Ministry of Education and Science of Ukraine
Sumy State University

Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP-2017)

2017, Part 2

Zatoka, Ukraine
September 10–15, 2017

Founded in 2012

Sumy
Sumy State University
2017

2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP – 2017)

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Electrical Conductivity of Aliovalent Substitution Solid Solution Pb$_{1-x}$Sm$_x$SnF$_{4+x}$

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Abstract—**The paper presents results of studies of the conductivity of aliovalent substitution solid solutions, which are formed in the system $(1-x)PbF_2 - xSmF_3 - SnF_2$ in the concentration range $0 < x \leq 0.2$ mole fraction and have a crystal lattice of hexagonal system isostructural with β-PbSnF$_4$. At a low aliovalent substituent content ($x \leq 0{,}07$), the conductivity of the synthesized fluorides is by an order of magnitude lower than that of β-PbSnF$_4$. At a higer content, it increases and reaches the largest values at $x = 0.15$. The fluorine anions in the synthesized samples of solid solutions are in three structurally nonequivalent positions, which differ in local environment and the nature of the M-F bond. The conductivity of the synthesized samples is provided by highly mobile interstitial fluorine anions.**

Keywords—electrical conductivity; transport numbers; aliovalent substitution solid solutions; lead, tin, samarium fluorides

I. INTRODUCTION

Nonstoichiometric fluorides with fluorite and tysonite structure are characterized by a high fluoride ion conductivity, which is due to anionic sublattice disorder. The concentration of structural defects in such compounds can reach a few tens of at %; therefore, it is proposed to call them "highly nonstoichiometric" [1] and to classify them as nanostructured compounds and the methods of controlling their properties as relating to the principles of nanotechnologies [2].

Isomorphic heterovalent substitution has a determining effect on the appearance of lattice defects of fluorides. In this case, the charge difference of M_1^{n+} and M_2^{m+} cations is compensated by extra fluorine anions and/or anionic vacancies. The cationic sublattice changes only the qualitative composition; all its nodal positions are fully occupied and actually retain their coordinates [3, 4].

Among the fluorides with fluorite and tysonite structure known to date, PbF$_2$- and SnF$_2$-based aliovalent substitution solid solutions, in which a part of Pb^{2+} or Sn^{2+} cations is substituted by rare-earth cations, are attractive for use in electrochemical devices [5]. Because of the structural changes of the anionic sublattice owing to the incorporation of aliovalent cations, the electrical conductivity of these solutions can greatly increase in comparison with the starting components [6]. The compounds based on PbSnF$_4$, whose electrical conductivity is ~ $3 \cdot 10^{-3}$ S/cm already at room temperature, are an object of special attention.

The change of cationic composition causes the formation of compounds that differ in structure and the energetics of ion motions. It is known that the aliovalen substitution of Pb^{2+} or Sn^{2+} cations in the PbSnF$_4$ compound contributes to increase in electrical conductivity owing to increase in the number of lattice defects [7, 8]. For instance, in the system $(1-x)PbF_2 - xYF_3 - SnF_2$, substitutional solid solutions isostructural with β−PbSnF$_4$ are formed in the concentration range $0 < x \leq 0{,}17$ [9]. At a low concentration of aliovalent Y^{3+} cations ($x \leq 0{,}07$), the electrical conductivity of solid solutions is much lower than that of the starting β-PbSnF$_4$. The samples of the composition Pb$_{0.91}$Y$_{0.09}$SnF$_{4.09}$ has much the same conductivity values as the β-PbSnF$_4$ compound. The sample containing 13,0 mol. % YF$_3$ has the highest conductivity [10].

However, no well-defined laws governing the influence of the concentration of aliovalent substituents on the ion mobility and electrical conductivity of lead (II) tetrafluorostannate (II) based fluoride ion conducting phases at different temperatures have been established. Therefore, the ascertainment of the interrelation between the nature of substituent and charge-transfer mechanism in the above fluorides is a topical not only scientific, but also applied problem.

