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RESEARCH ARTICLE

Synthesis and X-ray-graphical characteristics of the $MeSn_2F_5$ (Me = Na, K, Rb, Cs) fluoride-ion conductors

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Abstract

Objectives. *Pentafluorodistannates of alkali metals are promising materials for use as electrolytes in fluoride-ion batteries due to their electrophysical properties, such as high fluoride-ion conductivity. This work aims to synthesize crystals of alkali metals* $MeSn_2F_5$ *(Me = Na, K, Rb, Cs), carry out X-ray diffraction studies on them, and investigate the possibility of obtaining lithium fluorostannates.*
Methods. *Supersaturated aqueous solutions were employed to synthesize the crystals. The X-ray diffraction (XRD) analysis was carried out.*
Results. *Oversaturated solutions yield microcrystalline powders of sodium, potassium, rubidium, and cesium pentafluorodistannates. The presence of a single-phase was confirmed by XRD analysis of the powders corresponding to the* $MeSn_2F_5$ *(Me = Na, K, Rb, Cs) composition. XRD data analysis and literature indicated that* $MeSn_2F_5$ *(Me = K, Rb, Cs) have a fluorite-like structure, with the cations forming three-layer closest packing. The* $RbSn_2F_5$ *compound was discovered to be isostructural to* KSn_2F_5*. Based on this discovery,* $RbSn_2F_5$ *was reindexed to a hexagonal unit cell with parameters a = 7.40(3) Å, c = 10.12(6) Å (*KSn_2F_5 *P3, a = 7.29(3) Å, c = 9.86(2) Å). The* $CsSn_2F_5$ *compound was reindexed to a monoclinic unit cell (a = 10.03(4) Å, b = 5.92(7) Å, c = 11.96(9) Å, β = 107.4(5)°). A crystallochemical analysis of the pentafluorodistannates was carried out, and common structural motifs were discovered. The motifs are similar to lead tetrafluorostannate* $PbSnF_4$*, the best fluoride-ion conductor. The effect of the pentafluorodistannates structures on the ionic conductivity is considered. The* $LiF–SnF_2$ *system contains no compounds; the compositions were obtained by melting the original fluorides.*

Conclusions. *$MeSn_2F_5$ (Me = Na, K, Rb, Cs) were synthesized and investigated by XRD analysis. The structural characteristics of the $RbSn_2F_5$ and $CsSn_2F_5$ compounds have been redefined. The crystallochemical structure is analyzed in relation to the electrophysical properties of the alkali metal pentafluorodistannates. Pentafluorodistannates $MeSn_2F_5$ (Me = K, Rb, Cs) have a fluorite-like structural motif with cubic parameters a = 5.694 Å (KSn_2F_5), a = 5.846 Å ($RbSn_2F_5$), a = 6.100 Å ($CsSn_2F_5$), with the cations forming three-layer closest packing. The cationic layers alternate like Me–Sn–Sn–Me (Me = K, Rb, Cs). For KSn_2F_5 and $RbSn_2F_5$, they are normal to the three-fold axis and normal to the four-fold axis in the case of $CsSn_2F_5$.*

Keywords: *fluorostannates, X-ray diffraction analysis, fluoride-ion conductivity, tin fluoride, fluorides, crystal chemistry, layered structures*

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НАУЧНАЯ СТАТЬЯ

Синтез и рентгенографические характеристики фтор-ионных проводников $MeSn_2F_5$ (Me = Na, K, Rb, Cs)

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Аннотация

Цель. *Пентафтордистаннаты щелочных элементов являются перспективными материалами для практического применения в качестве электролитов во фторионных аккумуляторах за счет своих электрофизических характеристик, а именно высокой фторионной проводимости. Цель работы заключается в синтезе из раствора и рентгенографическом изучении кристаллов пентафтордистаннатов щелочных металлов $MeSn_2F_5$ (Me = Na, K, Rb, Cs) и исследовании возможности получения фторстаннатов лития.*
Методы. *Синтезировали кристаллы из пересыщенных водных растворов. Исследование проводили методом рентгенофазового анализа (РФА).*
Результаты. *Получены мелкокристаллические порошки пентафтордистаннатов натрия, калия, рубидия и цезия. Исследование методом РФА синтезированных порошков показало их однофазность и соответствие составу $MeSn_2F_5$ (Me = Na, K, Rb, Cs). Анализ данных рентгеновской дифрактометрии и литературных данных показал, что соединения $MeSn_2F_5$ (Me = K, Rb, Cs) являются флюоритоподобными – катионы образуют трехслойную плотнейшую упаковку. Было выявлено, что $RbSn_2F_5$ изоструктурен KSn_2F_5, на основании чего выполнено переиндицирование на гексагональную ячейку: a = 7.40(3) Å, c = 10.12(6) Å (KSn_2F_5 P3, a = 7.29(3) Å, c = 9.86(2) Å). Соединение $CsSn_2F_5$ переиндицировано на моноклинную ячейку (a = 10.03(4) Å, b = 5.92(7) Å, c = 11.96(9) Å; β = 107.4(5)°). Проведен кристаллохимический анализ указанных пентафтордистаннатов, выявлены общие структурные мотивы, подобные лучшему фторионному проводнику – тетрафторстаннату свинца $PbSnF_4$, и рассмотрено влияние строения пентафтордистаннатов на ионную проводимость. В системе LiF–SnF_2 соединений не обнаружено, взаимодействие исследовали сплавлением исходных фторидов.*

