O₃, SnO₂ [28]), the maximum conductivity values were observed when acidic oxide was used as an additive. Thus, it is rather unclear how the chemical nature of the oxide affects the transport properties in a particular class of substances.

Previously, composites based on OIPCs were studied in different scientific groups [29–31]. It has been shown that the introduction of nanosized inert additives of different chemical nature leads to a significant increase in the conductivity of salts. However, at the moment there are almost no systematic studies of composites based on OIPCs.

Earlier we have studied the composites based on one of the OIPC representatives – tetrabutylammonium tetrafluoroborate – with various nanosized inert additives (MgO [32], Al₂O₃ [29], nanodiamonds [33]), but composites with acidic oxides remain unexplored. In this work, we investigated the effect of the addition of acidic oxide SiO₂, characterized by high specific surface area, on the structural, thermal and transport properties of (n-C₄H₉)₄NBF₄ in comparison with previously used heterogeneous additives.

2. Materials and methods

2.1. Materials

Tetra-n-butylammonium tetrafluoroborate (n-C₄H₉)₄NBF₄ (hereafter Bu₄NBF₄) was synthesized by an exchange reaction between (n-C₄H₉)₄NBr (Sigma Aldrich, reagent grade) and an aqueous solution of HBF₄ (Sigma Aldrich, 48 mas.%).

The resulting white precipitate was filtered, then recrystallized from an aqueous-alcohol solution and dried at 120 °C. As a silicon dioxide SiO₂ additive, a mesoporous silica gel of the KSM grade (JSC "SKTB Katalizator", Russia, 99% pure, specific surface area $S_{BA} = 324 \pm 10 \text{ m}^2/\text{g}$, specific pore volume $0.193 \text{ cm}^3/\text{g}$, average pore size 2.392 nm) was used. Before use, SiO₂ was calcined at 500 °C for several hours to remove adsorbed water molecules. Composites (1-x) Bu₄NBF₄-xSiO₂ (0 ≤ x ≤ 1, x – molar fraction) were prepared by mixing stoichiometric quantities of initial components with the addition of a small amount of ethanol in an agate mortar. The resulting mixtures were then heated in a drying oven at 150 °C for one hour to remove any remaining solvent. In order to ensure a uniform distribution of particles throughout the composites, this process was repeated three times.

2.2. Methods

To investigate the phase composition of the composites, the X-ray diffraction was carried out on D8 Advance diffractometer (Bruker, Germany) using Cu Kα radiation, with Kβ filter and one-dimensional Lynx-Eye detector over the angle range of 5°<θ<90° with the angle step of $\Delta\theta = 0.0195^\circ$. Thermal properties were studied using a differential scanning calorimeter DSC-500 (Sam STU, Russia). For experiments, 5–10 mg of the powder sample was placed in a closed aluminum crucible and heated from 20 to 200 °C in an argon atmosphere at a rate of 10 °C/min. IR absorption spectra were measured on Vector 22 by the attenuated total reflectance (ATR) method. The transport properties were studied by impendence spectroscopy in a two-electrode mode on a Hewlett Packard 4284 A Precision LCR Meter (Hewlett-Packard, Japan) in a low-vacuum (5·10⁻² Torr) in the frequency range 30 Hz – 1 MHz. For measurements, the sample powders were compacted into pellets with a diameter of 6.2–6.3 mm and a thickness of 0.5–1.5 mm with silver powder electrodes at a pressure of 100 MPa. The resistance of the samples, $R$, at each temperature was calculated from the analysis of the Nyquist complex impedance plots $Z' = Z''$ by fitting the theoretical values calculated for the model equivalent circuits to the experimental ones using the Zview software (version 3.1, Scribner Associates, Inc., USA). The total conductivity was calculated using the ratio $\sigma = h/(R-S)$, where $h$ and $S$ are the thickness and electrode area of the pellet, respectively.

3. Results and Discussion

3.1. X-ray diffraction studies

The phase composition of (1-x) Bu₄NBF₄-xSiO₂ composites was studied by X-ray diffraction; the results are shown in Figure 1. In the diffraction patterns, only the reflections of the stable at room temperature low-temperature Bu₄NBF₄ phase (space group P2₁/c, according to our previous studies [33]) are present. Reflections of SiO₂ were not observed due to its amorphous structure.

