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CONDUCTIVITY OF NON-STOICHIOMETRIC FLUORIDE-CONDUCTING PHASES $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$

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Fluoride-conducting phases $Ba_{0.9-x}La_xSn_{1.10}F_{4+x}$ ($x \leq 0.12$), formed by the partial substitution of barium cations with lanthanum cations in the initial non-stoichiometric phase $Ba_{1-x}La_xF_{2+x}$ ($x \leq 0.12$), crystallize in a tetragonal syngony (*P4/nmm*) isotypic to $BaSnF_4$. The conductivity of the synthesized phases is higher than that of the parent compound and increases with temperature and substituent concentration. The highest conductivity is observed in the $Ba_{0.78}La_{0.12}Sn_{1.10}F_{4.12}$ phase, where fluoride anions are the primary charge carriers. The activation energy of conductivity decreases with increasing substituent content, which is characteristic of both high- and low-temperature regions. The synthesized fluoride-conducting phases remain stable within the potential range of −1.5 to +1.9 V.

Keywords: fluoride-conducting phases, tin fluorides, barium, lanthanum, solid substitution solutions, electrical conductivity, voltammetry.

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Introduction

Recent studies indicate the prospect of using fluoride-conducting phases with high mobility of anions in the solid state to develop existing and create fundamentally new electrochemical devices [1−6]. Such compounds can be used in the development of electrochemical energy storage systems, ion-selective electrodes, electrochemical sensors, supercapacitors, etc. [1,2]. In view of this, the development and synthesis of solid electrolytes with high fluoride conductivity at low temperatures is one of the current directions in the development of modern inorganic chemistry.

Relatively high ion conductivity values at low temperatures are typical for lead and tin fluoride-based systems. Thus, the stoichiometric compound β-$PbSnF_4$ has a conductivity of $\approx 10^{-3}$ S/cm at room temperature [1]. The shortcomings of this solid electrolyte include a narrow window of electrochemical stability. Complex fluorides $MSnF_4$ (where M − Pb, Ba, Sr) and solid solutions based on them are also characterized by high conductivity over fluorine anions at room temperature and a small fraction of electron conductivity.

The phases formed by the fluorides of tin and barium have a relatively high unipolar conductivity for anions F^- already at temperatures close to room temperature [3−5]. A specific feature of such systems is that their complex fluorides $BaSnF_4$, $BaSn_2F_6$ and solid solutions $(BaF_2)_x-(SnF_2)_{1-x}$ have conductivity several orders of magnitude higher than the original individual fluorides [3]. This behavior of the fluoride conducting phases formed by these compounds is due to the electronic configuration of the Sn^{2+} cation, which on the outer electron level has an undivided stereoactive pair $5s^2$ of electrons. It significantly affects the structure of the coordination polyhedron of cations and also the mobility of fluorine anions that surround their fluorides [4].

The crystalline lattice $BaSnF_4$ corresponds to tetragonal syngony (sp. group *P4/nmm)* isostructural with β-$PbSnF_4$. A characteristic feature of compounds of this type is the layered arrangement of −BaBaSnSnBaBa− cations in the crystal lattice parallel

to the axis with the unit cell [5]. Due to the structural features of the cationic framework, mobile anions are located mainly between the Ba–Sn and Sn–Sn layers, other anions located between the Ba–Ba layers have very low mobility, so the migration of fluorine anions is realized mainly due to their jumps into the Ba–Sn plane. Thus, the distribution of anions in the crystalline lattice fluoride-conducting phases and their localization around the cations significantly affects the conductivity of compounds of this type. The conductivity of fluoride conducting phases depends not only on the deformation of the coordination polyhedron of cations, but also on the deviation of their composition from stoichiometric and/or doping with heterovalent substituents. The first approach allows improving the migration of fluorine anions, and the second one provides an increase in the concentration of crystalline lattice defects [1–6].

Recent studies [3,6,7] indicates that deviation from stoichiometry significantly affects the conductivity of complex fluoride $BaSnF_4$. The highest electrical conductivity ($\sigma=4.1\cdot10^{-3}$ S/cm at room temperature) and the lowest activation energy of ionic conductivity ($E_a=17.9$ kJ/mol) are inherent in the composition $Ba_{0.47}Sn_{0.53}F_{4.00}$ phase [3].

