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SYNTHESIS AND ELECTRICAL CONDUCTIVITY OF FLUORIDE-CONDUCTING PHASES $SrSnF_4$ AND $Pb_xSr_{1-x}SnF_4$

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Abstract

In the article it is proposed to synthesize free of impurity phases complex fluoride $SrSnF_4$ by sintering lead and strontium fluorides in an equivalent ratio at temperatures higher than temperature of its phase transition from cubic modification into tetragonal (623 K). The duration of synthesis to obtain $SrSnF_4$ free from impurity phases at 773 K is 1 hour, and at 823 K – half an hour. Synthesis at temperatures lower than temperature of phase transition is associated with the formation of impurity phases different in composition and structure from $SrSnF_4$. The conductivity of such samples at 293 K is almost an order of magnitude higher than the conductivity of $SrSnF_4$, which is free from impurity phases ($1.18 \cdot 10^{-5}$ S/cm, Ea = 0.28 eV). The synthesis of fluoride-conducting phases $Pb_xSr_{1-x}SnF_4$ is proposed to be carried out by the method of sintering the initial components in a given ratio in two stages. First, the initial mixture is sintered in the temperature range of 423÷473 K for an hour. Then the temperature is raised to 773÷823 K and the reaction mixture is sintered for another hour. The crystal lattice of $Pb_xSr_{1-x}SnF_4$ samples of solid solutions of the isovalent substitution synthesized in this way, with the content of the substituent of $0 < x \le 0.25$, corresponds to tetragonal lattice (P4/nmm) and is similar to $SrSnF_4$. At a higher content of the substituent ($0.25 < x \le 0.30$), the symmetry of the crystal lattice does not change, but corresponds to another structural type (β-$PbSnF_4$). The highest conductivity ($1.12 \cdot 10^{-3}$ S/cm at 293 K) and the lowest activation energy (0.063 eV) has the $Pb_{0.25}Sr_{0.75}SnF_4$ phase, which corresponds to the region where the structural type of the crystal lattice is rearranged with increasing of content of the substituent.

Keywords: fluoride-conducting phases; tin; strontium; lead fluorides; synthesis; electrical conductivity.

СИНТЕЗ ТА ЕЛЕКТРОПРОВІДНІСТЬ ФТОРПРОВІДНИХ ФАЗ $SrSnF_4$ ТА $Pb_xSr_{1-x}SnF_4$

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Анотація

Запроновано синтез складного фториду $SrSnF_4$, вільного від домішкових фаз, методом спікання фторидів свинцю та стронцію в еквівалентному співвідношенні за температур, вищих за температуру фазового переходу його кубічної модифікації у тетрагональну (623 К). Тривалість синтезу для отримання вільного від домішкових фаз $SrSnF_4$ за 773 К складає 1 год., а за 823 К – пів години. Синтез за температур, нижчих за температуру фазового переходу, супроводжується утворенням домішкових фаз, відмінних за складом та структурою від $SrSnF_4$. Провідність таких зразків за 293 К майже на порядок величини вища за провідність $SrSnF_4$, вільного від домішкових фаз, і складає $1.18 \cdot 10^{-5}$ См/см, (E_a = 0.28 еВ). Синтез фторидпровідних фаз $Pb_xSr_{1-x}SnF_4$ запропоновано здійснювати методом спікання вихідних компонентів у заданому співвідношенні в дві стадії. Спочатку вихідну суміш спікають у температурному інтервалі 423÷473 К протягом години. Потім температуру піднімають до 773÷823 К та витримують реакційну суміш ще протягом години. Кристалічна гратка синтезованих таким чином зразків твердих розчинів ізовалентного заміщення $Pb_xSr_{1-x}SnF_4$ з вмістом замісника $0 < x \le 0.25$ відповідає тетрагональній сингонії (пр. гр. P4/nmm) та ізотипна $SrSnF_4$. За умови більшого вмісту ($0.25 < x \le 0.30$) симетрія кристалічної гратки не змінюється, але відповідає вже іншому структурному типу (β-$PbSnF_4$). Найвищу провідність ($1.12 \cdot 10^{-3}$ См/см за 293 К) та найменшу енергію активації (0.063 еВ) має фаза складу $Pb_{0.25}Sr_{0.75}SnF_4$, яка за вмістом замісника відповідає області, де відбувається перебудова структурного типу кристалічної гратки.