DOI: 10.15826/chimtech.2024.11.3.07
Figure 1 X-ray diffraction patterns of composites (1-x) Bu₄NBF₄–xSiO₂, recorded at ambient temperature.

With an increase in the molar fraction of SiO₂, a sharp decrease in the intensity of salt reflections was observed: for example, at x = 0.9 the intensity of the peak observed at 2θ = 9.12° decreases by 7 times, while the salt content in the composite was 42.8 vol.%. This effect can be explained by a partial amorphization of the salt in the composite.

3.2. Thermal properties
According to the literature data, the initial Bu₄NBF₄ is characterized by the presence of several phase transitions: polymorphic transition at 62–67 °C and melting at 159–161 °C (the temperature variation is due to different heating rates) [9, 13]. In addition, after fast cooling of the salt from the melt to room temperature, a metastable phase forms, which undergoes a phase transition to a high-temperature phase at 41 °C [33].

The thermal properties of the composites were studied by differential scanning calorimetry (DSC). In the DSC curves obtained upon heating, two phase transitions are observed, associated with the polymorphic transition: polymorphic transition (60–62 °C) and melting of Bu₄NBF₄ (163–164 °C) (Figure 2), respectively. The decrease of the polymorphic transition temperature from 67 °C to 60–62 °C is noteworthy. Most probably, this effect is due to the size effect as in earlier studies [34]. At the same time, it is quite unusual that along with the shift in the polymorphic transition temperature, there is no size effect during salt melting.

With increasing molar fraction of SiO₂ in composites, a sharp decrease in enthalpy of phase transitions of salts is observed. At high concentrations of SiO₂, phase transitions completely disappear. Previously, a similar effect was observed in other composites of the "ionic salt-oxide" type, such as LiClO₄ – MgO [26], RbNO₃ – Al₂O₃ [35], (n-C₄H₉)₃CH₃NBF₄ – nanodiamonds [36]. A similar phenomenon is associated with the salt amorphization near the salt-oxide phase contact.

As the amorphization of the salt occurs in the interfaces, the highest effect will be achieved at the maximal number of salt/additive contacts. Heterogeneous additives may differ in molar mass and density; therefore, in order to correct the effect of different additives, it is necessary to consider the relative change in enthalpy, expressed in J/cm³, and the volume fraction of the additive. For conversion of the molar fraction of SiO₂ x into the volume fraction f the following equation may be used:

\[ f = \frac{x}{x + (1-x) \cdot \frac{M_1 \cdot \rho_1}{M_2 \cdot \rho_2}} \]  

where M₁ and M₂ are the molar mass of salt and SiO₂, respectively, \( \rho_1 = 1.0 \text{ g/cm}^3 \) and \( \rho_2 = 2.2 \text{ g/cm}^3 \) are the density of salt and SiO₂. The experimental values of the relative enthalpy of melting differ significantly from those in the case of a random mixture of components without interfacial interaction (Figure 3). It is worth noting that although SiO₂ has an effect on the amorphization of (n-C₄H₉)₃NBF₄, the effect of other additives, such as nanodiamonds [31], is more pronounced.

Figure 2 DSC curves for (1-x) Bu₄NBF₄ – xSiO₂ composites on first (a) and second (b) heating.
Figure 3 Experimental values of relative melting enthalpy of Bu$_4$NBF$_4$ in (1-f) Bu$_4$NBF$_4$ - fA (where A = SiO$_2$ [this work] and nanodiamonds [33]) in comparison with the dependence expected for random mixture of components (line). The upper axis shows the molar fractions of SiO$_2$ in (1-x) Bu$_4$NBF$_4$-x SiO$_2$ composites.

3.3. IR spectroscopy study

The IR spectroscopy method was used to study the effect of SiO$_2$ on the local environment of atoms in Bu$_4$NBF$_4$. Vibrations in the BF$_4^-$ ion were used as a probe to determine the processes occurring in the system (1-x)Bu$_4$NBF$_4$-xSiO$_2$. According to the literature data, the BF$_4^-$ ion is characterized by four vibrations: totally symmetric stretching $\nu_1(A_1) \approx 770$ cm$^{-1}$, deformation $\nu_2(E) \approx 360$ cm$^{-1}$, antisymmetric stretching $\nu_3(F_2) \approx 1100$ cm$^{-1}$ and deformation vibrations $\nu_4(F_1) \approx 520$ cm$^{-1}$ [29, 37]. Only the last two are allowed in the IR spectra.