This paper present results of investigations of the transport properties of aliovalent substitution solid solutions in the system $(1-x)PbF_2 - xSmF_3 - SnF_2$.

II. EXPERIMENTAL

The starting substances in the synthesis were the following reagents: ultra-pure PbF_2, analytically pure Sm_2O_3, NH_4F, SnF_2. Samarium oxide was dissolved in nitric acid. Fluoride was precipitated from the resulting solution by adding it to an excess ammonium fluoride solution. The formed precipitate was dried and calcined at 673 K.

The aliovalent substitution solid solutions of the system $(1-x)PbF_2 - xSmF_3 - SnF_2$ were prepared by melting method [11]. A mixture of appropriate amounts of starting fluorides was thoroughly ground and heated in platinum crucibles to 773 K under argon, held for 20 min and cooled to room temperature with the furnace turned off.

The X-ray phase analysis (XPA) was performed on a DRON-3M diffractometer with $CuK\alpha$ radiation in an angle range of 10-80 deg. with a step of 0.02 deg. and an exposure time of 3 s. the diffraction patterns were processed using the computer programs Match and UnitCell and the JCPDS database powder diffraction patterns.

The electrical conductivity of the obtained compounds was studied by impedance spectroscopy using a two-electrode circuit with platinum blocking electrodes with the aid of an Autolab electrochemical module and a frequency response analyzer in a frequency range of 10^{-1}-10^6 Hz (at an output signal amplitude of 10 mV). Pressed samples of polycrystalline compounds with a diameter of 8 mm and a thickness of 2.0-3.0 mm were used for research. The measurements were made in a temperature range of 300-673 K.

The electrical conductivity was calculated from the equation $\sigma = l/(s \cdot R)$, where l is pellet thickness, s is contact area, R is ohmic resistance.

The electronic component of conductivity was studied by the Hebb-Wagner polarization method [12] in a $(-)Ni+NiF_2+CaF_2 \mid Pb_{1-x}Sm_xSnF_{4+x} \mid Pt(+)$ cell. The thermostated cell was gradually polarized with a B5-43 dc source in a potential range 0.1-2.5 V with a step of 0.1 V. the current flowing through the cell was measured with an AVM-4307 digital multimeter.

The ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer in a temperature range of 293-623 K. The chemical shift (δ in ppm) was measured relative to a C_6F_6 standard, with an accuracy of 1 ppm. The half-height width of the bands in the spectra (ΔH) was measured in kHz with an error of not over 1%. The obtained experimental data were processed using the computer programs MestReNova and MagicPlot.

III. RESULTS AND DISCUSSIONS

Based on XPA data, it has been found that in the system $(1-x)PbF_2 - xSmF_3 - SnF_2$, single-phase compounds of tetragonal system (space group P4/nmm) that are isostructural with β-$PbSnF_4$ are formed in the SmF_3 concentration range

$0 < x \leq 0.2$ (Fig 1). Lattice parameters of $Pb_{1-x}Sm_xSnF_{4+x}$ solid solutions are listed in Table 1.

TABLE 1 . LATTICE PARAMETERS OF SYNTHESIZED SAMPLES OF $Pb_{1-x}Sm_xSNF_{4+x}$ SOLID SOLUTIONS

Lattice parameters		
x	$a, Å$	$V, Å^3$
0.05	5.93827	209.4016
0.1	5.95048	210.6962
0.15	5.94345	209.9501
0.2	5.94870	210.401