Ключові слова: фторидпровідні фази; фториди олова; стронцію; свинцю; синтез; електропровідність.

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Introduction

The current level of science and technology development requires the creation of new energy sources that have high specific energy characteristics, that are safe and reliable while in operation, and that can be an alternative to modern lithium-ion batteries (LIBs). One of the promising ways to solve this problem is to create solid-state current sources in which the electromotive force is generated by Red/Ox processes accompanied by the reversible transfer of fluoride anions through the electrode/electrolyte interfacial surface, named fluoride-ion batteries (FIBs) [1–6].

The theoretical specific energy of such current sources is estimated to be 5 kW·h/dm^3 [1–3], which is significantly higher than that of lithium-ion batteries (LIBs). The large-scale commercial production and application of fluoride-ion batteries are limited by the lack of properly developed electrode and electrolyte materials that would ensure the reversible transfer of fluoride ions across the electrode/electrolyte interface in a wide range of values of potential [3–5].

Among a number of currently known fluoride-conducting phases that can be applied to create FIBs, there are at least three structural types of metal fluorides with high unipolar conductivity [1–15]. These are metal fluorides with the structure type of fluorite ($M_{1-x}M^*_xF_{2-x}$, M is alkaline earth element, lead and tin, M* is heterovalent substituent, including alkaline and rare earth elements with different numbers of oxidation), gagarinite ($MPbLnF_6$, M is alkaline metal) and tisonite ($Ln_{1-x}M_xF_{3-x}$, M is a heterovalent substituent). Compounds with structure of fluorite have the highest conductivity, in particular fluorides which are similar in structure to β-$PbSnF_4$. The lowest conductivity values are typical for representatives of the tisonite structure, but they have a much wider window of electrochemical stability. When selecting compounds to be applied for the creation of FIBs, not only their conductivity but also their decomposition voltage should be taken into account.

Fluoride-conducting phases formed by partial substitution of cations of complex fluorides $MSnF_4$ (M=Ca, Ba, Sr, Pb) with cations of various metals have the potential to be used to create electrode and electrolyte materials for FIBs [15-21]. A characteristic feature of compounds of this type is the layered arrangement of cations in the crystal lattice that is parallel to the *c*-axis [–M–M–Sn–Sn–M–M–]. The conductivity of such phases depends not only on the presence of crystal lattice defects, but also on the arrangement of fluorine anions between cation layers, and the size and electronic configuration of substituent cations [14; 20]. For example, the conductivity of tetragonal modification of β-$PbSnF_4$ at 373 K and its thermodynamic decomposition voltage are $1\cdot10^{-3}$ S/cm and 3.3 V, respectively [3; 12]. The conductivity of similar in structure $SrSnF_4$ compound at the same temperature is lower $3.5\cdot10^{-5}$ S/cm [13; 14]. Unlike lead and tin cations, the strontium cation does not have a lone electron pair (s^2), on its outer electron shell, which is stereoactive and significantly affects the stereometry of the coordination polyhedron of cations, and, consequently, affects the mobility of fluoride anions [15].

It was shown earlier [17] that partial substitution of lead cations in the fluoride-conducting phase of $Pb_{0.86}Sn_{1.14}F_4$ with isovalent barium cation, which also does not have a lone electron pair (s^2) on the outer electron shell, leads to increase in conductivity of obtained phases. The highest conductivity at 373 K and the lowest activation energy (σ = 0.12 S/cm, E_a = 0.11 eV) has the $Pb_{0.43}Ba_{0.43}Sn_{1.14}F_4$ phase.

Thus, the conductivity of fluoride-conducting phases formed by partial substitution of cations in $MSnF_4$ complex fluorides with cations of other metals depends not only on their quantity and quality of content but also on their electronic configuration.

In this regard, the studies of the effect of the electronic configuration of cation of the isovalent substituent on the mobility of fluorine anions and the conductive properties of $MSnF_4$ complex fluorides are of both scientific and practical interest.

This article presents the results of studies of the effect of partial isovalent substitution of strontium cations by lead cations in the $SrSnF_4$ complex fluoride and the conductivity of the formed phases. These cations have similar ionic radii (1.18 and 1.19 Å, respectively) [22] but different electronic configurations.