The formation of anionic supernatant solid solutions of the structure by replacing part of the barium cations with metal cations with an oxidation state of +3 (Nd^{3+}, Eu^{3+}, Ce^{3+}, and Y^{3+}) contributes to the formation of solid solutions whose conductivity is higher than the conductivity of the initial structure [6,8,9]. So, for example, a solid solution formed by replacing 0.10 m.p. of barium cations with yttrium cations has conductivity at room temperature ($1.5\cdot10^{-3}$ S/cm) almost 2 orders of magnitude higher than $BaSnF_4$ conductivity ($1.4\cdot10^{-5}$ S/cm) [9]. The phases formed by replacing part of the barium cations with cations Nd^{3+}, Eu^{3+}, and Ce^{3+} also have high conductivity: $Ba_{0.97}Nd_{0.03}SnF_{4.03}$ ($9\cdot10^{-4}$ S/cm) [8], $Ba_{0.98}Ce_{0.05}SnF_{4.05}$ ($5\cdot10^{-4}$ S/cm) [6], and $Ba_{0.98}Eu_{0.02}SnF_{4.02}$ ($4\cdot10^{-4}$ S/cm) [8]. It is believed [6,8,9] that the increase in conductivity of the formed fluoride conducting phases is due to an increase in the concentration of interstitial fluorine anions.

Information on anion deficient solid solutions based on $BaSnF_4$ formed by alloying with cation substituents with oxidation degree +1 is extremely limited. It is known [7] that solid solutions formed by replacing a part of barium cations with potassium cations have lower conductivity, however, replacing potassium cations in non-stoichiometric phases with $Ba_{(1-x)}Sn_{(1+x)}F_4$ ($0<x<0.1$) leads to an increase in conductivity in the high temperature range. The phase $(K_{0.10}Ba_{0.90})_{0.90}Sn_{1.10}F_{3.91}$ exhibits the best conductive properties ($\sigma=8.7\cdot10^{-3}$ S/cm at 573 K).

This study reports the conductivity of phases formed by replacing a part of the barium cations with La^{3+} cations in a solid solution of non-stoichiometric composition of $Ba_{0.9}Sn_{1.1}F_{4.0}$. Our aim was to identify the relationship between the composition and conductivity of fluoride-conducting phases.

Experimental

For the synthesis of fluoride-conducting phases $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$, analytical grade reagents from EMSURE® ACS were used, which contained the main substance of at least (wt.%): La_2O_3 99%, $Ba(NO_3)_2$ 99.95%, SnF_2 99% and NH_4F 99%.

The synthesis of solid solutions of the composition $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$ was carried out in several stages [7,10,11]. First, solid solutions of the composition $Ba_{1-x}La_xF_{2+x}$ were synthesized by coprecipitation from aqueous-alcoholic solutions. The initial solution 0.1 M $La(NO_3)_3$ was prepared by dissolving the La_2O_3 in concentrated nitrate acid, followed by dilution with an aqueous-alcoholic solution 1:1. A solution of 0.1 M $Ba(NO_3)_2$ was prepared by dissolving an equivalent amount of $Ba(NO_3)_2$ in an aqueous-alcoholic solution 4:1. The prepared solutions were then mixed in calculated amounts and magnetically stirred for 10 minutes. The resulting mixture was added dropwise to a solution of 1 M NH_4F taken in a seven-fold excess for complete compatible precipitation of barium and lanthanum fluorides. The resulting precipitate was separated from the reaction medium by centrifugation, washed with distilled water and dried in air for 24 hours at 333 K.

At the second stage, the synthesized solid solutions were sintered with SnF_2 in a molar ratio of 0.45:0.55 to obtain non-stoichiometric phases of the composition $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$. The synthesis was carried out under argon at 773 K for 30 minutes.

The synthesized phases were investigated by X-ray diffraction analysis (XRD) on a diffractometer DRON-3M with CuK_α radiation in the angle range from 10 to 80 degrees in increments of 0.04 degrees and exposure of 3 s at each point. Identification of the obtained XRD patterns was performed using the available JCPDS database. The XRD patterns were processed using the Match computer program, and unit cell volume was calculated in the UnitCell program.