Выводы. *Синтезированы и охарактеризованы методом РФА пентафтордистаннаты* $MeSn_2F_5$ *(Me = Na, K, Rb, Cs). Для соединений* $RbSn_2F_5$ *и* $CsSn_2F_5$ *переопределены структурные характеристики. Проанализировано кристаллохимическое строение в приложении к электрофизическим свойствам пентафтордистаннатов щелочных металлов. Пентафтордистаннаты* $MeSn_2F_5$ *(Me = K, Rb, Cs) имеют флюоритоподобный структурный мотив с приведенным параметром ячейки куба a = 5.694 Å (*KSn_2F_5*), a = 5.846 Å (*$RbSn_2F_5$*), a = 6.100 (*$CsSn_2F_5$*) Å, при этом катионы образуют трехслойную плотнейшую упаковку. Слои катионов чередуются в последовательности Me–Sn–Sn–Me (Me = K, Rb, Cs) в случае* KSn_2F_5 *и* $RbSn_2F_5$ *перпендикулярно оси третьего порядка, а в случае* $CsSn_2F_5$ *– оси четвертого порядка.*

Ключевые слова: *фторстаннаты, рентгенофазовый анализ, фторионная проводимость, фторид олова, фториды, кристаллохимия, слоистые структуры*

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The need for compact and rechargeable current sources has given rise to various types of lithium batteries development. Although the characteristics of lithium batteries have not yet reached their practical limits, it is clear that new classes of electrochemical devices are required. Sodium batteries are currently being actively developed. The use of other alkali metals is being considered, and the development of batteries based on metallic magnesium, titanium, or aluminum is drawing attention [1]. Batteries operate based on an electrochemical reaction involving the transfer of a cation in an electrochemical cell. Because cations are smaller than anions by nature, they have greater mobility and penetrating ability as charge carriers. Also, the electrolyte in an electrochemical cell must be solid (superionic), which significantly improves such cells' operational characteristics. Fluorine is likely to be the only anion that can be used in solid-state electrochemical cells, as it outperforms its closest competitors: oxygen and chlorine. Fluoride ionic conductors have several advantages over other solid-state anionic conductors: relatively high conductivity, solid electrolytes stability at room temperature, and a reasonably large theoretically possible potential difference of a charged cell. Fluorine has the highest electron affinity, second only to chlorine, suggesting the possibility of obtaining high potentials comparable to lithium batteries on electrochemical cells with a mobile fluorine anion. Fluoride ionic electrochemical cells allow using fluorides of less active metals as an anode and cathode, which is safer than lithium batteries, from which lithium metal or its highly active compounds are obtained, and the electrochemical cell can be depressurized and ignited. These advantages lead us to believe that fluoride ionic batteries will find practical applications and fill a niche in electronic devices that is both safe and compact.

The creation of fluoride ionic batteries requires the study of several practical issues, for example, the choice of electrochemical pairs for electrode materials. Tin(II) fluoride is one of the possible materials of the cathode; it exhibits a high fluoride ionic conductivity and a low electrochemical potential formation. Although using pure tin fluoride is promising, it imposes some restrictions. The first is the possibility of recrystallization into a monolithic material, resulting in a significant decrease in the phase boundary area, consequently decreasing the current characteristics of the electrochemical elements (current density decreases). Second, dendrites (crystals of metallic tin) may form, leading to the breakdown of the electrochemical cell. In this case, using fluorostannates is more advantageous because the released metal fluorides prevent the growth of tin particles with the ability to accumulate sorbed fluoride ions on themselves during the reduction of tin fluoride. Alkali metal fluorostannates are promising. The presence of trifluorostannates and pentafluorodistannates of sodium, potassium, cesium, and rubidium is demonstrated. Pentafluorodistannates are superior to trifluorostannates in terms of electrophysical characteristics, as they have a higher fluoride ionic conductivity, whereas the conductivity of trifluorostannates does not exceed the order of 10^{-9} S/cm [2].

The melting of tin fluoride with potassium, rubidium, and cesium fluorides leads to smoothing its phase transition from monoclinic to tetragonal modification with a concomitant increase in conductivity. At the same time, doping with rubidium ions (5% RbF, $6.31 \cdot 10^{-2}$ Cm/cm at 453 K) has the most significant influence, while doping with sodium ions with the formation of the $NaSn_2F_5$ phase ($2.62 \cdot 10^{-4}$ Cm/cm at 453 K) has the least. At 438 K, the conductivity of cesium pentafluorodistannate $CsSn_2F_5$ reaches $3.54 \cdot 10^{-3}$ Cm/cm, while that of potassium pentafluorodistannate KSn_2F_5 reaches $2.02 \cdot 10^{-2}$ Cm/cm at 463 K [3]. In the case of the phase formation of rubidium pentafluorodistannate $RbSn_2F_5$, its conductivity reaches $1.25 \cdot 10^{-1}$ Cm/cm at 473 K [4].