The objective of the work was to determine the optimal conditions for the synthesis of the $SrSnF_4$ and $Sr_{1-x}Pb_xSnF_4$ phases, and to study what affect the content of substituent and temperature have on their electrical conductivity and structural features.

Experimental and methods

Due to significant difference in the values of the melting points of strontium fluoride and barium fluoride [23], special conditions for the synthesis of complex $SrSnF_4$ fluoride by sintering the starting components are needed.

At least several methods for the synthesis of $SrSnF_4$ are known [13; 14]. One of them comprises the sintering of a mixture of strontium and tin fluorides thoroughly grinded in an agate mortar in an equal molar ratio [13]. The resulting mixture was pressed into tablets in stainless steel molds and then sintered. Sintering was carried out in a copper tube at a pressure reduced to $0.13 \cdot 10^{-3}$ MPa at 523 K for 12 hours. The resulting product was then annealed in vacuum quartz tubes in two stages: 1 hour at 473 K and 1 hour at 773 K followed by cooling to room temperature.

According to another method, $SrSnF_4$ was synthesized by the mechanochemical method using a ball mill [14]. The mechanochemical synthesis was carried out for at least 10 hours, after which the obtained samples were annealed at a temperature of 623 K for 4 hours [14]. Both known methods of synthesizing $SrSnF_4$ are quite laborious and time-consuming, and don’t always provide a single-phase compound that corresponds to the stoichiometric composition.

An individual metal fluorides with a basic compound content of at least 99.99 wt.% were used for the synthesis of fluoride-conducting phases. Summarizing the results of previous studies [12–14; 17], the synthesis of $SrSnF_4$ was carried out by sintering in two stages. At the first stage, the initial mixture of thoroughly dehydrated tin and strontium fluorides, taken in an equal molar ratio, was kept for 1 hour at temperature of 423÷473 K, which did not exceed the melting point of tin fluoride (488 K). The synthesis was carried out in a platinum crucible under a dry argon atmosphere. Then the temperature was raised to 773÷823 K and the reaction mixture was kept at this temperature for another hour. Before sintering, the mixture was thoroughly grinded in an agate mortar. After sintering, the resulting product was again thoroughly grinded in an agate mortar. A fraction of the synthesized sample with a particle size of no more than 20 μm was used for conductivity studies.

Samples of $Pb_xSr_{1-x}SnF_4$ fluoride-conducting phases were synthesized by a similar method. The mixtures of previously dehydrated initial components in a given ratio were thoroughly grinded in an agate mortar and sintered in a platinum crucible under a dry argon atmosphere first for 1 hour in the temperature range of 423÷473 K. Then the temperature was raised to 773÷823 K and the reaction mixture was kept at this temperature for another hour. After sintering, the product was grinded in an agate mortar to obtain fractions with a particle size of no more than 20 μm, which were used for further studies.

The X-ray analysis (XRD) of the synthesized samples was performed on a DRON-3M diffractometer applying CuK_{α} radiation, the measurements were conducted in the range of angles from 10 to 80 degrees. The JCPDS database and the Match and UnitCell PC programs were used to identify and process the obtained diffraction patterns [24]. The crystal lattice parameters of the synthesized phases were calculated by the Rietveld method using the «Jana2020» program [25].

The electrical conductivity of the synthesized samples of fluoride-conducting phases was determined by the method of electrochemical impedance spectroscopy using an Autolab electrochemical module (Ekochemie) and a frequency analyzer FRA (Frequency Response Analyzer) in the frequency range of 10^{-1}–10^{6} Hz (with an output signal amplitude of 10 mV) and by the bridge method of conductivity measurement at a frequency of 100 kHz using a two-electrode circuit. Pressed cylindrical polycrystalline samples with a diameter of 8 mm and a thickness of 2.0–3.0 mm were used for the study. Smooth polished platinum plates were used as current leads to the samples. The measurements were carried out while cooling in an argon atmosphere in the range of 298–773 K after preliminary thermostatting. In order to eliminate the influence of the porosity of the samples on the electrical conductivity measurements, samples were prepared from finely dispersed fractions with a particle size of no more than 20 μm under a pressure of 140 atm using the same molds. The specific conductivity was calculated using the formula $\sigma = l/s \cdot R$, where l is the thickness of the cylindrical sample, s is the contact area, and R is the active resistance based on the results of impedance or bridge measurements [12; 17].