The conductivity of solid electrolytes was determined by an alternating current method using a two-electrode circuit using an «immittance meter (RLC) E7-30» spectrometer. For studies, tableted compressed (10 MPa for 3 minutes) polycrystalline samples of cylindrical shape with a diameter of 8.0 mm and a thickness of 1.2–1.6 mm were taken

and placed in a cell with polished platinum current leads.

The temperature dependence of the electrical conductivity of the obtained phases was examined at a frequency of 100 kHz. Measurements were carried out after thermostating in a cooling mode in the temperature range of 298–623 K in an argon atmosphere. The measurement error of electrical conductivity did not exceed 4%, and the measurement error of the temperature was ±2 K.

Specific electrical conductivity was calculated from the equation:

$$\sigma = l/s \cdot R, \quad (1)$$

where l is the thickness of the cylindrical sample; s is the contact area; and R is the active resistance.

The contribution of the electronic component to the total electrical conductivity was determined by chronoamperometric measurements by the Hebb-Wagner method [14]. The study was carried out according to a two-electrode scheme using platinum blocking electrodes in the potential range of 0.6–3.2 V. The cell was polarized using a Masteram MR5010E power supply, and the current drop was measured with a laboratory multimeter Tektronix DMM4020. Measurements were made in the temperature range of 403–473 K in cooling mode.

The study of the electrochemical stability window was carried out by cyclic voltammetry using the MTech POL-21 device in a two-electrode cell with platinum electrodes at a potential scanning speed of 10 mV/s at a temperature of 100°C. For the studies, pressed polycrystalline samples of cylindrical shape with a diameter of 8.0 mm and a thickness of 1.2–1.6 mm were used.

Results and discussion

The results of XRD analysis revealed that the synthesized samples of solid solutions of $Ba_{1-x}La_xF_{2+x}$ have a cubic crystalline lattice (sp. group. *Fm3m*) and are isostructural with BaF_2 (JCPDS card No. 00-004-0452) (Fig. 1).

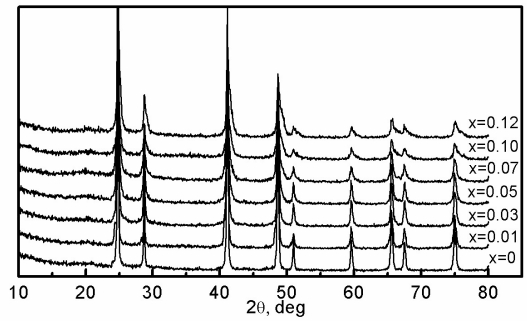

Fig. 1. XRD patterns of the synthesized samples of solid solutions $Ba_{1-x}La_xF_{2+x}$

Based on the results of XRD analysis, the volume of elementary cells of the obtained samples was calculated. The La^{3+} cation has a smaller effective ionic radius than that of Ba^{2+}, so for Ba^{2+} it is 0.135 nm, and for La^{3+} 0.101 nm (coordination number 6) [13]. This is why the unit cell volumes decrease from 2.386 nm^3 in BaF_2 to 2.371 nm^3 in $Ba_{0.88}La_{0.12}F_{2.12}$. This relationship is described by a linear function consistent with the rules of crystallographic substitution (Fig. 2). We determined the area of existence of single-phase solid solutions $Ba_{1-x}La_xF_{2+x}$, which is limited to 0.12 m.p., because the XRD pattern with the content of the substituent x=0.12 shows additional reflexes of the first four diffraction reflexes (Fig. 1). A further increase in the substituent leads to an increase in the intensity of these signals and a decrease in the main phase signals.