Works based on the structural studies of these compounds, for the most part, date back to the 1960s–1980s and contain ambiguous and even contradictory data on the structures. The structure of sodium pentafluorodistannate was determined by single-crystal X-ray diffraction (XRD) analysis in 1964. The compound crystallizes in tetragonal syngony with parameters $a = 6.37$ Å, $c = 13.71$ Å, $V = 556$ Å^3 according to [5] and the authors [6] decided the structure in the same year and specified that $NaSn_2F_5$ has the space group $P4_2$/nbc and parameters $a = 9.02$ Å, $c = 13.685$ Å.

Donaldson [5] gives the first data on the structure of potassium pentafluorodistannate, stating that fluorostannate corresponds to an orthorhombic system with parameters $a = 12.54$ Å, $b = 9.80$ Å, $c = 7.71$ Å, $V = 948$ Å^3. The structure of KSn_2F_5 was refined in [7, 8], and the authors captured the phase transition as follows: at room temperature, the hexagonal unit cell $P3$, $a = 7.291$ Å, $c = 9.861$ Å, and $V = 454$ Å^3, at 443 K, $P3m1$, $a = 4.268$ Å, $c = 9.911$ Å, and $V = 156.3$ Å^3. The results of the single-crystal XRD analysis in a later work [9] confirmed the identity of the crystals KSn_2F_5 to be a hexagonal crystal system $P3$, $a = 7.266$ Å, $c = 9.796$ Å, $V = 447.89$ Å^3 (at 200 K), $P3$, $a = 7.302$ Å, $c = 9.872$ Å, $V = 455.85$ Å^3 (at 350 K).

Cesium pentafluorodistannate $CsSn_2F_5$ crystallizes in the orthorhombic crystal system ($a = 19.20$ Å, $b = 12.44$ Å, $c = 8.54$ Å, $V = 2040$ Å^3). Rubidium pentafluorodistannate $RbSn_2F_5$ crystallizes in the orthorhombic crystal system ($a = 12.48$ Å, $b = 9.92$ Å, $c = 7.35$ Å. $V = 910$ Å^3) according to powder X-ray diffraction [10]. The structures of these fluorostannates' high-temperature phases were later determined using neutron powder diffraction [11]. At 538 K, $CsSn_2F_5$ has a space group $I4/mmm$ with parameters $a = 4.2606$ Å, $c = 19.739$ Å, $V = 358.31$ Å^3, and at 473 K, $RbSn_2F_5$ has the hexagonal crystal system: $P3$, $a = 4.3581$ Å, $c = 10.1704$ Å, $V = 167.29$ Å^3.

Our work aims to synthesize from a aqueous solution and carry out an X-ray study of crystals of alkali metal pentafluorodistannates, namely: sodium, potassium, cesium, and rubidium, and study the possibility of obtaining lithium fluorostannates.

EXPERIMENTAL

The synthesis was performed using tin(II) fluoride SnF_2 (*Sigma-Aldrich*, USA), cesium fluoride CsF (pure), sodium fluoride NaF (pure), lithium fluoride LiF (chemically pure), potassium carbonate K_2CO_3 (pure), rubidium carbonate Rb_2CO_3 (pure) and hydrofluoric acid HF (chemically pure). At 80°C, cesium fluoride was pre-dried. Potassium and rubidium fluorides were obtained by dissolving metal carbonates in hydrofluoric acid.

The method of crystallization from an aqueous solution was employed to synthesize the compounds $NaSn_2F_5$, KSn_2F_5, $CsSn_2F_5$, $RbSn_2F_5$. The calculated fluoride weighted amount based on molar ratios was placed in plastic tubes and dissolved in distilled water. The test tubes were heated to 70°C in an ultrasonic bath to obtain a concentrated solution and achieve supersaturation during cooling. An ice bath was utilized to increase the crystallization product yield as the solution was gradually cooled, resulting in abundant fluorostannates crystallization.

Some solutions were acidified with hydrofluoric acid to prevent the hydrolysis of tin(II) fluoride and tin oxide SnO precipitation.

Tin(II) fluoride and lithium fluoride were melted (in the stoichiometric ratios of 1:2, 2:1) in a glassy carbon crucible in a nitrogen atmosphere heated to 300°C and held at the specified temperature for 20 min to search for compounds in the LiF–SnF_2 system.

The size and morphology control of the obtained crystals were implemented using an optical microscope POLAM S-111 (*LOMO*, Russia) with crossed polarizers. Sodium pentafluorodistannate $NaSn_2F_5$ formed needle-like crystals, KSn_2F_5 and $CsSn_2F_5$—bulk crystals, $RbSn_2F_5$—hexagonal-shaped platy crystals.