Figure 2 show typical plots of the complex conductivity of polycrystalline $Pb_{1-x}Sm_xSnF_{4+x}$ samples for a $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ solid solution as an example. The impedance plots exhibit in the high-frequency region only one semicircle, which transform into a straight-line dependence on transition to the low-frequency region. The radius of deformed semicircles decreases with rising temperature, and they shift to the higher-frequency region owing to an increase in the electrical conductivity of materials. The absence of another semicircle from the complex plane of impedance indicates a fairly high homogeneity of samples and that there is no contribution of the surface conductivity of crystallites. The calculated values of the complex-conductivity capacity of samples at the frequencies corresponding to the change of semicircle into a straight-line dependence on impedance plots also speak for this (Fig 2). The obtained values of $(1.0-4.0) \times 10^{-11}$ F are much smaller that the surface conductivity capacity of crystallites (10^{-9}-10^{-7} F) [13].
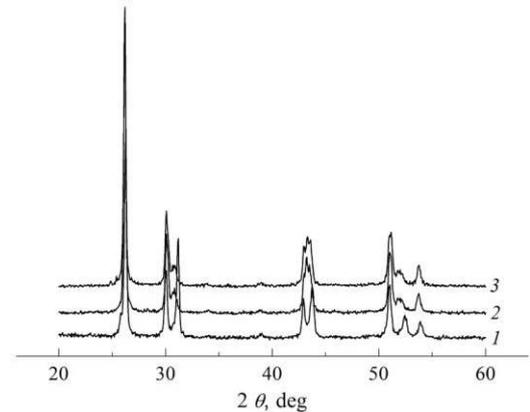
Fig. 1. Diffraction patterns of synthesized samples: (1) β-$PbSnF_4$; (2) $Pb_{0.95}Sm_{0.05}SnF_{4.05}$; (3) $Pb_{0.85}Sm_{0.15}SnF_{4.15}$

At low temperatures, the impedance spectra are described by the circuit shown in Fig 3 (a). The high-frequency region of the impedance hodograph is described by the element R1 and CPE1, which characterize the bulk properties of samples. A stage connected in series, which consists of a resistor R2 and constant phase element CPE2 and CPE3, describes the low-frequency region of impedance spectrum and corresponds to a set of processes occurring at the electrode/electrolyte interface, i.e. polarization effect manifest themselves. The resistor R1 of the equivalent circuit corresponds to the total conductivity of samples.

At high temperatures, the impedance spectra can by described by means of an equivalent circuit, which consists of the elements R1 and CPE1, which characterize the conductivity of the synthesized sample, and the constant phase element CPE3, which describes polarization effects at the electrode/electrolyte interface (Fig 3 (b)).
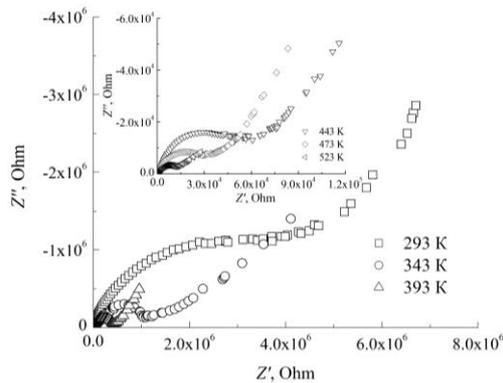
Fig. 2. Impedance spectra of $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ solid solution under temperature change

a)   b)

Fig. 3. Equivalent impedance circuits of cell with $Pb_{1-x}Sm_xSnF_{4+x}$ at 293 (a) and 473 K (b)

The appearance of the impedance plots in Bode coordinates, which are shown in Fig 4, is typical of disordered ion conducting compounds with relaxation processes, which are caused by the structural and energetic nonequivalence of charge carriers (in this particular case, fluorine anions) [13]. They can by arbitrarily divided into three portions. The first low-frequency region exhibits variations of the electrical conductivity of the samples under investigation, which are associated with polarization effects, which arise in the near-electrode layers of the samples under investigation. They are caused by the formation of a space charge at the electrode/electrolyte interface, and the higher the temperature and the lower frequency of the external electric field, the more markedly they manifest themselves. The average statistical intrinsic bulk conductivity σ_0 is characterized by the portion of the plot that is in the medium-frequency region. And, finally, in the high-frequency region (over 1×10^4 Hz), the Bode plots show the regions that characterize the increase in conductivity caused by an increase in the amount of fluorine anions that are able to escape the potential barrier between the sites of their localization by the action of an external electric field [13].