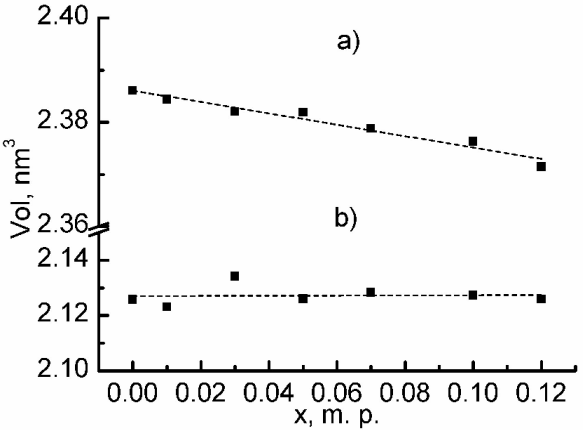

Fig. 2. Unit cell volumes of the synthesized samples of solid solutions (a) $Ba_{1-x}La_xF_{2+x}$ and (b) $Ba_{1-x}La_xSnF_{4+x}$

The synthesized samples of solid solutions $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$ have a tetragonal crystal lattice (P4/nmm) isotype $BaSnF_4$ (JCPDS card No. 00-038-0738) (Fig. 3). The concentration of the substituent in them is in the $0<x\leq0.12$ region and practically affects the volume of the unit cell. In the field of existence of solid solutions, it is estimated to be 2.125±0.0084 nm^3. The calculated parameters of the crystalline lattice are presented in Fig. 2.

Analysis of the obtained results shows that with an increase in both temperature and concentration of the substituent, the conductivity of the synthesized phases increases (Fig. 4, Table 1). This may be due to the fact that both an increase in temperature and an increase in the concentration of the substituent contribute to an increase in the concentration of charge carriers, inter-node fluorine anions. When the temperature increases, their concentration increases due to the jump of fluorine anions from sedentary

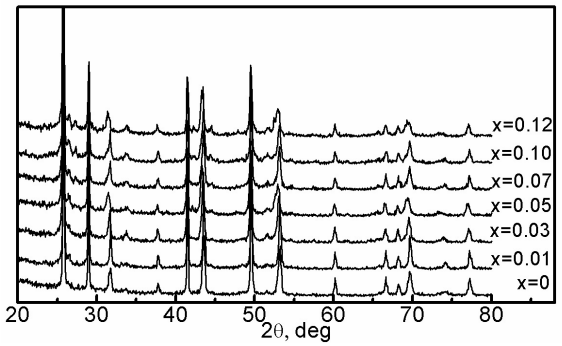

Fig. 3. XRD patterns of solid solutions $Ba_{1-x}La_xSnF_{4+x}$

positions of the anionic subgroup to more highly mobile [3–6,10,11]; and when the concentration of the substituent increases due to the formation of excess fluorine anions (replacement of the cation with a lower oxidation state (Sn^{2+}) with a cation of a higher oxidation state (La^{3+}) according to Kroger-Vink schemes:

$$LaF_3(BaF_2) \rightarrow La^{*}_{Ba} + F_i^{'}.$$

The $Ba_{0.78}L_{0.12}Sn_{1.10}F_{4.12}$ phase shows the highest conductivity (Fig. 4, Table 1).

The electrical conductivity relationships of the synthesized fluoride conducting phase samples are satisfactorily approximated by the following Arrhenius-Frenkel equation:

$$\sigma T = A \cdot \exp\left(-\Delta E_a/kT\right), \quad (2)$$

where A is the pre-exponential factor; ΔE_a is the activation energy of ion conductivity; and k is the Boltzmann constant.

The determination coefficients estimated for high-temperature and low-temperature have values close to unity, from 0.98 to 0.99 (Table 1).

The synthesized samples of solid solutions $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$ have a lower energy of activation of conductivity compared to the initial $Ba_{0.90}Sn_{1.10}F_{4.00}$ phase and in the studied temperature range it is the less, the greater the content of the substituent (Table 1).

An important requirement for solid fluoride conductive electrolytes is low electron conductivity. The electron conductivity of the sample with the best ionic conductivity ($Ba_{0.78}La_{0.12}Sn_{1.12}F_{4.12}$) was determined by chronoamperometric measurements using the Hebb-Wagner method. Figure 5a shows a rapid decrease in current to a stationary state, in which conductivity is realized exclusively by electrons. A plateau (Fig. 5b) has been established for which electronic conductivity can be determined from the following equation:

$$I_S = \frac{RTS\sigma_n}{Fl}. \quad (3)$$

Given the obtained values (Table 2) of electron conductivity, it can be assumed that the conductivity for the composition of the $Ba_{0.78}La_{0.12}Sn_{1.12}F_{4.12}$ is realized mainly by fluorine anions.