Figure 4 shows the IR spectra of (1-x)Bu$_4$NBF$_4$-xSiO$_2$. The resulting spectra are the sum of the spectra of individual components. With an increase in the proportion of SiO$_2$, the intensities of all bands decrease slightly. It was previously shown that the disordering of Bu$_4$NBF$_4$ leads to a decrease in the symmetry of the BF$_4^-$ anion, which leads to the appearance of the forbidden mode $\nu_1(A_1)$ [29]. In pure Bu$_4$NBF$_4$, a low-intensity peak is observed at 800 cm$^{-1}$, which can be attributed to the forbidden mode $\nu_1(A_1)$, while with increasing x a shift of this peak from 800 cm$^{-1}$ to 789 cm$^{-1}$ is observed. Thus, during the transition from pure salt to composite, the structure of Bu$_4$NBF$_4$ becomes disordered.

3.4. Transport properties

The transport properties of the composites were studied by impedance spectroscopy. At each temperature point, an impedance hodograph was recorded, the typical form of which in Nyquist coordinates is shown in Figure 5. The hodographs were described by an equivalent electrical circuit consisting of three impedances connected in series: the bulk impedance $Z_{\text{bulk}}$, which includes a parallel-connected resistance $R_{\text{bulk}}$ and a constant-phase element $CPE_{\text{bulk}}$, the impedance $Z_{\text{surface}}$, consisting of a parallel-connected resistance $R_{\text{surface}}$ and a constant-phase element $CPE_{\text{surf}}$, as well as an electrode impedance described by a constant-phase element $CPE_{\text{el}}$. The impedance $Z_{\text{bulk}}$ describes the resistance of the bulk phase of the salt; the impedance $Z_{\text{surface}}$ describes the resistance of the salt located in the SiO$_2$ pores.

Figure 6a shows the temperature dependence of the conductivity of (1-x) Bu$_4$NBF$_4$-xSiO$_2$ composites. The conductivity of composites increased monotonously with temperature and was reproduced in heating-cooling cycles, which indicates the absence of influence of water adsorbed on the oxide surface on the conductivity values.

Figure 5 Typical complex impedance plots: 0.5Bu$_4$NBF$_4$-0.5 SiO$_2$ at 140 °C (a); 0.15Bu$_4$NBF$_4$-0.85SiO$_2$ at 123 °C, 137 °C and 151 °C (b); (1-x) Bu$_4$NBF$_4$-xSiO$_2$ (x = 0.5, 0.7, 0.85) (c). The inset in Figure 5a shows the equivalent electrical circuit used for the simulation.
The presented dependences obey the Arrhenius equation \( \sigma T = A \exp(-E_b/RT) \) (\( A \) is the pre-exponential factor, \( E_b \) is the activation energy of conductivity) throughout the studied range of \( \text{SiO}_2 \) concentrations. The introduction of \( \text{SiO}_2 \) leads to a slight decrease in the activation energy of the conductivity, while the \( E_b \) values within the measurement accuracy are the same for all compositions (Table 1). Compared to a pure BuNBF\(_4\), in the composites the values of the pre-exponential factor decrease and then increase with increasing \( \text{SiO}_2 \) concentration (Table 1).

It is known that in composites of the «ionic salt – oxide» type the excess conductivity is caused by ionic transport along interfaces. The maximum electrical conductivity is exhibited at the highest number of interfaces, which is usually observed at a volume ratio of the components close to 1:1. In this regard, it is more correct to analyze the dependences of conductivity on the volume fraction of the oxide.

Figure 6b shows the concentration dependence of the composites (1-x) BuNBF\(_4\)-\( x \)SiO\(_2\) on the oxide volume fraction \( f \) (bottom) and mole fraction \( x \) (top). The conductivity of the composites may be qualitatively described by percolation model with two percolation thresholds. At low fractions of the additive the total conductivity is provided mainly by the bulk contribution of BuNBF\(_4\). At the first percolation threshold the contribution of the interface conductivity increases up to maximum values where this contribution dominates. With further increase in the oxide additive content near the second percolation, conductivity decreases due to the destruction of the interconnected network of highly conductive interface regions. Actually, percolation thresholds may be strongly diffused, hindering the application of the percolation model.