The dependence of the specific conductivity of the samples under investigation is satisfactorily described by the Arrhenius-Frenkel equation in the lg $\sigma T - 10^3/T$ coordinates (Fig 5). The resistance of the samples was determined at the frequencies corresponding to the projection of the point of change of the semicircle in the impedance plot into a straight-line dependence onto the abscissa axis [14]. The plots of electrical conductivity against temperature (Fig 2) exhibit in the

temperature range 435-475 K a kink ("faradaic phase transition" [16]), which is characteristic of most solid electrolytes with fluorite and antifluorite structure.
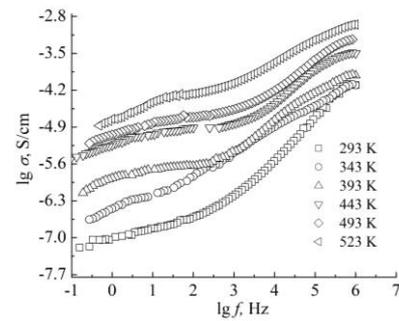
Fig. 4. Dependence of the real conductivity component of a $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ solid solution on frequency at different temperatures

It was noted than on substitution by a small amount of SmF_3 (x $\leq$ 0.07), the conductivity of synthesized samples decreases by almost an order of magnitude as compared with further increase of samarium trifluoride content. The compound $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ has the highest conductivity (Table 2).
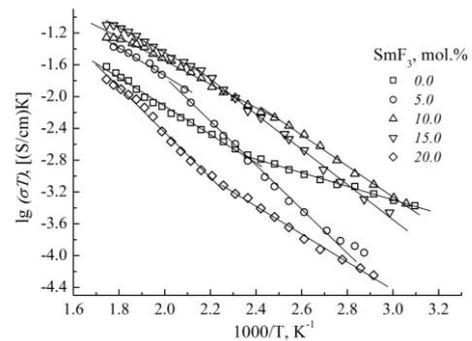
Fig. 5. Plots of electrical conductivity against temperature in the coordinates of the Arrhenius-Frenkel equation for polycrystalline samples of $Pb_{1-x}Sm_xSnF_{4+x}$ solid solutions

TABLE 2. ELECTRICAL CONDUCTIVITY PARAMETERS OF $PB_{1-X}SM_XSNF_{4+X}$ SOLID SOLUTION

Sample	ΔEa (eV)	lg (A) ((S/cm)·K)	σ (S/cm)	T (K)
β-PbSnF₄	0.2	2.27	$1.88\cdot10^{-2}$	573
	0.36	4.19	$9.02\cdot10^{-4}$	353
$Pb_{0.95}Sm_{0.05}SnF_{4.05}$	0.39	4.92	$4.21\cdot10^{-2}$	573
	0.55	6.44	$1.32\cdot10^{-4}$	353
$Pb_{0.9}Sm_{0.1}SnF_{4.1}$	0.35	4.68	$5.51\cdot10^{-2}$	573
	0.41	5.45	$1.07\cdot10^{-4}$	353
$Pb_{0.85}Sm_{0.15}SnF_{4.15}$	0.36	4.9	$7.97\cdot10^{-2}$	573
	0.48	6.25	$8.43\cdot10^{-4}$	353
$Pb_{0.8}Sm_{0.2}SnF_{4.2}$	0.38	4.51	$1.31\cdot10^{-2}$	573
	0.47	6.14	$6.94\cdot10^{-5}$	353

At temperatures below 350 K, the electrical conductivity of the synthesized compounds is practically independent of rare-earth fluoride concentration, and at temperatures above 430 K, it increases with lanthanide trifluoride content (Fig 6). In this case, the activation energy of ionic conductivity decreases, which speaks for change transfer by interstitial fluorine anions.
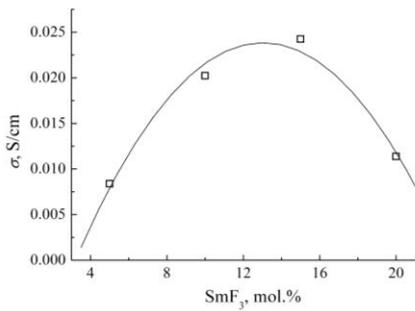
Fig. 6. Conductivity-composition isotherm of $Pb_{1-x}Sm_xSnF_{4+x}$ solid solutions at 473 K

An additional information on the effect of aliovalent substituent on the electrical conductivity of synthesized phases was obtained from an examination of a plot of conductivity against frequency in the dimensionless $\lg \sigma_f/\sigma_0 - \lg f/f_0$ coordinates [15, 16].