The obtained mixed fluorides crystals were ground in a jasper mortar and examined by XRD analysis on a Shimadzu XRD 6000 diffractometer (*Shimadzu*, Japan). Powder diffraction patterns were taken in the range of angles 2θ from 10° to 60° with a step of 0.02°, 1 s exposure time per point and CuKα radiation.

The peak positions were determined using the Profit program [12], and indexing by the least-squares technique was performed using the Powder program[1]. The difference between the experimental and calculated indexing parameters ΔQ expressed as $Q = 10^4/d^2$, where d is the interplanar distance (Å), determines the indexing quality. $\Delta Q < 5$ indicates high imaging and indexing quality.

RESULTS AND DISCUSSION

The samples obtained by melting SnF_2 and LiF in the molar ratio 1:2 and 2:1 did not form co-phases. According to the card 04-0857 of powder database PCPDFWIN, all the samples were two-phase and showed a predominantly monoclinic modification of tin(II) fluoride and smaller amounts compared to the amount of lithium fluoride (peaks at angles 2θ ~ 38.696°, 44.996°). The calculated cell parameters ($C2/c$, $a = 13.35$ Å, $b = 4.908$ Å, $c = 13.78$ Å, $\beta = 109.1°$, $V = 853.97$ Å^3) correspond to the card 15-0744 SnF_2. The immutability of the SnF_2 parameters implies that lithium fluoride does not form solid solutions with tin difluoride.

Alkali metals (Na, K, Rb, Cs) form pentafluorodistannates and trifluorostannates with tin(II) fluoride. The pentafluorodistannates of interest to us are those synthesized and crystallized from the aqueous solutions. Figure 1 shows the powder diffraction patterns of the $NaSn_2F_5$, KSn_2F_5, $RbSn_2F_5$, $CsSn_2F_5$ compounds.

The sodium and potassium pentafluorodistannates diffraction patterns indexing showed good convergence with the powder database cards (Table 1).

The sodium salt diffraction pattern differs significantly from the similar diffraction patterns of potassium, rubidium, and cesium salts (Fig. 1). The diffraction patterns of KSn_2F_5 and $RbSn_2F_5$ are almost identical. All of this indicates that these compounds have a similar structural motif, and potassium and rubidium pentafluorodistannates are isostructural. Based on these assumptions, reindexing was performed on a powder diffraction pattern of $RbSn_2F_5$ on a hexagonal cell similar to KSn_2F_5 (Table 2). The obtained primitive unit cell parameters for rubidium pentafluorodistannate are $a = 7.40(3)$ Å, $c = 10.12(6)$ Å. Compared to the cell proposed in [10] with a volume twice as large, this indexing is characterized by higher quality.

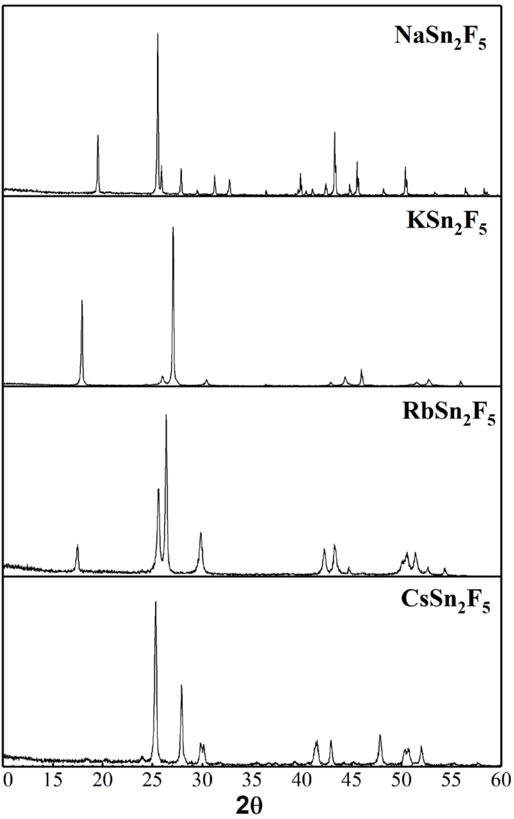

Fig. 1. Powder diffraction patterns of $NaSn_2F_5$, KSn_2F_5, $RbSn_2F_5$, $CsSn_2F_5$.

A distorted fluorite-like cell with the given parameter $a = 5.694$ Å, formed by tin and potassium cations, can be distinguished in the structure of potassium pentafluorodistannate (hexagonal syngony, according to [7]). Figure 2 depicts the unit cell of KSn_2F_5. For convenience, only the cations are left in the model. As shown, the tin cations at the hexagonal cell's base are arranged according to the law of the three-layer closest packing, while the cations above and below it are located above and below its voids. Both layers are represented by the closest packing, having different positions above the voids and indicating the formation of a three-layer closest packing (ABCABC). Layers A and B are represented by Sn cations in the three-layer packaging sequence, while K cations represent layer C. Such layer sequence is perpendicular to the crystallographic axis c of the hexagonal structure, corresponding to the fluorite-like cube's large diagonal, and equal to the parameter