Results and Discussion

The analysis and processing of the obtained results allowed to indicate that the temperature regime of synthesis significantly affects both the phase composition and electrical conductivity of $SrSnF_4$.

The X-ray diffraction patterns of the samples synthesized under different conditions correspond to the diffractograms of $SrSnF_4$ samples synthesized by the method of mechanochemical synthesis in ball mills [14] (Fig. 1).

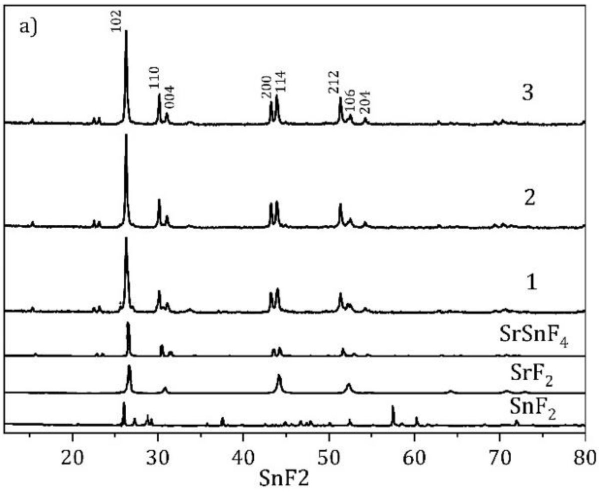

Fig. 1. X-ray diffraction patterns of the initial stannum and strontium fluorides, $SrSnF_4$ complex fluoride synthesized by the mechanochemical method [14] and by sintering under different conditions: 1 – sample 1 – synthesis for 1 h at 473 K + 1 h at 773 K (* - specified in text); 2 – sample 2 – synthesis for 1 h at 773 K; 3 – sample 3 – synthesis for 0.5 h at 823 K

Interpretation with the use of Match and UnitCell PC programs and «Jana2020» [25] indicates that the synthesized samples form a tetragonal lattice (P4/nmm space group) similar to the $BaSnF_4$. The crystal lattice parameters of $SrSnF_4$ samples synthesized under different conditions are given in Table 1. The crystal lattice parameters of the $SrSnF_4$ sample synthesized by the mechanochemical method were used for the calculations [14]. From the data presented, it is clear that the $SrSnF_4$ sample synthesized in two stages (sintering for 1 h at 473 K and 1 h at 773 K) has slightly larger cell dimensions. In addition, the X-ray diffraction pattern (Fig. 1, curve 1) shows reflexes (marked with an *), which may indicate the presence of ather phases with a chemical composition and crystal lattice different from $SrSnF_4$. For example, the reflexes at 2θ = 26.50, 30.60, 52.20 may indicate the presence of a small amount of SrF_2.

Table 1

Crystal lattice parameters of $SrSnF_4$ samples synthesized by sintering at different temperatures

Sample	a = b, Å	c, Å	V, Å^3	Goodness of fitting (GOF)
1	4.17(6)	11.48(0)	200.15(2)	1.80
2	4.16(9)	11.46(6)	199.28(6),	1.69
3	4.16(9)	11.47(1)	199.37(8),	1.47
mechanochemical synthesis [14]	4.1762(1)	11.4529(8)	199.7473(7)	5.7

Approximately in the same interval of 2θ values, reflexes which are characteristic to SnF_2 (Fig. 1) and complex fluorides of stannum and strontium of a composition different from $SrSnF_4$, such as $Sr(SnF_3)_2$, are recorded [26]. It has been noted [14] that the X-ray diffraction patterns of $SrSnF_4$ samples obtained by the mechanochemical method also show additional reflexes, the intensity of which decreases with increasing in synthesis duration. After reaching a certain synthesis duration which is sufficient for the complete reaction of the initial components, no additional reflexes are recorded on the patterns.

The fact that the $SrSnF_4$ samples synthesized under different temperature conditions have a different composition and lattice parameters is also evidenced by the results of studies of their conductivity. The impedance patterns of $SrSnF_4$ samples synthesized under different conditions in the Z\`-Z\`\` coordinates look like deflected semicircles, the radius of which decreases with increasing temperature, and its center shifts to the high frequency region. A typical diagrams of the example of sample 1 synthesized by sintering at different temperatures (1 h at 473 K and 1 h at 773 K) are shown in Fig. 2.