Figure 7 shows plots of electrical conductivity against frequency and temperature in dimensionless reduced coordinates for a $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ solid solution as an example. In the case of temperature rise, such plots for all synthesized samples are described by one function, indicating that there is no considerable effect of temperature on electrical conductivity and charge-transfer mechanism in fluorides of such composition.
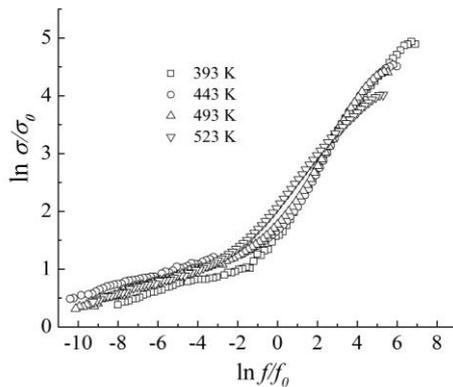
Fig. 7. Dependence of the electrical conductivity of $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ on frequency in reduced coordinates at different temperatures

Figure 8 shows conductivity-frequency spectra of polycrystalline samples of $Pb_{1-x}Sm_xSnF_{4+x}$ solid solutions of different composition at 298 K. an examination of electrical conductivity spectra at 298 K at different SmF_3 content showed that in the low- and medium-frequency region, the curves in the dimensionless $\lg \sigma_f/\sigma_0 - \lg f/f_0$ coordinates are superimposed on one another, indicating that there is no considerable effect of lanthanide trifluoride concentration on the electrical conductivity of samples. In the region of high frequencies (higher than f_0), these plots are different for the samples with different substituent (SmF_3) content. This may indicate on influence of relaxation effects ("dynamic response of the cell" [17]) in the case of increasing the substituent concentration.

The contribution of electronic component of the total electrical conductivity of the synthesized compounds has been estimated, and the transport numbers of F-ions have been calculated by the Hebb-Wagner method [12] from current-potential curves for a $(-)Ni+NiF_2+CaF_2 \mid Pb_{1-x}Sm_xSnF_{4+x} \mid Pt(+)$ electrolytic cell. It has been found that the transport numbers of fluorine anions in the synthesized compounds are over 0.91 and are practically independent of SmF_3 concentration.
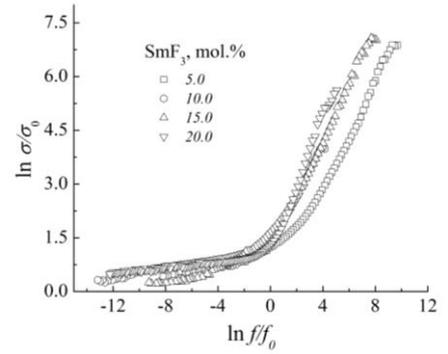
Fig. 8. Conductivity-frequency spectra of polycrystalline $Pb_{1-x}Sm_xSnF_{4+x}$ samples at 298 K

The information on the nature of charge carries in the system under investigation was obtained by high-temperature ^{19}F NMR spectroscopy. Figure 9 shows ^{19}F NMR spectra, which are typical of $Pb_{1-x}Sm_xSnF_{4+x}$ compounds, under temperature change for a $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ solid solution as an example. Unlike the spectra of $PbSnF_4$ sample of tetragonal β-modification, which are described at 500 K by a narrow almost symmetrical Lorentz unit function with a chemical shift of ~ 126 ppm and ΔH of ~ 3 kHz [8]. The 19F NMR spectra for $Pb_{1-x}Sm_xSnF_{4+x}$ solid solutions are a set of board bands (Fig 9) and are similar to the ^{19}F NMR spectra of solid electrolytes with tysonite structure [18, 19].