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Table 1. Results of $NaSn_2F_5$, KSn_2F_5 powder diffraction patterns indexing

Compound	Cell parameters from the results of the indexing	Cell parameters from the literature data
$NaSn_2F_5$	$P4_2/nbc$, a = 9.035(2) Å, c = 13.715(5) Å, V = 1119.6(4) Å^3	$P4_2/nbc$, a = 9.020(3) Å, c = 13.686(3) Å, V = 1113.50 Å^3 (Card PCPDFWIN 21-1233)
KSn_2F_5	$P3$, a = 7.293(6) Å, c = 9.862(2) Å, V = 454.2(7) Å^3	$P3$, a = 7.291(1) Å, c = 9.862(1) Å, V = 453.97 Å^3 (Card PCPDFWIN 76-1977)

Table 2. $RbSn_2F_5$ powder diffraction pattern indexing

No.	2θ	*d*, Å	Q_{exp}	I/I_o	*h k l*	Q_{calc}	ΔQ
1	17.50	5.0668	389.5	16	0 0 2	390.1	−0.6
2	25.64	3.4730	829.1	87	1 1 1	827.3	1.8
3	26.38	3.3772	876.8	100	0 0 3	877.7	−0.9
4	27.86	3.2019	975.4	1	2 0 0	973.1	2.3
5	29.88	2.9902	1118.4	53	1 1 2	1119.9	−1.5
6	42.28	2.1371	2189.5	24	3 0 0	2189.4	0.1
7	43.32	2.0887	2292.2	43	1 1 4	2290.2	2.0
8	44.74	2.0252	2438.2	6	0 0 5	2438.1	0.1
9	50.06	1.8221	3012.0	18	2 2 1	3016.8	−4.8
10	50.52	1.8068	3063.3	29	3 0 3	3067.2	−3.9
11	51.44	1.7765	3168.6	31	1 1 5	3168.0	0.6
12	52.70	1.7367	3315.5	9	2 2 2	3309.3	6.2
13	54.36	1.6878	3510.4	5	0 0 6	3510.9	−0.5

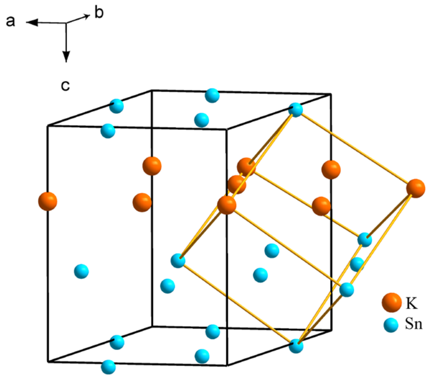

Fig. 2. Transformation of the unit cell of KSn_2F_5: fluorine atoms are removed from the model; hexagonal cell accords to [7] (the coordinate system is for this lattice); orange cubic cell is fluorite-like cell.

c = 9.862 Å of the KSn_2F_5 cell. Fluorine atoms do not fill all tetrahedral voids; instead, the majority of them are statistically located. There are no fluorine anions in the interlayer space of Sn cations.

A similar motif is observed in the $RbSn_2F_5$ structure (Fig. 3). From [11], rubidium cations are located at the hexagonal cell's base according to the law of the closest packing. According to the same law, tin cations are located above and below the voids of this layer, and their positions do not coincide with the rubidium cations, indicating the formation of a three-layer closest packing of cations with alternating Sn–Sn–Rb layers. The parameter c for the orthorhombic cell proposed in [10] is equal to the hexagonal cell's parameter c = 10.126 Å. Rubidium cations are also located at the orthorhombic cell's

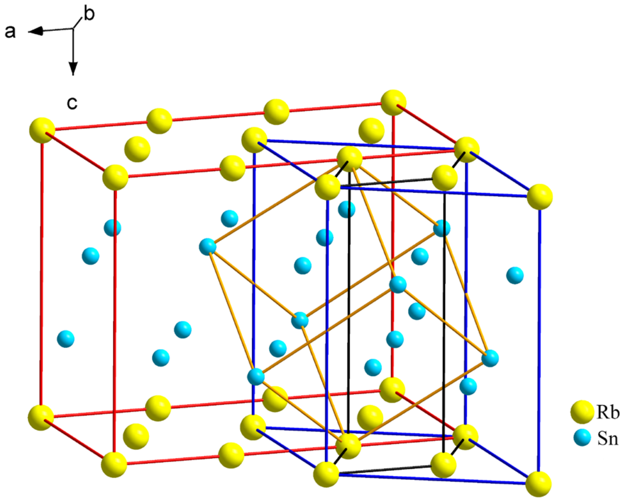

Fig. 3. Transformation of the unit cell of $RbSn_2F_5$: fluorine atoms are removed from the model; black hexagonal cell accords to [11] (the coordinate system is for this lattice); red orthorhombic cell accords to [10]; the orange cubic cell is fluorite-like cell; the blue hexagonal cell is obtained by the indexing results.

base, having an area six times larger than the cell area [11]. The hexagonal cell's base obtained by reindexing due to the isostructure of potassium and rubidium pentafluorodistannates is similarly represented by rubidium cations; however, its area is three times larger than the cell area [11]. The three-layer closest packing of cations, the fluorite motif with the given parameter a = 5.846 Å, is preserved in all cases. The parameter of the fluorite-like cell increased by 2.6% compared to potassium pentafluorodistannate, indicating the isostructure of these compounds.

