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## Mechanism of electrotransport in superionic conductor $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$ with the fluorite-type structure

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Received September 1, 2022

Revised September 1, 2022

Accepted September 9, 2022

The ionic conductivity of the superionic conductor  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  with the fluorite-type structure (type  $\text{CaF}_2$ , sp.gr.  $Fm\bar{3}m$ ) had measured by the impedance spectroscopy in the temperature range 385–794 K. Bulk crystals of a three-component solid solution (lattice parameter  $a = 5.7726(1) \text{ \AA}$ ) had obtained from the melt by the directed crystallization technique. Temperature dependence ionic conductivity  $\sigma_{dc}(T)$  satisfies the Arrhenius–Frenkel equation with the activation enthalpy of the electrical conductivity  $\Delta H_\sigma = 0.706 \pm 0.05 \text{ eV}$ . The value of  $\sigma_{dc}$  is  $1.5 \cdot 10^{-5} \text{ S/cm}$  at 500 K. Based on the analysis of electrophysical and structural studies of fluorite-type solid solutions in  $\text{SrF}_2\text{–LaF}_3$  and  $\text{SrF}_2\text{–LuF}_3$  systems, the microscopic model of ion transport in the  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  crystal was proposed. The concentration and mobility of charge carriers were calculated:  $n_{mob} = 7.8 \cdot 10^{20} \text{ cm}^{-3}$  and  $\mu_{mob} = 1.2 \cdot 10^{-7} \text{ cm}^2/\text{Vs}$  at 500 K.

**Keywords:** superionic conductors, impedance spectroscopy, single crystals, fluorides, rare earth ions, fluorite structure.

DOI: 10.21883/PSS.2023.01.54979.467

### 1. Introduction

Multicomponent fluorides significantly expand the scope of traditional applications of single crystals of individual fluorides. Isomorphic heterovalent substitutions make it possible to create new functional monocrystalline fluoride materials, improving their physical and operational properties. The work continues the publications [1–8] devoted to the growth of single crystals of fluorite nonstoichiometric phases  $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$  ( $R$  — rare earth elements La–Lu, Y), the study of their defect structure and structurally sensitive ionic conductivity. Alkaline earth metal difluorides (Ca, Sr, Ba) belonging to the fluorite family ( $\text{CaF}_2$ ), are high-temperature (at temperatures over 1000°C) superionic conductors [9]. Matrix doping  $\text{MF}_2$  ( $M = \text{Ca, Sr, Ba}$ ) by fluorides of metals I, III and IV groups of the periodic system of elements  $\text{RF}_n$  allows the creation of multicomponent fluorite solid solutions  $\text{M}_{1-x}\text{R}_x\text{F}_{2+(n-2)x}$  with superionic conductivity in the medium temperature range (200–300°C).

Of particular interest are the processes of alloying fluorite matrices  $\text{MF}_2$  with trifluorides of rare earth metals  $\text{RF}_3$  ( $R = \text{La–Lu, Y}$ ), as a result of which large families of fluorite solid solutions have been synthesized  $\text{Ca}_{1-x}\text{R}_x\text{F}_{2+x}$ ,  $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$  and  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$ . Nonstoichiometric crystals  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  belong to impurity superionic conductors, the level of conductivity of which is determined by the content and chemical nature of the components. To realize the high ionic conductivity ( $\sigma_{dc} > 10^{-4} \text{ S/cm}$ ) a doping level of tens mol.%  $\text{RF}_3$  is required, leading to the formation of concentrated solid solutions ( $x > 0.1$ ) [10].

The structural mechanism of ion transport in two-component solutions of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  is well studied. The high ionic conductivity of crystals  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  is due to the migration of anions  $\text{F}^-$  in structurally distorted sections of fluorite matrices  $\text{MF}_2$  ( $M = \text{Ca, Sr, Ba}$ ) located near clusters of defects („model of defective areas“ [10–12]). Analysis of structural data [13–15] shows that the most likely clusters in concentrated solid solutions  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  are rare-earth tetrahedral clusters  $[\text{R}_4\text{F}_{26}]$  [16] and octahedral clusters  $[\text{R}_6\text{F}_{36-37}]$  [17]. Clusters  $[\text{R}_6\text{F}_{36-37}]$  are the core of more complex octahedron-cubic clusters  $[\text{M}_8\text{R}_6\text{F}_{68-69}]$  [18,19]. The type of defective structure of fluorite crystals  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  depends both on the nature of matrix ( $M$ ) and rare-earth ( $R$ ) cations and on their quantitative ratio in solid solution [14,19,20].