The electrochemical stability of the synthesized samples of fluoride conducting phases $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$ was evaluated by cyclic voltammetry (Fig. 5). Voltammograms were recorded from the stationary potential to +2.0 V, and then from 2.0 V to −2.0 V (line I) and reverse from −2.0 V to 2.0 V (line II) (Fig. 5a). Analysis of the obtained results shows that a sharp increase in the current flowing through the cell is recorded on the voltammetric responses of samples in the cathode region when the polarization of electrodes is higher than −1.5 V. An increase in current strength is observed on the reverse scan of the voltamperogram in the anode region (line II) at potential values above 1.9 V. The obtained

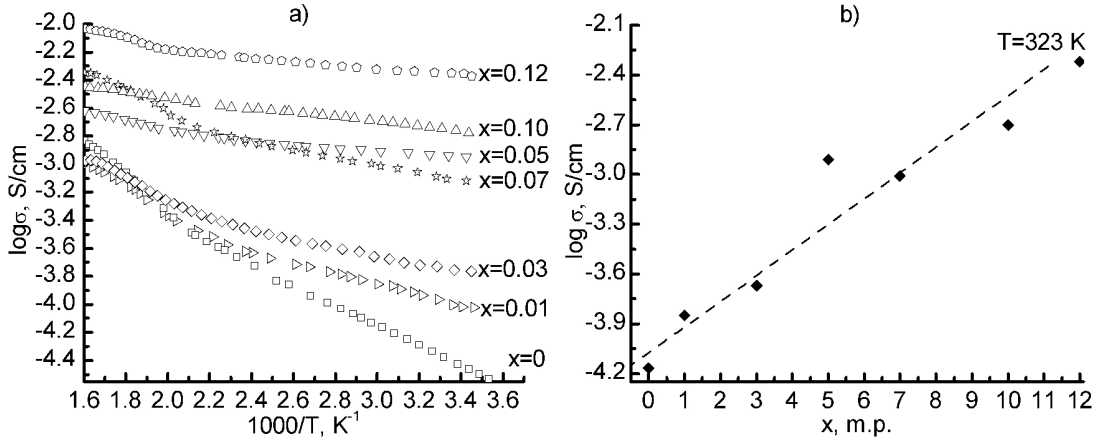

Fig. 4. Dependence of electrical conductivity of solid solutions $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$ with different content (x) of heterovalent substituent on temperature (a) and its content (b)

results suggest that in the potential region of −1.5 V ... + 1.9 V in the studied fluoride conducting phases there are no electrochemical transformations, which does not significantly depend on the content of the substituent. At potentials higher than −1.5 V in the cathode region, processes of electrolyte degradation occur on platinum electrodes due to reduction processes, and in the anode region at potentials higher than 2.0 V degradation occurs due to oxidation processes. When cycling in the specified region of potentials, the voltammogram practically does not change (Fig. 5b).

Conclusions

The sintering of solid solutions $Ba_{1-x}La_xF_{2+x}$ (x≤0.12) with tin (II) fluoride in a molar ratio of 0.45:0.55 at 773 K in an argon atmosphere allows preparing the solid solutions of substitution $Ba_{0.90-x}La_xSn_{1.10}F_{4+x}$ (x≤0.12), whose crystal lattice is isotypic with $BaSnF_4$ and corresponds to tetragonal syngony (P4/nmm).

The conductivity of the synthesized phases is higher than the conductivity of the initial fluoride conducting phase $Ba_{1-x}La_xF_{2+x}$ (x≤0.12) and increases with the concentration of the substituent. The activation energy decreases, and to a greater extent, the greater the content of the substituent. The $Ba_{0.78}La_{0.12}Sn_{1.10}F_{4.12}$ phase reveals the highest conductivity, which is realized mainly by fluorine anions.

In the potential region of −1.5 V ... +1.9 V in the studied fluoride conducting phases, no electrochemical transformations occur regardless of the content of the substituent.