The structure of $CsSn_2F_5$ shows a fluorite structural motif, similar to that of potassium and rubidium pentafluorodistannates (Fig. 4). Due to the larger ionic radius of cesium than potassium and rubidium, the reduced cubic cell is larger than in the first two cases, and its parameter is a = 6.100 Å. The $CsSn_2F_5$ powder diffraction pattern was reindexed to a monoclinic primitive unit cell with parameters a = 10.03(4) Å, b = 5.92(7) Å, c = 11.96(9) Å, β = 107.4(5)°, V = 679.0(1) Å^3 (Table 3).

The Miller indices were redefined based on a crystal-chemical analysis of the literature data [5–11]. A densely packed layer of cesium atoms lies at the monoclinic cell's base, with tin atoms forming dense layers above and below it in the voids. As Fig. 4 shows, the rectangular face of a monoclinic cell with dimensions b = 5.927 Å and c = 11.969 Å corresponds to two faces of a fluorite cube with cesium atoms at the base, and the parameter a = 10.034 Å connects the two nearest layers of cesium atoms. Compared to potassium pentafluorodistannate, the fluorite cube's parameter a = 6.100 Å increased by 7.1%, explaining the difference between the cationic motif and the two previous structures. Unlike KSn_2F_5 and $RbSn_2F_5$, the Sn–Sn–Cs layers are now located perpendicular to one of the fourth-fold axes (the fluorite cell), rather than the fluorite motif's third-fold axis, causing cations to be collected in the dense layers, rather than the densest layers. The planes of cesium cations limit the orthorhombic cell presented in [10], forming its bases. The side of cell b's base is the diagonal of the fluorite cube's face, and the side a is the doubled diagonal. The height of cell c corresponds to the tripled side of the cube. The base area is four times that of the base area of a fluorite-like cell, and the volume is 12 times larger. The authors of [11] presented a much more simplified tetragonal cell. According to [10], its height coincides with the parameter c of the orthorhombic cell. The base area is half that of the fluorite-like cell's face, implying that the cell parameter "a" differs from the cubic cell parameter by a factor $\sqrt{2}$.

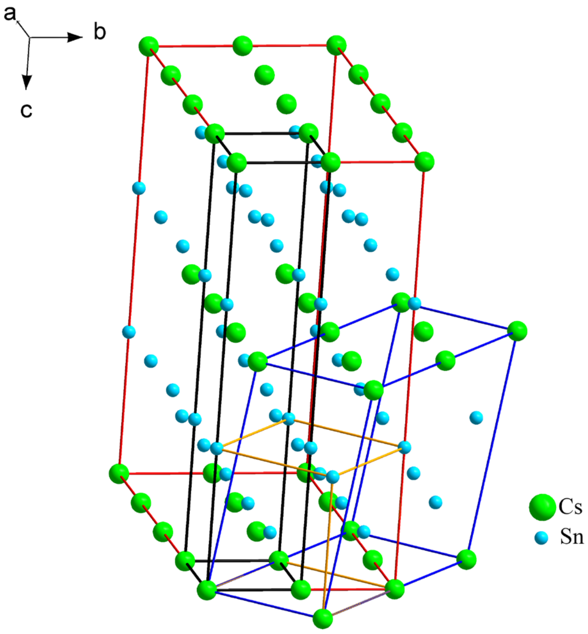

Fig. 4. Transformation of the unit cell of $CsSn_2F_5$: fluorine atoms are removed from the model; black tetragonal cell according to [11] (the coordinate system is for this lattice); red orthorhombic cell according to [10]; the orange cubic cell is fluorite-like cell; the blue monoclinic cell is obtained by the indexing results.

Let us consider the influence of the structure of pentafluorodistannates on their fluoride-ion conductivity. Fluorostannates have a significant ionic conductivity and compete with fluoride-ion conductors containing rare earth elements (REE). High-conducting fluorides have fluorite or tisonite