The defect structure of solid solutions  $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$  varies along the series  $R$  from La to Lu [1,21–25]. At the beginning of the series, tetrahedral clusters are formed  $[\text{R}_4\text{F}_{26}]$ , at the end of the row — octahedral clusters  $[\text{R}_6\text{F}_{37}]$ . Therefore, the structural and electrophysical properties of solid solutions  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  and  $\text{Sr}_{1-x}\text{Lu}_x\text{F}_{2+x}$  attracted the increased attention.

In the  $\text{SrF}_2\text{–LaF}_3$  system the homogeneity region of the fluorite phase  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  corresponds to the composition range  $0 \leq x \leq 0.49$  at eutectic temperature 1723 K [26]. This phase has a congruent melting character at  $x = 0.31 \pm 0.02$  and a temperature of  $1843 \pm 10 \text{ K}$ . Defect crystal structure  $\text{Sr}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$  was studied by the neutronographic method [27], crystals of the concentration series  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  ( $x = 0.11\text{–}0.47$ ) — by X-ray

diffraction analysis [21]. Composition  $\text{Sr}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ , corresponding to the maximum fusibility, has a high ionic conductivity [5,6].

In the  $\text{SrF}_2\text{--LaF}_3$  [26] the homogeneity region of the fluorite phase  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  corresponds to the composition range  $0 \leq x \leq 0.37$  at eutectic temperature 1278 K. There is no temperature maximum on the melting curves. The defect structure was studied for crystals  $\text{Sr}_{0.815}\text{Lu}_{0.185}\text{F}_{2.185}$  [22] and  $\text{Sr}_{0.84}\text{Lu}_{0.16}\text{F}_{2.16}$  [28] by neutron and X-ray methods, respectively. The ionic conductivity of  $\text{Sr}_{1-x}\text{Lu}_x\text{F}_{2+x}$  crystals is significantly lower compared to  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  crystals [5,7].

Studies of the electrophysical properties of three-component solid solutions, in which the composition of a rare-earth ( $R, R'$ ) or matrix ( $M, M'$ ) sublattice varies, are just beginning. To date, measurements have been made of the ionic conductivity of crystals  $\text{Sr}_{0.8}(\text{La}_{1-x}\text{Lu}_x)_{0.2}\text{F}_{2.2}$  [4],  $(\text{Ca}_{1-x}\text{Sr}_x)_{0.85}\text{Nd}_{0.15}\text{F}_{2.15}$ ,  $\text{Ba}_{0.75}(\text{La}_{1-x}\text{Nd}_x)_{0.25}\text{F}_{2.25}$  [29],  $(\text{Sr}_{1-x}\text{Ba}_x)_{0.7}\text{La}_{0.3}\text{F}_{2.3}$  [29,30] and solid solutions whose compositions correspond to saddle points on the phase diagrams of the ternary systems  $\text{CaF}_2\text{--SrF}_2\text{--RF}_3$  ( $R = \text{La--Nd}$ ) [31,32].

To study the nature of ion transport in fluorite structures of three-component solid solutions, crystals of  $\text{Sr}_{1-x}(\text{La,Lu})_x\text{F}_{2+x}$  are of particular interest, the defect structure of which simultaneously contains tetrahedral  $[\text{La}_4\text{F}_{26}]$  and octahedral  $[\text{Lu}_6\text{F}_{37}]$  clusters. In [4] it was found that the nonmonotonic course of the dependence  $\sigma_{dc}(x)$  for three-component crystals  $\text{Sr}_{0.8}(\text{La}_{1-x}\text{Lu}_x)_{0.2}\text{F}_{2.2}$  correlates with the conductivity behavior of two-component crystals  $\text{Sr}_{0.8}\text{R}_{0.2}\text{F}_{2.2}$  when changing  $R$  in a row from La to Lu. Solid solution  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  can be considered as a model crystal for studying the effect of a defect structure on ion transport in the three-component solid solutions with a fluorite structure.

