Transport Properties of Aliovalent Substitution Solid Solutions of the System (1-x)PbF₂-xYF₃-SnF₂

Y V Pogorenko¹, R M Pshenychnyi¹, V I Lutsyk²,³ and A O Omel’chuk¹

¹Vernadskii Institute of General & Inorganic Chemistry of the Ukrainian NAS, 03680 Kyiv, Ukraine
²Institute of Physical Materials Science, SB RAS, 670047 Ulan-Ude, Russia
³Chemical Department, Buryat State University, 670000 Ulan-Ude, Russia

Abstract. In polycrystalline solid solution of Pb₁₋ₓYₓSnF₄⁺₄ (0 < x ≤ 0.17) with a structure of β-PbSnF₄ in temperature 293 – 523 K the fluoride anions occupy three structurally nonequivalent positions which differ in the local environment and mobility. The concentration of mobility fluoride anions at 300 K is almost independent of the content of heterovalent substituent on YF₃ and at temperatures above 430 K increases with grow concentration of the YF₃. Fluoride ion exchange between nonequivalent subsystems increases with raising temperature, which causes an increase in conductivity. The electronic component of conductivity the synthesized samples by 2 orders of magnitude lower than the ion.

Keywords: solid fluoride-conducting electrolytes, heterovalent substitution solid solutions, lead, tin, and yttrium fluorides, conductivity, transport numbers

1. Introduction

The researchers are completed at recent time have been shown that a compound with a high unipolar conductivity that provided by the fluoride ions are interested for the development of new electrolyte and electrode materials of electrochemical devices for various purposes such as chemical power sources, sensors, analyzers, ion-selective electrodes, etc. [1, 2]. For many of them characterized by a high ionic conductivity (10⁻¹ – 10⁻¹⁴ S cm⁻¹) and a small electronic component.

Among currently known solid electrolytes fluoride conductive particular interest are solid solutions based on PbF₂, SnF₂, LnF₃ (where Ln is rare-earth elements). In particular the attractive transport properties, in particular, has lead (II) tetrafluorostannate(II), which has conductivity even at room temperature is approximately 3·10⁻³ S cm⁻¹.

The replacement of Pb²⁺ or Sn²⁺ cations by heterovalent Zr⁴⁺, In³⁺, Al³⁺, Ga³⁺, and Na⁺ cations favored the formation of solid solutions, which generally have higher conductivity than β-PbSnF₄ [3]. As is known, some substituents (e.g., Y³⁺) favor a decrease in conductivity, while others (Bi⁷⁺) increase it [4, 5].

Despite the large amount of currently available information [4-7], the effect of heterovalent substituents on the character of the dependence of solid solutions based on lead(II) tetrafluorostannate(II) on the composition and temperature has not yet been determined unambiguously.
Therefore, it is of interest to reveal the relationship between the nature of the heterovalent substituent and the charge transfer in multicomponent fluoride systems from both scientific and practical viewpoints.

The present communication presents the results of our studies of the charge transfer in the polycrystalline samples of \( \text{PbF}_2-\text{SnF}_2-\text{YF}_3 \) solid solutions.

2. Experimental details

The heterovalent substitution solid solutions \( \text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x} \) were synthesized in two stages. At first, \( \text{Pb}_{1-x}\text{Y}_x\text{F}_{2+x} \) solid solutions were obtained by solid-state synthesis [8]. \( \text{PbF}_2 \) and \( \text{YF}_3 \) were thoroughly ground, mixed in an appropriate ratio, and pelletized. The resulting pressed mixtures were heated to 973 K in quartz tubes under highly pure argon, kept at this temperature for 5 h, and cooled to room temperature in the switched-off furnace mode.

At the second stage, the resulting solid solutions were fused with an equimolar amount of tin difluoride in platinum crucibles under argon, kept at 773 K for 20 min, and cooled to room temperature in the switched-off furnace mode. This gave nonstoichiometric \( \text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x} \) phases.

The conductivity of the synthesized compounds was studied by impedance spectroscopy and bridge method using a P5083 DCAC bridge in the frequency range 10–70 kHz. The impedance spectra were recorded in a cell with platinum electrodes using an Autolab (Ekochemie) electrochemical module and a frequency response analyzer (FRA) in the frequency range \( 10^{-1}-10^{6} \) Hz (at an output signal amplitude of 10 mV). Pelletized samples of the synthesized compounds with a diameter of 8 mm and a thickness of 2.0–3.0 mm were used. Platinum electrodes were used as current leads. The measurements were performed in an argon atmosphere at temperatures of 293–573 K in the cooling mode.