The percolation-like conductivity behavior of such composites can be described within the framework of the mixing model proposed by Uvarov [38]. Within the framework of this model, it is assumed that the experimental values of the electrical conductivity of the composites are described by three contributions: the contribution of the crystalline phase of the salt \( \sigma \text{bulk} \), silicon oxide \( \sigma_s \) and the highly conductive regions of the salt \( \sigma_f \) (equation 2):

\[
\sigma_{\text{mix}}(f) = \sigma_{\text{bulk}}(1-f) + \sigma_s(a_f) \cdot f + \sigma_f(a_f) \cdot f
\]

where \( f \) and \( f_s \) are the volume fraction of \( \text{SiO}_2 \) and the interface amorphous phase of the salt, respectively. The \( f_s \) values were calculated from the dependence of the relative enthalpy of melting on \( f \) according to equation 3:

\[
f_s = \beta \cdot \frac{\lambda}{L} \cdot f \cdot (1-f), \quad (f_s \leq 1-f),
\]

where \( \beta \) is the geometric factor, \( \lambda \) is the thickness of the amorphous interface layer, and \( L \) is the average size of \( \text{SiO}_2 \) crystallites. The coefficient \( a(f) \) takes into account the morphology of the composite. In the simplest case, \( a(f) \) is approximated by a linear function:

\[
a(f) = a_1 \cdot (1-f) + a_2 \cdot f
\]

where \( a_1 \) and \( a_2 \) are the coefficients determined by the morphology of the composite in limiting cases.

As seen from Figure 6b, the mixing equation fairly describes the experimental data. The modelling results confirm the qualitative explanation of the variation in conductivity with the composition described above.

**Table 1** Experimental conductivity parameters for composites (1-x) BuNBF\(_4\)-\( x \)SiO\(_2\).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \text{SiO}_2 )</th>
<th>( E_a ) (eV)</th>
<th>( \log A ) (S-K\text{-cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.95±0.01</td>
<td>8.04±0.1</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.82±0.01</td>
<td>6.92±0.03</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.82±0.01</td>
<td>7.14±0.03</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.80±0.01</td>
<td>7.23±0.03</td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>0.80±0.01</td>
<td>7.43±0.03</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.81±0.01</td>
<td>7.41±0.03</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 6** Dependences of the conductivity of composites (1-x) BuNBF\(_4\)-\( x \)SiO\(_2\) from: the reciprocal temperature (a); the volume fraction \( f \) and molar fraction \( x \) of \( \text{SiO}_2 \) at temperatures of 100, 120 and 140 °C (b).
Estimation shows that the electrical conductivity of the amorphous phase is 3 orders of magnitude greater than that for the crystalline phase of the salt (Table 2).

The fraction of amorphous phase of the salt increases with $x$ or $f$, so at high concentrations of SiO$_2$ the contribution of the interface conductivity of the salt becomes dominant. The maximum conductivity value of $2\times10^{-7}$ S/cm is observed at 150 °C for the composition $x = 0.85$, which corresponds to the volume fraction of the additive $f = 32\%$. Previously, a similar effect of increased conductivity was observed in other the ionic salt-type composite electrolytes [26, 35]. The conductivity increase is attributed to the contribution of the highly-conducting amorphous interface phase of the salt formed as a result of the interface interaction between SiO$_2$ and Bu$_4$NBF$_4$.

Figure 7 shows a comparison of temperature dependences of conductivity for Bu$_4$NBF$_4$-based composites with various oxides. The conductivity of Bu$_4$NBF$_4$-oxide composites strongly depends on both the specific surface area, concentration of the dopant and the chemical nature of the heterogeneous additive. For the comparison only oxide additives with specific surface area of 200–300 m$^2$/g and the compositions corresponding to the highest conductivity value were selected.