The purpose of this work is temperature measurements of ionic conductivity, investigation of the ion transfer mechanism and calculation of the concentration and mobility of charge carriers in a superionic conductor  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$

## 2. Experiment

Crystals  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  obtained from the melt by the Bridgman method in a fluorinating atmosphere. The crystal growth technique is described in detail in [3]. The rate of withdrawal of the crucible with the melt from the growth zone was 5 mm/h, the cooling rate was  $\sim 100$  K/h, the loss of substance to evaporation did not exceed 0.5 mass.%. The crystal was not subjected to heat treatment and was in the state „as grown“.

X-ray examination was performed on a powder X-ray diffractometer Rigaku MiniFlex 600 (radiation  $\text{CuK}_\alpha$ ). The crystal is a solid solution with a fluorite structure (sp.gr.  $Fm\bar{3}m$ ), the cubic lattice parameter is

$a = 5.7726(1)$  Å. The radiographic density and molar volume of the solid solution are  $\rho_X = 5.25$  g/cm<sup>3</sup> and  $V_{mol} = 28.96$  cm<sup>3</sup>/mol, respectively. The density measured (by hydrostatic weighing in distilled water)  $\rho_{exp} = 5.20 \pm 0.03$  g/cm<sup>3</sup> coincides well with the theoretical value  $\rho_X$ .

The values  $a, \rho_X$  and  $V_{mol}$  for a three-component solid solution  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  are well modeled by the values of these parameters calculated according to the law of additivity from the characteristics of two-component solid solutions  $\text{Sr}_{0.7}\text{La}_{0.3}\text{F}_{2.3}$  and  $\text{Sr}_{0.7}\text{Lu}_{0.3}\text{F}_{2.3}$ :  $a^{cal} = 5.769$  Å,  $\rho_X^{cal} = 5.27$  g/cm<sup>3</sup> and  $V_{mol}^{cal} = 28.92$  cm<sup>3</sup>/mol. This fact and the results of the study [33] indicate the possibility of using a data bank on lattice parameters and densities of two-component crystals  $M_{1-x}R_x\text{F}_{2+x}$  [14,34,35] to calculate the characteristics of a large number of multicomponent (with the number of components three or more) of fluorite solid solutions.

The electrical conductivity of the crystal was measured by impedance spectroscopy on a Tesla BM-507 device (frequency range 0.005–500 kHz) in vacuum  $\sim 1$  Pa in the temperature range 385–794 K. A sample for electrophysical measurements in the form of a plane-parallel plate with a thickness of  $h = 2.45$  mm was made from an optically homogeneous, transparent section in the middle part of a crystal boule. A detailed description of the conductometric set-up is given in [5]. Silver paste of the Degussa brand (Germany) was used as electrodes. The area of the electrodes  $S$  was 35 mm<sup>2</sup>.

The presence of a blocking effect from inert (silver) electrodes in the impedance spectra indicates the ionic nature of electrical conductivity. The bulk resistance  $R_b$  of the crystal was found by the intersection of the impedance hodograph with the axis of the actual resistances. The value of the ionic conductivity  $\sigma_{dc}$  was calculated from the bulk resistance data  $R_b$  taking into account the geometry of the crystal sample ( $h$  and  $S$ ):

$$\sigma_{dc} = h/(R_b S). \quad (1)$$

The relative error of determination  $\sigma_{dc}$  did not exceed 5%. Conductometric isothermal measurements with an exposure time of 30 min were carried out in a heating-cooling cycle. When cooled, the value of  $\sigma_{dc}$  turned out to be higher than when heated. So, at 500 K, the values of  $\sigma_{dc}$  are  $7.7 \cdot 10^{-6}$  and  $1.5 \cdot 10^{-5}$  S/cm when heated and cooled, respectively. This phenomenon is characteristic of crystals of nonstoichiometric fluorides [36] and is apparently caused by annealing of thermal stresses in the samples. Processing of electrophysical data was carried out for the cooling mode.