Table 1

Electrical conductivity parameters of solid solutions

Sample	Temperature range, K	ΔE_a, eV (±0.01)	lg A, (S/cm)·K	σ, S/cm (±4%)	R	T, K (±2 K)
$Ba_{0.90}Sn_{1.10}F_4$	624–415	0.284	2.24	$1.46\cdot10^{-3}$	0.99	624
	415–282	0.168	0.91	$2.94\cdot10^{-5}$	1.00	282
$Ba_{0.89}La_{0.01}Sn_{1.10}F_{4.01}$	622–414	0.219	1.58	$1.01\cdot10^{-3}$	0.99	622
	414–288	0.104	0.24	$9.44\cdot10^{-5}$	1.00	288
$Ba_{0.87}La_{0.03}Sn_{1.10}F_{4.03}$	623–432	0.192	1.39	$1.06\cdot10^{-3}$	0.99	623
	432–289	0.088	0.21	$1.73\cdot10^{-4}$	0.99	289
$Ba_{0.85}La_{0.05}Sn_{1.10}F_{4.05}$	624–441	0.108	1.04	$2.42\cdot10^{-3}$	0.99	624
	441–292	0.054	0.44	$1.13\cdot10^{-3}$	0.99	292
$Ba_{0.83}La_{0.07}Sn_{1.10}F_{4.07}$	624–446	0.197	2.07	$4.48\cdot10^{-3}$	1.00	624
	446–290	0.087	0.83	$7.79\cdot10^{-4}$	1.00	290
$Ba_{0.80}La_{0.10}Sn_{1.10}F_{4.10}$	623–449	0.091	1.09	$3.57\cdot10^{-3}$	1.00	623
	449–296	0.061	0.76	$1.73\cdot10^{-3}$	1.00	296
$Ba_{0.78}La_{0.12}Sn_{1.12}F_{4.12}$	623–492	0.128	1.81	$9.22\cdot10^{-3}$	0.99	622
	492–296	0.056	1.06	$4.26\cdot10^{-3}$	0.99	293

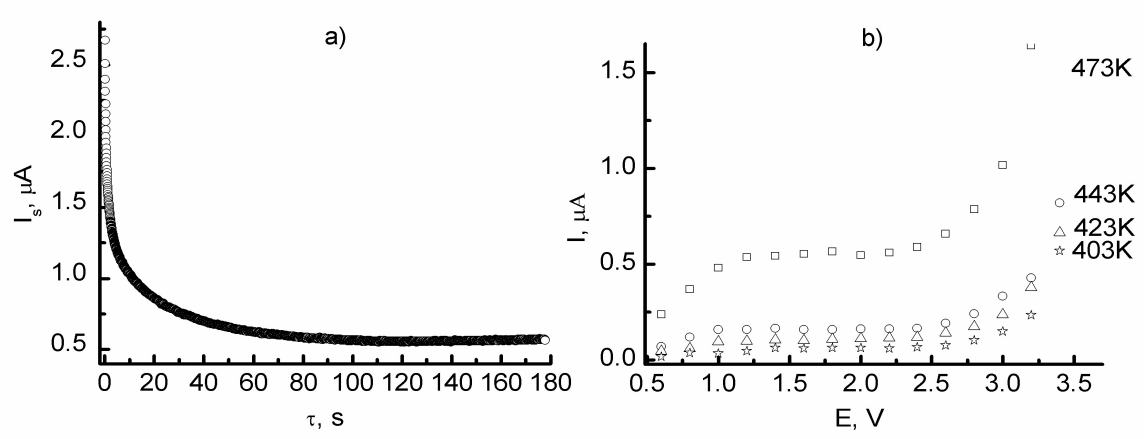

Fig. 5. Chronoamperometry of solid electrolyte $Ba_{0.78}La_{0.12}Sn_{1.12}F_{4.12}$: dependences of current strength on polarization time (E=2.0 V at 473 K) (a) and applied voltage (b)