The \( ^{19}\text{F} \) NMR spectra have recorded on Bruker AVANCE 400 spectrometer at the temperature range 293 – 573 K. The chemical shift (\( \delta \) in ppm) relative to a reference set \( \text{C}_6\text{F}_6 \) an accuracy of 1 ppm. The width (at half height \( \Delta H \)) has measured in kHz with an error less than 1 %. Experimental data processed using computer programs MestReNova and MagicPlot.

3. Results and discussion

At the first stage of the synthesis in the concentration range 1.0–29.0 mol % \( \text{YF}_3 \), \( \text{Pb}_{1-x}\text{Y}_x\text{F}_{2+x} \) solid solutions of cubic crystal system formed, which had a fluorite structure as in the case of the starting \( \text{PbF}_2 \), but with smaller unit cell dimensions. For example, for the \( \text{Pb}_{0.71}\text{Y}_{0.29}\text{F}_{2.29} \) solid solution, \( a = 5.886(1) \) Å, while for \( \text{PbF}_2 \) it is 5.940(1) Å.

At the second stage, \( \text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x} \) \( (0 < x \leq 0.17) \) solid solutions of the tetragonal crystal system isostructural with \( \beta-\text{PbSnF}_4 \) formed (Fig. 1). The replacement of some part of \( \text{Pb}^{2+} \) ions by \( \text{Y}^{3+} \) ions leads to an increase in the unit cell volume of the resulting compounds. The unit cell volume of the \( \text{Pb}_{0.83}\text{Y}_{0.17}\text{SnF}_{4.17} \) sample was 103.301 Å\(^3\), while for pure \( \beta-\text{PbSnF}_4 \) it is 101.51 Å\(^3\). The dependences of the unit cell parameters of the synthesized compounds on the yttrium trifluoride content in them obey the Vegard and Rutgers rules [9].

Figure 1 presents the typical frequency and temperature dependences of complex conductivity of the synthesized polycrystalline samples of \( \text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x} \) solid solutions with different compositions in Nyquist coordinates.

At 293 K the impedance diagrams of all the samples contain only one deformed semicircle in the region of high frequencies, which transforms into a linear dependence in the region of low frequencies. This segment of the impedance diagram suggests polarization of the solid solution/blocking electrode interface due to the change in the ion balance in the near-electrode layer of the solid electrolyte under the action of the external electric field.

As the temperature and yttrium fluoride content in the solid solution increase, the radius of the deformed semicircles decreases, and they shift toward higher frequencies. The shape of the obtained impedance diagrams suggests that the total bulk conductivity of crystallites has no significant contribution of surface conductivity. To verify this assumption, the capacity of the complex
conductivity of the samples at frequencies $f_{\text{max}}$ corresponding to the maximum $Z''$ values of the deformed semicircles and the sites of hypothetical intersection with the abscissa axis was evaluated by the equation $2\pi f_{\text{max}} RC = 1$. The resulting values $(1.0 - 4.0) \times 10^{-11}$ F have a substantially lower order of magnitude than the capacity component that characterizes the surface conductivity of crystallites $(10^{-9} - 10^{-7})$ F.

Figure 1. Impedance diagrams of the synthesized samples of (a) $\text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x}$ solid solutions at 293 K and (b) of the $\text{Pb}_{0.87}\text{Y}_{0.13}\text{SnF}_{4.13}$ sample at 373 and 473 K

The temperature dependence of the conductivity of the synthesized compounds in the frequency-independent region of the impedance spectrum is satisfactorily approximated by the Arrhenius–Frenkel equation. For each sample including $\beta$-$\text{PbSnF}_4$, the dependence has an inflection (“Faraday phase transition” [10]) in the range 435–475 K inherent in the majority of solid electrolytes with a fluorite and antifluorite structure (Fig. 2).

Figure 2. Temperature dependences of specific electric conductivity of the polycrystalline $\text{Pb}_{1-x}\text{Y}_x\text{SnF}_{4+x}$ solid solutions
The conductivity of the synthesized samples at low contents of yttrium ions ($x \leq 0.07$) is much lower than for the starting $\beta$-PbSnF$_4$. The Pb$_{0.91}Y_{0.09}$SnF$_{4.09}$ sample has almost the same conductivity as the stoichiometric $\beta$-PbSnF$_4$ phase in the high-temperature range (Fig. 2). In the samples containing more than 10.0 mol % YF$_3$, a considerable contribution to the total conductivity is from the structural changes in the solid electrolyte on heating. The activation energy in the high temperature range is higher than in the low-temperature one and increases with the concentration of the heterovalent substituent. The highest conductivity is inherent in the Pb$_{0.87}Y_{0.13}$SnF$_{4.13}$ sample. In the high temperature range, it is an order of magnitude higher than for $\beta$-PbSnF$_4$.