Temperature dependence of the ionic conductivity of the crystal  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  is shown in Fig. 1. The parameters of ionic electrical conductivity were calculated using the Arrhenius-Frenkel equation

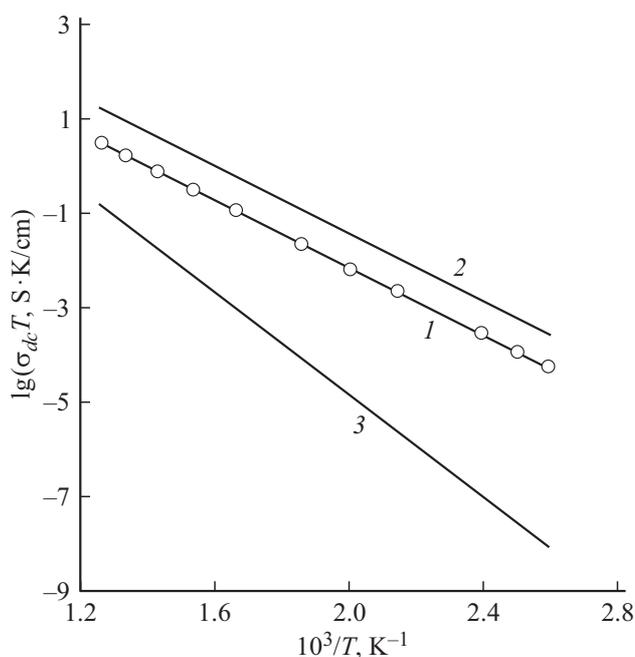
$$\sigma_{dc} T = \sigma_0 \exp(-\Delta H_\sigma / kT), \quad (2)$$

where  $\sigma_0$  — preexponential multiplier,  $\Delta H_\sigma$  — enthalpy of ion transfer activation,  $k$  — Boltzmann constant,  $T$  —

Parameters of ionic conductivity of fluorite solid solutions in systems  $\text{SrF}_2\text{--LaF}_3$ ,  $\text{SrF}_2\text{--LuF}_3$  and  $\text{SrF}_2\text{--LaF}_3\text{--LuF}_3$  (single crystals)

Crystals	Multiplier $\sigma_0$ , SK/cm	Enthalpy $\Delta H_\sigma$ , eV	Conductivity $\sigma_{dc}$ at 500 K, S/cm	References
System $\text{SrF}_2\text{--LaF}_3\text{--LuF}_3$				
$\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$ $a = 5.7726 \text{ \AA}$	$9.53 \cdot 10^4$	0.706	$1.5 \cdot 10^{-5}$	This study
$\text{Sr}_{0.8}\text{La}_{0.17}\text{Lu}_{0.03}\text{F}_{2.2}$ $a = 5.8195 \text{ \AA}$ [33]	$4.1 \cdot 10^5$	0.71	$6.0 \cdot 10^{-5}$	[4]
$\text{Sr}_{0.8}\text{La}_{0.14}\text{Lu}_{0.06}\text{F}_{2.2}$ $a = 5.8021 \text{ \AA}$ [33]	$3.5 \cdot 10^5$	0.75	$1.8 \cdot 10^{-5}$	
System $\text{SrF}_2\text{--LaF}_3$				
$\text{Sr}_{0.85}\text{La}_{0.15}\text{F}_{2.15}$ $a = 5.820 \text{ \AA}$ [37]	$5.4 \cdot 10^5$	0.71	$7.6 \cdot 10^{-5}$	[5,6]
$\text{Sr}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ $a = 5.842 \text{ \AA}$ [37]	$9.6 \cdot 10^5$	0.66	$4.3 \cdot 10^{-4}$	
System $\text{SrF}_2\text{--LuF}_3$				
$\text{Sr}_{0.84}\text{Lu}_{0.16}\text{F}_{2.16}$ $a = 5.745 \text{ \AA}$ [37]	$1.1 \cdot 10^6$	1.08	$2.9 \cdot 10^{-8}$	[5,7]
$\text{Sr}_{0.75}\text{Lu}_{0.25}\text{F}_{2.25}$ $a = 5.714 \text{ \AA}$ [37]	$1.3 \cdot 10^6$	1.08	$3.4 \cdot 10^{-8}$	

temperature. In the range from 794 to 385 K values of  $\sigma_{dc}$  decrease from  $3.9 \cdot 10^{-3}$  to  $1.4 \cdot 10^{-7}$  S/cm, which is approximately four orders of magnitude. The values of the multiplier  $\sigma_0$  and the activation enthalpy  $\Delta H_\sigma$  are  $9.53 \cdot 10^4 \text{ Scm}^{-1} \text{ K}$  and  $0.706 \pm 0.005 \text{ eV}$ , respectively.