Table 3. $CsSn_2F_5$ powder diffraction pattern indexing

No.	2θ	*d*, Å	Q_{exp}	I/I_o	*h k l*	Q_{calc}	Δ*Q*
1	18.530	4.7844	436.86	1	2 0 0	436.53	0.33
2	20.343	4.3620	525.57	2	1 1 1	525.36	0.20
3	23.936	3.7147	724.69	2	2 1 0	721.20	3.49
4	25.310	3.5161	808.87	100	1 1 2	810.33	−1.46
5	27.908	3.1944	979.99	48	3 0 0	982.20	−2.21
6	29.823	2.9935	1115.94	14	−1 0 4	1116.87	−0.93
7	30.143	2.9624	1139.50	12	0 2 0	1138.66	0.83
8	31.869	2.8058	1270.24	2	−1 2 1	1269.63	0.61
9	35.630	2.5178	1577.46	4	2 2 0	1575.19	2.26
10	36.637	2.4509	1664.75	3	1 2 2	1664.32	0.42
11	39.258	2.2930	1901.92	3	3 1 2	1902.86	−0.94
12	40.644	2.2180	2032.72	1	−3 2 1	2032.96	−0.25
13	41.339	2.1823	2099.77	17	1 2 3	2102.69	−2.92
14	41.557	2.1714	2120.90	14	3 2 0	2120.86	0.04
15	42.917	2.1056	2255.53	17	−1 2 4	2255.53	0
16	44.256	2.0450	2391.19	2	2 1 4	2387.32	3.86
17	45.159	2.0062	2484.57	3	−5 0 2	2486.47	−1.90
18	47.471	1.9137	2730.56	1	5 0 0	2728.33	2.23
19	47.843	1.8997	2770.96	25	−5 1 2	2771.14	−0.18
20	50.281	1.8132	3041.65	16	0 1 6	3045.86	−4.21
21	50.671	1.8001	3086.08	15	1 3 2	3087.65	−1.57
22	51.985	1.7577	3236.76	14	−4 2 4	3234.14	2.62
23	55.314	1.6595	3631.16	4	−6 0 3	3631.51	−0.35
24	57.631	1.5982	3915.05	3	−6 1 3	3916.18	−1.12

structure. Usually pure fluorites and tisonites have low conductivity. Their conductivity is increased by introducing heterovalent cation substitution. REE is introduced into the fluorites, resulting in the additional interstitial fluorine ion into the fluorite cell. Alkaline earth fluoride dopant elements are introduced into the composition of tisonites, causing fluorine vacancies to form in the structure. All of this allows the increase of the initial compounds' fluoride ionic conductivity.

Despite all attempts to increase the fluoride ionic conductivity of tisonites and fluorites, the compound lead tetrafluorostannate $PbSnF_4$ is the best fluoride-ion conductor at room temperature [13]. Although this compound is stoichiometric, it has a rich polymorphism. Attempts to increase its conductivity by introducing impurities have been ineffective. Only by doping lead tetrafluorostannate with lithium fluoride this was possible [4]. Increasing the conductivity of $PbSnF_4$ is a promising task. It is possible to understand this compound's fluoride ionic conductivity mechanism by considering the structure of the compounds with fragments, such as $PbSnF_4$. Studying lead tetrafluorostannate directly [14] is very difficult due to its polymorphism and inhibition of phase transitions. A three-layer closest packing of cations represents all polymorphic modifications of the $PbSnF_4$ compound. The cations forming the packing are collected in dense layers that alternate with Sn–Sn–Pb–Pb pairs; there are no fluorine anions in the gaps between the layers of tin atoms. A similar layered structure is observed on the pentafluorodistannates of alkali metals. They are stoichiometric compounds with high mobility fluorine ions. Analysis of their structure and ionic conductivity parameters will allow us to understand better the ionic conductivity mechanism of the $PbSnF_4$ compound and possibly identify ways to increase it.

Let us consider the pentafluorodistannates of alkali metals successively. In fluorostannates, the fluorine atoms that coordinate tin(II) are located in one hemisphere. Lithium fluorostannates are not formed because the tin atoms coordinate alkali metals with their fluorine. Sterically, a lithium atom with its small size will not be able to coordinate such large structural fragments.

The sodium pentafluorodistannate structure consists of chains of tin cations located along the fourth-fold axis' direction. Tin cations form tetrahedra, which are connected along their edges. The fluorine anions in the tin atom's coordination sphere have angles between them that are slightly less than a right one and are turned outward from the tin tetrahedra's axis. In this case, the fluorine atoms coordinate the sodium atoms located in the channels between the chains. Compared to other alkali metal fluorostannates, all the fluorine atoms are strongly bound to the tin atoms, which explains the worst fluoride-ion conductivity.

The cations are arranged according to the law of the closest three-layer cubic packing (not ideal) for the potassium, rubidium, and cesium compounds. In the case of potassium and rubidium (Figs. 2 and 3), the densest layers alternate as A_{Sn}, B_{Sn}, C_{Me} (Me = K, Rb). There are no fluorine atoms in the space between the tin layers. The fluorine atom is quite firmly fixed, and the bond with the tin atom is located perpendicular to the plane of the tin atoms. The remaining fluorine atoms form almost a plane near the atomic layer of tin. The fluorine anions in these layers are statistically located under or near the tetrahedral voids. These fluorine atoms carry out charge transfer. The conductivity in the crystal volume is anisotropic and two-dimensional. By increasing the distances in the layers of the tin atoms, which creates broader and deeper valleys on the atomic surface of tin atoms for the movement of fluorine ions, rubidium pentafluorodistannate has a higher fluoride-ion conductivity (Table 4) compared to potassium pentafluorodistannate.