The conductivity parameters of the synthesized phases were estimated with the aid of the Arrhenius-Frenkel equation:

$$\sigma = A \exp\left(-\Delta E_\sigma / kT\right),$$

where $A$ is pre-exponential factor, $\Delta E_\sigma$ is the activation energy of conductivity, $k$ is Boltzmann constant (Table 1).

Table 1. Parameters of electric conductivity of Pb$_{1-x}$Y$_x$SnF$_{4+x}$ solid solutions

| Sample            | $\Delta E_\sigma$, eV | $\log(A)$, S/(cm·K) | $\sigma$, S/cm | $T$, K |
|-------------------|-----------------------|----------------------|----------------|--------|
| $\beta$-PbSnF$_4$ | 0.36                  | 4.19                 | 9.02·10$^{-4}$ | 373    |
|                   | 0.2                   | 2.27                 | 1.88·10$^{-2}$ | 573    |
| Pb$_{0.97}$Y$_{0.03}$SnF$_{4.03}$ | 0.48                  | 4.49                 | 7.84·10$^{-3}$ | 373    |
|                   | 0.25                  | 1.92                 | 2.65·10$^{-3}$ | 573    |
| Pb$_{0.95}$Y$_{0.05}$SnF$_{4.05}$ | 0.40                  | 3.83                 | 2.47·10$^{-4}$ | 373    |
|                   | 0.18                  | 1.39                 | 3.34·10$^{-3}$ | 573    |
| Pb$_{0.91}$Y$_{0.09}$SnF$_{4.09}$ | 0.47                  | 5.42                 | 5.36·10$^{-4}$ | 373    |
|                   | 0.30                  | 3.32                 | 3.07·10$^{-2}$ | 573    |
| Pb$_{0.89}$Y$_{0.11}$SnF$_{4.11}$ | 0.17                  | 3.01                 | 1.67·10$^{-3}$ | 373    |
|                   | 0.54                  | 7.18                 | 0.0606         | 573    |
| Pb$_{0.87}$Y$_{0.13}$SnF$_{4.13}$ | 0.24                  | 4.28                 | 4.41·10$^{-3}$ | 373    |
|                   | 0.53                  | 7.42                 | 0.21           | 573    |
| Pb$_{0.83}$Y$_{0.17}$SnF$_{4.17}$ | 0.30                  | 4.7                  | 3.25·10$^{-4}$ | 373    |
|                   | 0.72                  | 9.99                 | 0.128          | 573    |

Below 300 K, the conductivity of the synthesized compounds is almost independent of the concentration of the heterovalent substituent (Fig. 3a). Above 400 K in the samples containing more than 7.0–9.0 mol % yttrium trifluoride, the electric conductivity increases with the concentration of the heterovalent substituent.

Figure 3. Conductivity isotherms (a) of the synthesized Pb$_{1-x}$Y$_x$SnF$_{4+x}$ samples and dependence of the activation energy of conductivity (b) of the samples of Pb$_{1-x}$Y$_x$SnF$_{4+x}$ solid solutions on the YF$_3$ content for the temperature range (1) before and (2) after the “Faraday phase transition” temperature.
Figure 3b presents the dependence of the activation energy of conductivity of the synthesized samples before and after the “Faraday phase transition” on the concentration of the heterovalent substituent. Below 400 K at 9–10 mol % YF₃, the concentration is the dominant factor that determines the total electric conductivity. The activation energies of the synthesized samples are almost independent of the concentration of the heterovalent substituent and are close to the energy of the starting β-PbSnF₄ (table).

In the samples containing more than 10.0 mol % YF₃, a considerable contribution to the total conductivity is from the structural changes in the solid electrolyte on heating. The activation energy in the high-temperature range is higher than in the low-temperature one and increases with the concentration of the heterovalent substituent. The highest conductivity is inherent in the Pb₀.₈₇Y₀.₁₃SnF₄.₁₃ sample. In the high-temperature range, it is an order of magnitude higher than for β-PbSnF₄.

The contribution of the electronic component of the total electric conductivity of the synthesized compounds was evaluated from the voltammetric characteristics of the(-)Ni/NiF₂+CaF₂[Pb₁₋ₓYₓSnF₄+x]Pt(+) electrochemical cell by the Hebb–Wagner method [11]. The transport numbers of fluoride anions in the synthesized samples of solid solutions are almost independent of the concentration of the heterovalent substituent, and the electron component of conductivity exceeds the ion conductivity by more than two orders of magnitude.