**Figure 1.** Temperature dependences of ionic conductivity for crystals  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  (1),  $\text{Sr}_{0.85}\text{La}_{0.15}\text{F}_{2.15}$  [5,6] (2) and  $\text{Sr}_{0.84}\text{Lu}_{0.16}\text{F}_{2.16}$  [5,7] (3).

The following table shows conductometric data for fluorite solid solutions (single crystals) in systems with the participation of  $\text{SrF}_2$ ,  $\text{LaF}_3$  and  $\text{LuF}_3$ . It can be seen that the ionic conductivity of fluorite solid solutions is higher the higher the content of lanthanum trifluoride in them.

### 3. Microscopic mechanism of electrical transfer in a superionic conductor $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$

The ionic conductivity of fluorite solid solutions  $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$  and  $\text{Sr}_{1-x}(\text{La}, \text{Lu})_x\text{F}_{2+x}$  determines their nonequilibrium defect structure. Structural studies of crystals  $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$  and  $\text{Sr}_{1-x}\text{Lu}_x\text{F}_{2+x}$  [19,21–25] showed that the  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  cations embedded in the  $\text{SrF}_2$  fluorite matrix are coordinated by interstitial fluorine ions of a certain type and different clusters of defects are formed: tetrahedral  $[\text{La}_4\text{F}_{26}]$  and octahedral  $[\text{Lu}_6\text{F}_{37}]$  (or in a more generalized form, octahedron-cubic clusters  $[\text{Sr}_8\text{Lu}_6\text{F}_{69}]$ ).

According to NMR data  $^{19}\text{F}$  [38,39], the reason for the high electrical conductivity of crystals is  $M_{1-x}\text{R}_x\text{F}_{2+x}$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) is the intensive diffusion of ions  $\text{F}^-$  by the interstitial mechanism. To increase the ionic conductivity of nonstoichiometric fluorites, it is necessary to increase the concentration of charge carriers and/or reduce the height of potential barriers to their migration (increase the mobility of charge carriers).

Enthalpy of ion transfer activation in a crystal  $Sr_{0.69}La_{0.31}F_{2.31}$  with tetrahedral clusters  $[La_4F_{26}]$  ( $\Delta H_\sigma = 0.66 \pm 0.01$  eV) is significantly less than in the crystal  $Sr_{0.75}Lu_{0.25}F_{2.25}$  with octahedral clusters  $[Lu_6F_{37}]$  ( $\Delta H_\sigma = 1.08$  eV). Conductivity values (at 500 K) of crystals  $Sr_{0.69}La_{0.31}F_{2.31}$  and  $Sr_{0.75}Lu_{0.25}F_{2.25}$  differ in  $\sim 1.3 \cdot 10^4$  times (see table).

It can be assumed that the conductivity value of the crystal  $Sr_{0.7}La_{0.15}Lu_{0.15}F_{2.3}$  is related to the existence of structurally distorted fluorite sites around tetrahedral clusters  $[La_4F_{26}]$  in the structure of this solid solution (the lattice parameters  $a$  are 5.800 and 5.7726 Å for the matrix  $SrF_2$  and solid solution  $Sr_{0.7}La_{0.15}Lu_{0.15}F_{2.3}$  respectively). Indeed, this assumption is directly confirmed by the relationship of electrophysical data for the fluorite phases  $Sr_{1-x}La_xF_{2+x}$  and  $Sr_{1-x}(La, Lu)_x F_{2+x}$  in Fig. 2. The values of conductivity and enthalpy of ion transfer activation in  $Sr_{1-x}(La, Lu)_x F_{2+x}$  crystals (depending on the content of lanthanum trifluoride in them) correspond well to the curves  $\sigma_{dc}(x)$  and  $\Delta H_\sigma(x)$  for the solid solution  $Sr_{1-x}La_xF_{2+x}$ .