This structure changes during the transition to cesium pentafluorodistannate (Fig. 4); cations also form a three-layer closest packing, and tin and cesium planes form closely packed layers perpendicular to the fourth-fold axis [11]. There are no fluorine atoms in the space between the tin cations, and a firmly fixed fluorine atom is perpendicular to the plane of the tin atoms by its Sn–F bond. Because the cesium atoms are located above the tin packaging's voids, the mobile fluorine atoms form a plane parallel to the tin cation layer's surface and are located in the gaps between the nearest neighbors, preventing the fluorine atoms' free movement along the tin layer's atomic surface. This explains the sharp drop in the cesium salt's fluoride-ion conductivity by three orders of magnitude and increased activation energy (Table 4).

Table 4. Comparison of the electrophysical and crystallochemical characteristics of fluorostannates

Compound	Conductivity at the room temperature, S/cm [2]	Activation energy, eV [2]	Interlayer distance between the Sn cation layers, Å	Distance between the Sn cations inside the layer, Å
$NaSn_2F_5$	$8\cdot10^{-9}$	0.57	–	–
KSn_2F_5	$5\cdot10^{-6}$	0.55	3.444	4.200
$RbSn_2F_5$	$2\cdot10^{-5}$	0.68	3.491	4.358
$CsSn_2F_5$	$4\cdot10^{-8}$	0.76	3.227	4.260
$PbSnF_4$	$(1–10)\cdot10^{-3}$	0.11–0.42	3.042	4.224

CONCLUSIONS

This study investigates the possibility of obtaining lithium fluorostannates in the LiF–SnF_2 system by fusing lithium fluoride and tin(II) fluoride in molar ratios of 1:2 and 2:1. There were no compounds and solid solutions found in the XRD data. This is due to the lithium atom's inability to coordinate large structural fragments characteristic of alkali metal pentafluorodistannates.

Crystals of alkali metal pentafluorodistannates (sodium, potassium, rubidium, and cesium) were synthesized from aqueous solutions, and their X-ray phase study was conducted. The results of indexing the XRD data confirmed the single-phase nature of the obtained samples and good correspondence to the composition of $MeSn_2F_5$ (Me = Na, K, Rb, Cs). The cells parameters for $NaSn_2F_5$ ($P4_2/nbc$, a = 9.035(2) Å, c = 13.715(5) Å, V = 1119.6(4) Å^3), and KSn_2F_5 ($P3$, a = 7.293(6) Å, c = 9.862(2) Å, V = 454.2(7) Å^3) calculated by a least-square technique has shown good agreement with the literature data and cards of PCPDFWIN powder database. It was revealed during a crystal-chemical analysis of pentafluorodistannates that the compounds $MeSn_2F_5$ (Me = K, Rb, Cs) with high fluoride-ion conductivity have a layered structure corresponding to the three-layer packing type of fluorite, in which a pair of tin layers alternate with the layers of cations of alkali metal Sn–Sn–Me (Me = K, Rb, Cs) pentafluorodistannate. The reduced fluorite-like cells parameters naturally increase down the group: 5.694 Å (KSn_2F_5), 5.846 Å ($RbSn_2F_5$), 6.100 Å ($CsSn_2F_5$). For potassium and rubidium pentafluorodistannates, the Sn–Sn–Me (Me = K, Rb) layers are the densest, and the conductivity increases from KSn_2F_5 to $RbSn_2F_5$. Rubidium pentafluorodistannate $RbSn_2F_5$ is isostructural with KSn_2F_5, and the compound was reindexed to a hexagonal cell with parameters a = 7.40(3) Å and c = 10.12(6) Å. In the $CsSn_2F_5$ compound, the Sn–Sn–Cs layers are dense but not the densest and oriented along one of the axes of the fourth-fold of the fluorite motif. The fluoride-ion conductivity is significantly reduced due to the cationic packaging's global rearrangement. Cesium pentafluorodistannate $CsSn_2F_5$ was reindexed from orthorhombic (according to literature data) to a monoclinic system with cell parameters a = 10.03(4) Å, b = 5.92(7) Å, c = 11.96(9) Å, β = 107.4(5)°. Surprisingly, $CsSn_2F_5$ is the closest to $PbSnF_4$ in terms of the structure and packing of the layers. This suggests that their conductivity mechanisms are distinct. Perhaps, suppose a $PbSnF_4$ compound or a similar $BaSnF_4$ compound with the same type of cation layer packing as KSn_2F_5 and $RbSn_2F_5$ can be obtained. In that case, a higher value of fluoride ionic conductivity can be achieved. It is still not completely clear how to accomplish this.

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Authors' contribution

R.M. Zakalyukin – conducting synthesis, X-ray diffraction analysis, and crystallochemical analysis, writing the text of the article, powder diffraction patterns indexing;

E.A. Levkevich – conducting synthesis, working with the literature, writing and editing the text of the article, powder diffraction patterns indexing;

A.V. Nikolaeva – conducting synthesis, working with the literature, powder diffraction patterns indexing.

The authors declare no conflicts of interest.

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