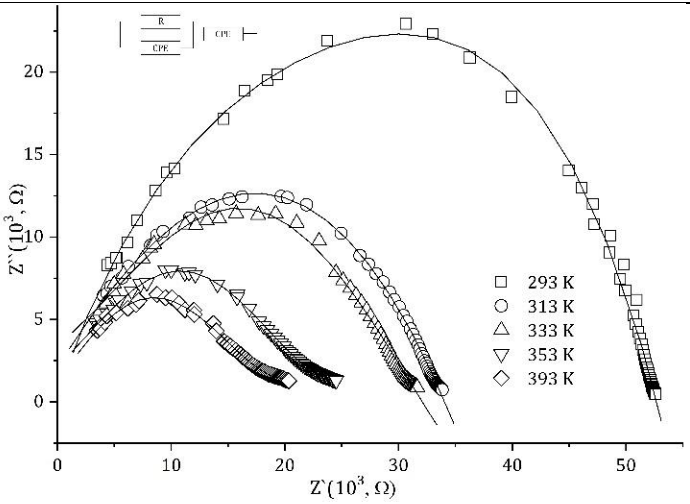

Fig. 2. Impedance pattern of the $SrSnF_4$ sample at different temperatures synthesized by sintering (1 h at 473 K and 1 h at 773 K) and its equivalent circuit

Impedance spectra of this shape are typical for the vast majority of solid ionic conductors, and are approximated successfully by model concepts of the jump conduction mechanism, and indicate that charge transfer is realized mainly by charging carriers localized in the volume of the conducting phase [27–28]. To estimate the conductivity of the synthesized samples at different temperatures from the impedance spectroscopy data, the *R* values of the equivalent circuit were used. The values of conductivity calculated from the impedance spectra and determined by the bridge method in the frequency range of 80÷100 kHz satisfactorily coincide with each other.

Conductivity curves of the synthesized $SrSnF_4$ samples in coordinates: $\ln\sigma - 1000/T$ are satisfactorily approximated by the Arrhenius-Frenkel equation $\sigma T = A\exp(-\Delta E/kT)$, where *A* is the pre-exponential factor, ΔE is the activation energy of conductivity, and *k* is the Boltzmann constant. The polyterms of each of the synthesized $SrSnF_4$ samples at temperatures of 450–500 K show a shift (the so-called «Faraday phase transition») typical for the fluoride-conducting phases of the fluorite structure (Fig. 3).

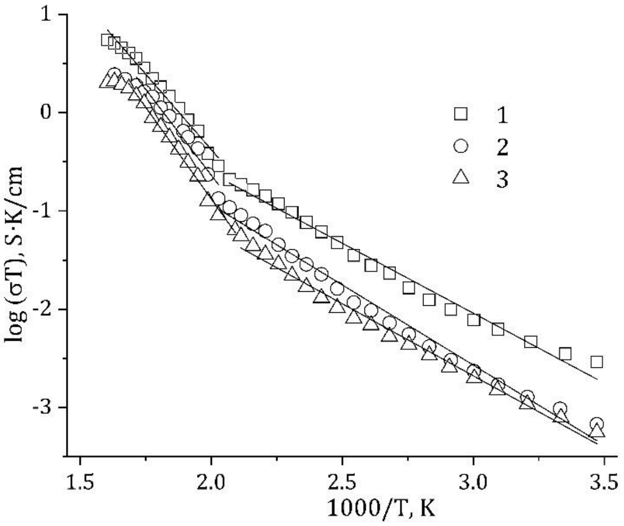

Fig. 3. Conductivity versus temperature curves of $SrSnF_4$ samples synthesized in different temperature regimes in the coordinates of the Arrhenius-Frenkel equation

It is usually caused by the fact that at a certain temperature, not only inter-node fluorine anions participate in charge transfer, but also those that occupy other positions in the anionic sublattice, and additional conduction channels appear due to thermal vibrations of cations [29–30].