Concentration of charge carriers in a solid solution  $Sr_{0.7}La_{0.15}Lu_{0.15}F_{2.3}$  is temperature-independent and is determined by the mechanism of heterovalent substitutions of the cations  $Sr^{2+}$  to  $La^{3+}$ . Substitutions of  $Sr^{2+}$  by  $La^{3+}$  lead to charge heterogeneity of the cation subsystem and spatial heterogeneity of the anionic sublattice caused by the appearance of additional fluorine ions in interstitial positions  $F_{32f}$  sp.gr.  $Fm\bar{3}m$  with coordinates  $(w, w, w)$ ,  $w = 0.41-0.42$  [21,27]. The structurally disordered state of the anionic sublattice has a crystallochemical nature and persists at low temperatures.

For heterovalent substitutions  $Sr^{2+}$  to  $La^{3+}$  in crystals  $Sr_{1-x}La_xF_{2+x}$  and  $Sr_{1-x}(La, Lu)_x F_{2+x}$  the interstitial fluorine ions are formed for two reasons: firstly, due to compensation of the excess charge of impurity cations (the designations of defects are given in the symbols of Kroeger–Vink [40]):



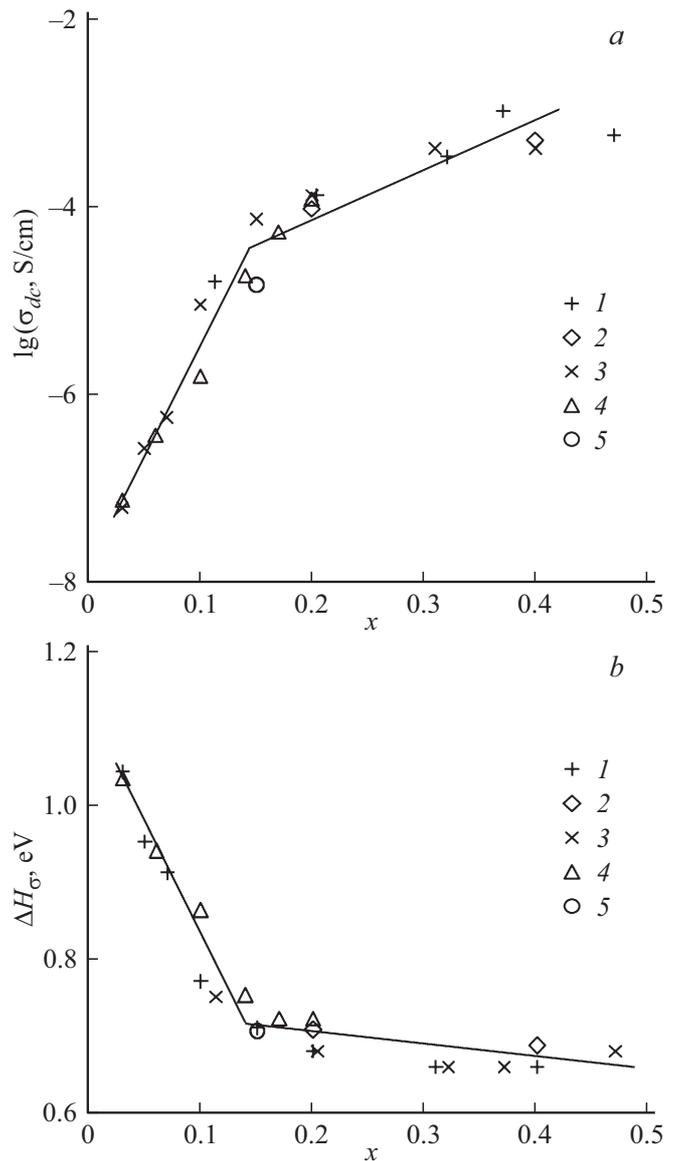
and, secondly, due to the formation of fluorine vacancies to overcome short cation-fluorine bonds (formation of anti-Frenkel defects):