The shape of the observed spectrum (superposition of several signals) points to the structural nonequivalence of fluorine ions in the crystal lattice. The obtained results indicate that in the crystal lattice of synthesized samples, the fluorine anions are in three different positions already at temperatures close to room temperatures (300 K), viz: in the position of immobile (F_1) and locally mobile (F_2) fluoride subsystems, as well as in highly mobile interstitial positions F_3. At temperatures above 500 K, the of position F_3 is typical of the investigated samples, which manifests as a narrow components (P_3) in NMR spectra.
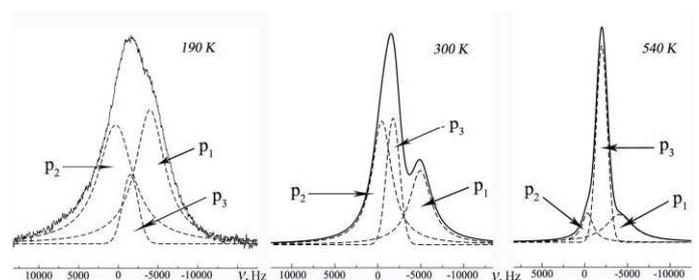
Fig. 9. Evolution of the component composition of ^{19}F NMR spectra of the $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ compound with rising temperature

NMR spectra may be represented as a superposition of three compounds: P_1 and P_2 of Gaussian shape and P_3 of Lorentzian shape (Fig 10). The presence of several components in the spectra is due to the structural nonequivalence of fluorine ions, whose concentration can be estimated from the integral intensity of the components. The contribution of the "highly mobile" forms of ions (component P_3) at 190 K is not over 8%; at 360 K, it is over 30% and increases with temperature, reaching 84-85% at 623 K owing to the involvement of the fluoride ions of the locally mobile (P_2) and immobile (P_1) subsystems (Fig 10).
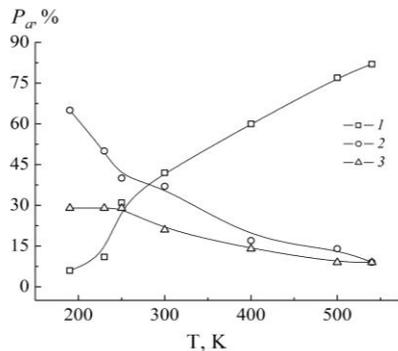
Fig. 10. Distribution of fluorine anions over the sites of localization in the crystal lattice of $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ at different temperatures: (1) P_3; (2) P_1; (3) P_2.

As the temperature rises, a redistribution between the positions of fluoride ions in the structure of the synthesized samples takes place. The narrow component, which corresponds to mobile (interstitial) fluorine ions, becomes predominant in integral intensity in superposition.

IV. CONCLUSIONS

Aliovalent substitution solid solutions with β-$PbSnF_4$ structure in the system $(1-x)PbF_3 - xSmF_3 - SnF_2$ are formed at $0 < x \leq 0.2$. It has been found that substitution by a small amount of SmF3 ($x \leq 0.07$) reduces the electrical conductivity of compounds by an order of magnitude as compared with β-$PbSnF_4$. The conductivity increases with further increase in lanthanide trifluoride content. The solid solution of the composition $Pb_{0.85}Sm_{0.15}SnF_{4.15}$ has the highest electrical conductivity.

The fluorine anions occupy three structurally nonequivalent positions. The mobile fluorine anions are localized mainly in the interstitial position F_3. Their concentration in over 30% and increases with temperature, reaching 83-85% at 623 K. The electrical conductivity of solid solutions is provided by highly mobile interstitial fluorine anions, as indicated by the transformation of NMR spectra and by the calculated values of the activation energy of ion mobility.

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