The data show that sample 1, which contains traces of additional phases and has the largest crystal lattice volume, has the highest conductivity in the range of temperatures close to room temperature. At 293 K, its conductivity is σ = $1.18 \cdot 10^{-5}$ S/cm, E_a = 0.28 eV. The conductivity of samples 2 and 3 at 293 K is almost identical and almost an order of magnitude lower (σ = $3.36 \cdot 10^{-6}$ S/cm, E_a = 0.32 eV). The conductivity of the $SrSnF_4$ sample synthesized by the mechanochemical method [14] is comparable to that of sample 1 ($\sigma = 1.16 \cdot 10^{-5}$ S/cm, $E_a = 0.48$ eV).

It is known [14] that SrSnF4, in addition to the tetragonal modification, forms a low-temperature metastable cubic modification (*Fm*-3*m* space group, a = 5.7746(3) Å), which, after annealing at 623 K in a nitrogen atmosphere, transforms into a stable tetragonal modification. The conductivity of the low-temperature cubic modification of the $SrSnF_4$ modification at room temperature is almost an order of magnitude lower ($\sigma = 2.05 \times 10^{-6}$ S/cm) [14]. This value is close in order of magnitude to the conductivity of samples 1 and 2, but it cannot be interpreted as evidence that these samples are contaminated with the metastable phase of $SrSnF_4$ of the cubic modification. Firstly, the X-ray diffraction patterns (Fig. 1) do not show the reflexes typical for this phase, and secondly, they were synthesized at a temperature of 773 K, which is much higher than the temperature of the phase transition of the cubic modification to the tetragonal one (623 К) [14]. The higher electrical conductivity of sample 1 may be due to the fact that it contains impurities of foreign fluoride-conducting phases, the chemical composition and crystal lattice of which differ from $SrSnF_4$. Previously, on the example of fluoride-conducting phases $(CeF_3)_{1-m}(CaF_2)_m$ ($m \leq 0.08$) of the tisonite structure, it was shown [31], that a small amount of the secondary phase (excess of the substituent (CaF_2) of the fluorite structure, which practically does not distort the structure of the main phase $(CeF_3)_{0.92}(CaF_2)_{0.08}$) contributes to an increase in its conductivity. This effect can be applied to the development of new electrode and electrolyte materials for fluoride batteries.

According to the results of X-ray phase analysis of the system xPbF$_2$ – (1-x)SrF$_2$ – SnF$_2$ when part of the strontium cations is replaced by lead cations, solid solutions of isovalent substitution are formed, the crystal lattice of which in the interval $0 < x \leq 0.25$ corresponds to tetragonal syngony (*P4/nmm* space group) and is similar to $SrSnF_4$. With a further increase in the concentration of the substituent ($0.25 < x \leq 0.30$) the crystal lattice is rearranged, as evidenced by the absence of reflexes, which are characteristic of this structure in the interval 2θ = 15÷25 degrees, and their merging at 2θ = 30÷31; 43÷44; 51÷53°(Fig. 4).

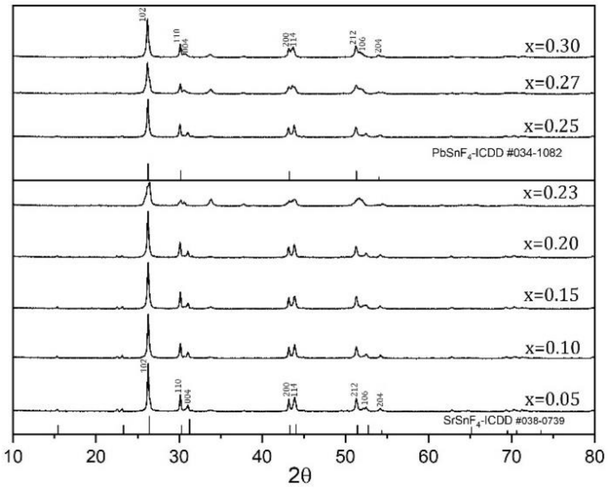

Fig. 4. X-ray diffraction patterns of synthesized samples of $Pb_xSr_{1-x}SnF_4$ solid solutions with different content of an isovalent substituent

Such shape of the diffraction patterns is typical for the structural type of β-$PbSnF_4$, so JCPDS cards No. 034-1082 (β-$PbSnF_4$) and No. 038-0739 ($SrSnF_4$) were used to index the X-ray diffraction patterns and estimate the parameters of the synthesized samples (table 2).