The presence of ions  $F_i'$  in interstitial positions  $32f$  and vacancies  $V_F^{\bullet}$  in the main positions  $8c$  sp.gr.  $Fm\bar{3}m$  fluorite structure  $Sr_{1-x}La_xF_{2+x}$  was detected by neutron and X-ray diffraction analysis [21,27]. This fact indicates the formation of cation-anion clusters in the structure of solid solutions  $[La_4F_{26}]$  [16,19]. For non-stoichiometric crystals, there is a scheme of heterovalent substitutions (block isomorphism [41]):



where  $F'_{mob}$  — mobile fluorine ions in positions  $4b$  sp.gr.  $Fm\bar{3}m$ , located outside the cluster [13]. Concentration



**Figure 2.** Dependences of conductivity at 500 K (a) and enthalpy of ion transfer activation (b) on the content of  $LaF_3$  for fluorite solid solutions  $Sr_{1-x}La_xF_{2+x}$  (1 — [2], 2 — [4], 3 — [5,6]) and  $Sr_{1-x}(La, Lu)_x F_{2+x}$  (4 —  $Sr_{0.8}(La_{1-x}Lu_x)_{0.2}F_{2.2}$  [4], 5 —  $Sr_{0.7}La_{0.15}Lu_{0.15}F_{2.3}$ ).

of mobile interstitial fluorine ions  $F'_{mob}$ :

$$n_{mob} = Zx/4a^3, \quad (6)$$

where  $Z$  is the number of formula units in the fluorite structure  $Z = 4$ ,  $x$  — molar fraction of  $LaF_3$  in solid solution,  $a$  — unit cell parameter. For a crystal  $n_{mob} = 7.8 \cdot 10^{20} cm^{-3}$  and is 1.6% of the total number of anions.

The resulting value  $n_{mob}$  in the crystal  $Sr_{0.7}La_{0.15}Lu_{0.15}F_{2.3}$  exceeds by  $\sim 10^7$  times the concentration of anti-Frenkel defects in the fluorite matrix  $SrF_2$  ( $n_{mob} = 3.2 \cdot 10^{13} cm^{-3}$  [42] at 500 K), which

is proof of a strong structural disordering of the anionic subsystem.

Knowing the static conductivity of  $\sigma_{dc}$  and the concentration of charge carriers  $n_{mob}$ , it is possible to estimate the mobility of carriers  $\mu_{mob}$ :

$$\mu_{mob} = \sigma_{dc} / qn_{mob}, \quad (7)$$

where  $q$  is an elementary charge. Mobility of charge carriers at 500 K  $\mu_{mob} = 1.2 \cdot 10^{-7} \text{ cm}^2/\text{sV}$  in the superionic crystal  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  higher mobility of fluorine vacancies  $V_{\text{F}}^{\bullet}$  in crystal  $\text{SrF}_2$  ( $\mu_{vac} = 9.4 \cdot 10^{-9} \text{ cm}^2/\text{sV}$  [42]), and is comparable to the mobility of interstitial fluorine ions  $\text{F}_i'$  in this crystal ( $\mu_{int} = 1.1 \cdot 10^{-7} \text{ cm}^2/\text{sV}$  [42]).

## 4. Conclusion

To study the nature of the processes of electrical transfer and defect formation in fluoroconductive systems, multi-alloying (with ions  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$ ) of the fluorite matrix  $\text{SrF}_2$  was used. Crystals of the superionic conductor  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  were grown by the Bridgman method in the atmosphere  $\text{CF}_4$ . This superionic is a three-component solid solution with a fluorite structure (sp.gr.  $Fm\bar{3}m$ ), for which the lattice parameter  $a = 5.7726(1) \text{ \AA}$  and experimental density  $\rho_{exp} = 5.20 \pm 0.03 \text{ g/cm}^3$ . Temperature measurements of the ionic conductivity of the crystal  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  by impedance spectroscopy. Defect crystal structure  $\text{Sr}_{0.7}\text{La}_{0.15}\text{Lu}_{0.15}\text{F}_{2.3}$  contains two types of defect clusters — tetrahedral  $[\text{La}_4\text{F}_{26}]$  and octahedral  $[\text{Lu}_6\text{F}_{37}]$  clusters. Based on the analysis of electrophysical and structural data, the mechanism of ion transfer is proposed, the concentration and mobility of charge carriers are calculated. The results of the study are useful for the directed synthesis of new fluoride superionic materials of complex chemical composition.