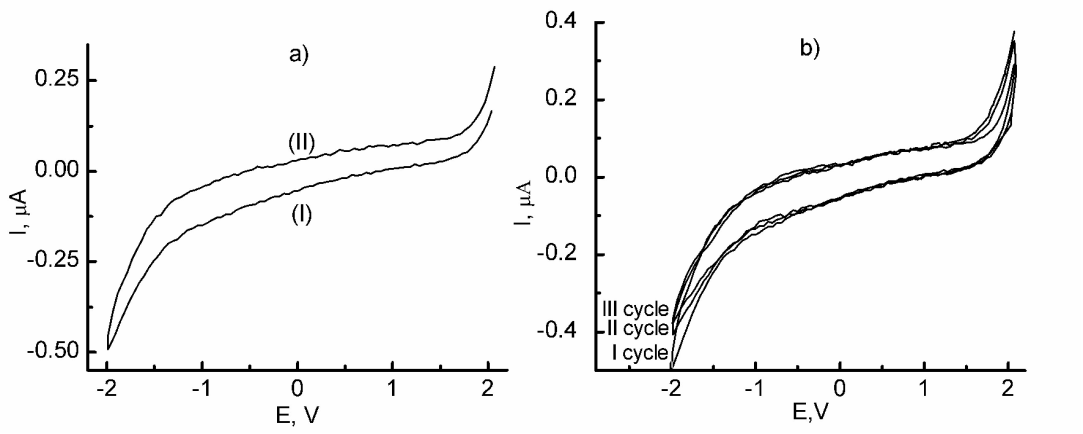

Fig. 6. Cyclic voltammograms of the phase $Ba_{0.87}La_{0.03}Sn_{1.10}F_{4.03}$ at T=373 K

Table 2

Electronic conductivity of the sample composition $Ba_{0.78}La_{0.12}Sn_{1.12}F_{4.12}$

T, K	I_s, μA	σ_n, S/cm	t_{F^-}
473	0.56	$3.80 \cdot 10^{-6}$	1.00
443	0.16	$1.18 \cdot 10^{-6}$	1.00
423	0.10	$7.95 \cdot 10^{-7}$	1.00
403	0.06	$4.82 \cdot 10^{-7}$	1.00

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ПРОВІДНІСТЬ НЕСТЕХІОМЕТРИЧНИХ ФТОРИД-ІОН-ПРОВІДНИХ ФАЗ $Ba_{0,9-x}La_xSn_{1.1}F_{4+x}$

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Фторидні провідні фази $Ba_{0,9-x}La_xSn_{1,10}F_{4+x}$ (x≤0,12), утворені заміщенням частини катіонів барію катіонами лантану у вихідній нестехіометричній фазі $Ba_{1-x}La_xF_{2+x}$ (x≤0,12), утворюють кристалічну решітку тетрагональної сингонії (P4/nmm) ізотипну $BaSnF_4$. Провідність синтезованих фаз вища провідності вихідної сполуки, зростає з підвищенням температури і концентрації замісника. Найбільшу електропровідність має фаза складу $Ba_{0,78}La_{0,12}Sn_{1,10}F_{4,12}$, яка реалізується переважно аніонами фтору. Зі збільшенням вмісту замісника енергія активації провідності зменшується, що характерно як для високотемпературної, так і для низькотемпературної зон. Синтезовані зразки фторидпровідних фаз не розкладаються в інтервалі потенціалів −1,5 ... +1,9 В.

Ключові слова: фторидпровідні фази, фториди стануму, барію, лантану, тверді розчини заміщення, електропровідність, вольтамперометрія.

CONDUCTIVITY OF NON-STOICHIOMETRIC FLUORIDE-CONDUCTING PHASES $Ba_{0.9-x}La_xSn_{1.1}F_{4+x}$

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Fluoride-conducting phases $Ba_{0.9-x}La_xSn_{1.10}F_{4+x}$ (x≤0.12), formed by the partial substitution of barium cations with lanthanum cations in the initial non-stoichiometric phase $Ba_{1-x}La_xF_{2+x}$ (x≤0.12), crystallize in a tetragonal syngony (*P4/nmm*) isotypic to $BaSnF_4$. The conductivity of the synthesized phases is higher than that of the parent compound and increases with temperature and substituent concentration. The highest conductivity is observed in the $Ba_{0.78}La_{0.12}Sn_{1.10}F_{4.12}$ phase, where fluoride anions are the primary charge carriers. The activation energy of conductivity decreases with increasing substituent content, which is characteristic of both high- and low-temperature regions. The synthesized fluoride-conducting phases remain stable within the potential range of −1.5 to +1.9 V.

Keywords: fluoride-conducting phases; tin fluorides; barium; lanthanum; solid substitution solutions; electrical conductivity; voltammetry.

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