It can be seen from the data that when content of the substituent is low $x<0.23$, the values of lattice parameters and the unit cell volume are almost identical. This may be due to the fact that the radii of strontium and lead ions are similar in size (1.18 and 1.19 Å, respectively. Only in the range of substituent concentrations ($x \geq 0.23$), at which a change in the structural type of the unit cell occurs, a change in the unit cell parameters was noted.

The conductivity of solid electrolytes in general and fluoride conductors in particular largely depends on the structural features of their structure [8; 9; 15] and can be used as a tool to detect structural changes in compounds that are similar in structural type and chemical composition.

Table 2

Crystal lattice parameters of synthesized samples of $Pb_xSr_{1-x}SnF_4$ solid solutions with different content of an isovalent substituent

Content of an isovalent substituent, x	a = b, Å	c, Å	V, Å^3	Goodness of fitting (GOF)
0.05	4.17(3)	11.48(6)	200.01(6)	1.78
0.10	4.17(4)	11.47(3)	199.88(6)	1.65
0.15	4.17(4)	11.48(7)	200.12(0)	1.84
0.20	4.17(5)	11.47(0)	199.92(9)	1.72
0.23	4.25(4)	11.79(7)	213.48(5)	1.69
0.25	4.17(6)	11.47(7)	200.14(7)	1.59
0.27	4.17(9)	11.60(2)	202.61(8)	1.76
0.30	4.16(8)	11.57(0)	200.99(7)	1.73

The analysis of the results characterizing the relation of the conductivity of the synthesized samples of $Pb_xSr_{1-x}SnF_4$ solid solutions and their unit cell volume on the substituent content showed that there is a certain correspondence between them. Both functions reach their maximum values in the range of substituent concentrations in which the structural type of the fluoride-conducting phase changes (Fig. 5).

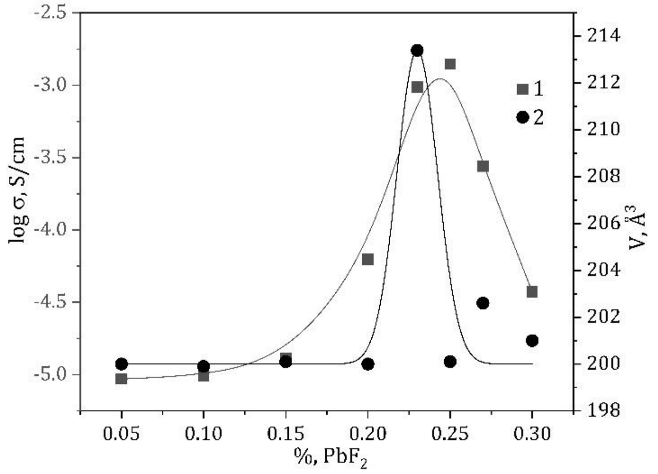

Fig. 5. Conductivity (1) and volume (2) of fluoride-conducting phases of $Pb_xSr_{1-x}SnF_4$ versus the substituent content curves at 373 K

The discovered effect can be used for the targeted search for fluoride-conducting phases with high values of conductivity of other composition and structure and requires further research.

The temperature dependences of the conductivity of the synthesized samples of the $Pb_xSr_{1-x}SnF_4$ fluoride-conducting phases are satisfactorily approximated by the Arrhenius-Frenkel equation, and in the temperature range of 450–500 K show a characteristic shift typical for fluoride-ion conductors of the fluorite structure (Fig. 6).

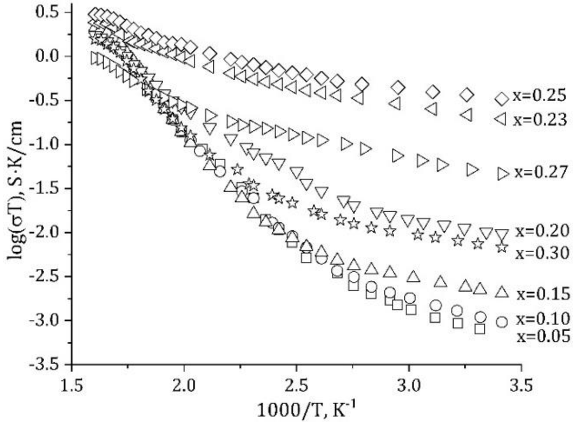

Fig. 6. Conductivity versus temperature curves of $Pb_xSr_{1-x}SnF_4$ samples in the coordinates of the Arrhenius-Frenkel equation

Based on the data obtained, the activation energies of the conductivity of each of the synthesized samples were estimated. The general characterization of the conductivity of samples of $Pb_xSr_{1-x}SnF_4$ solid solutions of different composition is given in table 3.