Additional information about the nature of charge carriers in the system was obtained by high-temperature ¹⁹F NMR spectroscopy. The results indicate that, like in the starting β-PbSnF₄, the fluoride anions occupy three structurally nonequivalent positions in the synthesized samples (F1, F2, and F3), which differ in the local environment and in the character of the Me–F bond, which agrees with the data of [12].

Unlike ¹⁹F NMR spectra for tetragonal β-modification PbSnF₄ that at 300 K describes a narrow symmetric Lorentz function with a chemical shift of about 126 ppm and ΔH about 3 kHz the ¹⁹F NMR spectra for solid solutions Pb₁₋ₓYₓSnF₄ₓ⁺ are the set of broad lines (Fig. 4).

![Figure 4](image.png)

Figure 4. Evolution component of ¹⁹F NMR spectra of solid solution Pb₀.₈₉Y₀.₁₁SnF₄.₁₁ with increasing temperature

There is the redistribution of fluoride anions between places in the structure of synthesized samples with increasing temperature. Dominating the integrated intensity of superposition becomes narrow component (P₃) corresponding mobile ions.

The presence in the spectra of several components due to structural nonequivalence of fluoride ions, whose concentration can be measured by integrated intensities components. Contribution high mobility forms ions (component P₃) at 300 K greater than 32 % and increases with raise temperature, reaching values of 72–80 % at 523 K by attracting fluoride ions locally a mobile (P₂) and motionless (P₁) subsystems (Fig. 5). This largely reduces the area component P₂ and P₁ component in it remains unchanged until 400 – 450 K, and only further increase the temperature starts to drop, due to the sedentary growth rate of diffusion of fluoride ions.
The distribution of fluoride ions localization in the crystal lattice $\text{Pb}_{0.89}\text{Y}_{0.11}\text{SnF}_{4.11}$ at different temperatures

Figure 5. The distribution of fluoride ions localization in the crystal lattice $\text{Pb}_{0.89}\text{Y}_{0.11}\text{SnF}_{4.11}$ at different temperatures

The concentration of moving fluoride anions at 300 K does not depend on the concentration of heterovalent substituent YF$_3$, and at temperatures higher than 430 K increases with the concentration of the YF$_3$. Exchange of the fluoride ion between unequal subsystems are increases with increasing of the temperature and degree of substitution. This fact is reflected in the temperature dependences of electrical conductivity.

4. Conclusions
Heterovalent substitution solid solutions of the tetragonal crystal system isostructural with $\beta$-PbSnF$_4$ are formed in the range of concentrations $0 < x \leq 0.17$ in the $(1-x)$PbF$_2$ – $x$YF$_3$ – SnF$_2$ system. Like in $\beta$-PbSnF$_4$, the fluoride anions occupy three structurally nonequivalent positions. The mobile fluoride anions are mainly localized in the interstitial positions (F3). Their concentration exceeds 50% already at 300 K and increases with temperature. An inflection (“Faraday phase transition”) was recorded in the temperature range 435–475 K for each composition of the synthesized samples, which is inherent in the majority of solid electrolytes with a fluorite and antifluorite structure. Below 300 K, the conductivity of the synthesized compounds is almost independent of the concentration of the heterovalent substituent. Above 400 K in the samples containing more than 7.0–9.0 mol % yttrium trifluoride, the electric conductivity increases with the concentration of the heterovalent substituent.

References
[1] Gurevich Y Y and Harkats Y I 1992 Superionic conductors (Moscow: Nauka)
[2] Sorokin N I and Fedorov P P 1997 Inorganic Materials 33 1
[3] Donaldson J D and Senior B J 1967 J. Chem. Sot. A. 1821
[4] Ito Y, Koto K, Yoshikado S and Ohachi T 1986 Solid State Ionics 18–19 1202
[5] Nikiforov A E, Zakharov A Yu, Chernyshev V A, Ugryumov M Yu and Kotomanov S V 2001 Fiz. Tverd. Tela 44 1446
[6] Kanno R, Nakamura S and Kawamoto Y 1992 Solid State Ionics 51 53
[7] Kavun V Ya, Ryabov A I, Telin I A, Podgorbunskii A B, Sinebryukhov S L, Gnedenkov S V and Goncharuk V K 2012 Zh. Strukt. Khim 53 292
[8] Patwe S J, Balaya P, Goyal P S and Tyagi A K 2001 Mater. Res. Bull. 36 1743
[9] Urusov V S 1987 Theoretical Crystal Chemistry. Manual (Moscow: Mosk. Gos. Univ.) (In Russian)
[10] Sorokin N I and Sobolev B P 2007 Kristallografiya 52 870
[11] Wagner C 1956 Z. Elektrochem 60 4
[12] Ito Y, Mukoyama T, Funatomi H, Yoshikado S and Tanaka T 1994 Solid State Ionics 67 301-305