It is seen that the introduction of any heterogeneous oxide additive into the dielectric salt Bu$_4$NBF$_4$ leads to an increase in its conductivity by 1–3 orders of magnitude over the entire temperature range. There is a clear tendency: conductivity increases with basicity of the oxide additive in a series SiO$_2$–Al$_2$O$_3$–MgO.

Table 2. Conductivity parameters obtained from the mixing equation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>100 °C</th>
<th>120 °C</th>
<th>140 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{bulk}}$ (S/cm)</td>
<td>$3.5\times10^{-8}$</td>
<td>$1.6\times10^{-7}$</td>
<td>$5.9\times10^{-7}$</td>
</tr>
<tr>
<td>$\sigma$ (S/cm)</td>
<td>$3.8\times10^{-5}$</td>
<td>$1.2\times10^{-4}$</td>
<td>$3.5\times10^{-4}$</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>0.29±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.09±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta\lambda/L$</td>
<td>1.6±0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Limitations

One of the limitations is the difficulty of indexing salt reflections in the X-ray diffraction patterns. At the moment, there are no crystallographic data on the ($n$-C$_{5}$H$_{11}$)$_{3}$NBF$_{4}$ phase that is stable at room temperature in the databases. Structural analysis of the crystals of this salt is complicated by a number of factors: the low quality of the grown single crystals, disordered structure and the presence of only light atoms in the substance. In this regard, it is not possible to decipher the structure of ($n$-C$_{5}$H$_{11}$)$_{3}$NBF$_{4}$ from single-crystal X-ray diffraction data, and as a consequence, it is not possible to index the reflections. It is known that in some cases phase indexing can be carried out using powder X-ray diffraction data, but correct analysis requires the presence of well-separated reflections with high intensity. In our case, a large number of difficult to separate reflections with low intensity are observed. Thus, X-ray powder diffraction cannot help in phase indexing either.

Another limitation is the mechanism of interaction of the components of the system, which leads to the formation of a highly conductive composite, remains unclear.

5. Conclusions

In this work, the properties of the composites based on ($n$-C$_{5}$H$_{11}$)$_{3}$NBF$_{4}$ and highly dispersed SiO$_2$ ($S_p = 3244\pm10$ m$^2$/g) were studied for the first time. The addition of SiO$_2$ does not lead to the formation of new bulk phases, while it contributes to the amorphization of the salt. The conductivity of the composites under study increases with the SiO$_2$ concentration, reaching a maximum of 0.02 mS/cm at 150 °C for the composite $0.15(n$-C$_{5}$H$_{11}$)$_{3}$NBF$_{4}$–0.85SiO$_2$, which is 1.5 orders of magnitude higher than for pure salt. The concentration dependences of conductivity are well described using the general mixing equation. Modelling using the mixing equation shows that the interface amorphous phase of the salt gives the main contribution to the overall conductivity. The conductivity of this phase is 3 orders of magnitude higher than that in the bulk crystalline phase of ($n$-C$_{5}$H$_{11}$)$_{3}$NBF$_{4}$. It has also been shown that the addition of SiO$_2$ causes much less conductivity enhancement effect compared to the nanocrystalline alumina or magnesia. Nevertheless, the results obtained may be useful for further development of highly conductive solid electrolytes based on organic ionic plastic crystals.

- **Supplementary materials**

No supplementary materials are available.

**Funding**

This work was supported by the Russian Science Foundation (project 20-13-00302), [https://www.rscf.ru/en](https://www.rscf.ru/en).
Acknowledgments

None.

Author contributions

Conceptualization: I.S., Y.M., N.U. 
Data curation: Y.M. 
Formal analysis: Y.M. 
Funding acquisition: N.U. 
Investigation: I.S. 
Methodology: I.S., Y.M. 
Project administration: N.U. 
Resources: N.U. 
Supervision: N.U. 
Validation: Y.M., N.U. 
Visualization: I.S. 
Writing - original draft: I.S. 
Writing - review & editing: Y.M., N.U.

Conflict of interest

The authors declare no conflict of interest.

Additional information

Author IDs:
Ivan Stebnitskii, Scopus ID 58488613400; Yulia Mateyshina, Scopus ID 6506782050; Nikolai Uvarov, Scopus ID 700694152.

Websites:

References


DOI: 10.15826/chimtech.2024.11.3.07