Table 3

Conductivity parameters of samples of $Pb_xSr_{1-x}SnF_4$ solid solutions with different content of isovalent substituent

Sample	Temperature range, K	ΔEa, eV	lg(A), (S/cm)·K	σ, S/cm	T, K
$Pb_{0.05}Sr_{0.95}SnF_4$	613–433	0.567	1.05	$1.77\cdot10^{-3}$	573
	423–300	0.227	0.15	$2.68\cdot10^{-6}$	298
$Pb_{0.1}Sr_{0.9}SnF_4$	613–418	0.566	1.05	$1.79\cdot10^{-3}$	573
	413–293	0.168	0.19	$3.28\cdot10^{-6}$	293
$Pb_{0.15}Sr_{0.85}SnF_4$	623–423	0.595	1.08	$1.92\cdot10^{-3}$	573
	413–293	0.124	0.14	$6.94\cdot10^{-6}$	293
$Pb_{0.2}Sr_{0.8}SnF_4$	623–423	0.363	0.86	$1.74\cdot10^{-3}$	573
	413–293	0.112	0.23	$3.32\cdot10^{-5}$	293
$Pb_{0.23}Sr_{0.77}SnF_4$	623–443	0.157	0.56	$2.62\cdot10^{-3}$	573
	433–293	0.076	0.13	$6.64\cdot10^{-4}$	293
$Pb_{0.25}Sr_{0.75}SnF_4$	623–443	0.163	0.61	$3.86\cdot10^{-3}$	573
	433–293	0.063	0.14	$1.12\cdot10^{-3}$	293
$Pb_{0.27}Sr_{0.73}SnF_4$	623–483	0.274	0.70	$1.04\cdot10^{-3}$	573
	473–293	0.099	0.21	$1.58\cdot10^{-4}$	293
$Pb_{0.3}Sr_{0.7}SnF_4$	623–447	0.499	0.99	$1.56\cdot10^{-3}$	573
	437–293	0.106	0.25	$2.32\cdot10^{-5}$	293

The fluoride-conducting phase of the $Pb_{0.25}Sr_{0.75}SnF_4$ composition has the highest conductivity and the lowest activation energy value in the entire studied temperature range.

Conclusions

A necessary condition for the synthesis of stoichiometric $SrSnF_4$ complex fluoride free of impurity phases is the sintering of individual stannum and strontium fluorides in an equivalent ratio at temperatures higher than the phase transition temperature of $SrSnF_4$ cubic modification to tetragonal (623 K). The synthesis time decreases with increase of temperature. Thus, for example, the duration of the synthesis of $SrSnF_4$ free of impurities of the initial components at 773 K is 1 hour, and at 823 K it is half an hour. Samples synthesized under conditions that include a sintering stage at 473 K followed by annealing at 773 and 823 K contain impurities of phases that differ in composition and structure from $SrSnF_4$. The conductivity of such samples is almost an order of magnitude higher than the conductivity of $SrSnF_4$ free of impurity phases.

When strontium cations are partially substituted in the $SrSnF_4$ complex fluoride by lead cations in the concentration range of $0.0 < x \leq 0.3$ $Pb_xSr_{1-x}SnF_4$ solid solutions of isovalent substitution are formed, the crystal lattice of which at a range of substituent content $0 < x \leq 0.25$ corresponds to tetragonal syngony (P4/nmm space group) and is similar to $SrSnF_4$, and at a higher content ($0.25 < x \leq 0.30$) corresponds to the structural type of β-$PbSnF_4$. For the synthesis of such fluoride-conducting phases, a two-step sintering method was proposed: isothermal sintering for an hour in the temperature interval of 423÷473 and for an hour at 773÷823 K. The highest conductivity is observed in phases in which the substituent content corresponds to the transition of the crystal lattice from the structural type $SrSnF_4$ to the structural type of β-$PbSnF_4$.

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