## Acknowledgments

The authors thank N.A. Ivanovskaya for her help in obtaining densitometric data.

## Funding

The work was carried out with the support of the Ministry of Science and Higher Education within the framework of the State assignment of the Federal Scientific Research Center „Crystallography and Photonics“ of the Russian Academy of Sciences.

## Conflict of interest

The authors declare that they have no conflict of interest.

## References

- [1] E.A. Sulyanova, D.N. Karimov, B.P. Sobolev. *Kristallografiya* **65**, 569 (2020). (in Russian).
- [2] N.I. Sorokin, D.N. Karimov, E.A. Sulyanova, Z.I. Zhmurova, B.P. Sobolev. *Kristallografiya* **55**, 707 (2010). (in Russian).
- [3] B.P. Sobolev, D.N. Karimov, S.N. Sulyanov, Z.I. Zhmurova. *Kristallografiya* **54**, 129 (2009). (in Russian).
- [4] N.I. Sorokin, M.W. Breiter. *Solid State Ionics* **104**, 325 (1997).
- [5] A.K. Ivanov-Shits, N.I. Sorokin, P.P. Fedorov, B.P. Sobolev. *Solid State Ionics* **31**, 253 (1989).
- [6] A.K. Ivanov-Shits, N.I. Sorokin, P.P. Fedorov, B.P. Sobolev. *FTT* **25**, 1748 (1983). (in Russian).
- [7] A.K. Ivanov-Shits, N.I. Sorokin, B.P. Sobolev, P.P. Fedorov. *FTT* **28**, 2552 (1986). (in Russian).
- [8] N.I. Sorokin. *ZhNKh* **40**, 233 (1993). (in Russian).
- [9] A.V. Chadwick. *Solid State Ionics* **8**, 209 (1983).
- [10] B.P. Sobolev, N.I. Sorokin, N.B. Bolotina. In: *Protonic & Electronic Properties of Fluoride Materials / Eds. A. Tressaud, K. Poepplmeier*. Elsevier, Amsterdam (2016). P. 465.
- [11] K.E.D. Wapenaar, J.L. van Koesveld, J. Schoonman. *Solid State Ionics* **2**, 145 (1981).
- [12] H.W. den Hartog, J.C. Langevoort. *Phys. Rev. B* **24**, 3547 (1981).
- [13] N.I. Sorokin, A.M. Golubev, B.P. Sobolev. *Kristallografiya* **59**, 275 (2014). (in Russian).
- [14] B.P. Sobolev. *The rare earth trifluorides. Pt. 1 and 2*. Institute of Crystallography, Moscow & Institut d'Estudis Catalans, Barcelona (2000–2001). 980 p.
- [15] P.P. Fedorov. *Butll. Soc. Cat. Cien.* **12**, 349 (1991).
- [16] L.A. Muradyan, B.A. Maksimov, V.I. Simonov. *Koordinatsionnaya khimiya* **12**, 1398 (1986). (in Russian).
- [17] D.J.M. Bevan, J. Strahle, O. Greis. *J. Solid State Chem.* **44**, 75 (1982).
- [18] A.M. Golubev, V.I. Simonov. *Kristallografiya* **31**, 478 (1986). (in Russian).
- [19] E.A. Sulyanova, B.P. Sobolev. *Cryst. Eng. Commun.* **24**, 3762 (2022).
- [20] N.I. Sorokin. *Kristallografiya* **35**, 793 (1990). (in Russian).
- [21] E.A. Sulyanova, N.B. Bolotina, A.I. Kalyukanov, N.I. Sorokin, D.N. Karimov, I.A. Verin, B.P. Sobolev. *Kristallografiya* **64**, 47 (2019). (in Russian).
- [22] E.A. Sulyanova, I.A. Verin, B.P. Sobolev. *Kristallografiya* **57**, 79 (2012). (in Russian).
- [23] E.A. Sulyanova, D.N. Karimov, B.P. Sobolev. *Kristallografiya* **64**, 874 (2019). (in Russian).
- [24] E.A. Sulyanova, N.B. Bolotina, D.N. Karimov, I.A. Verin, B.P. Sobolev. *Kristallografiya* **64**, 196 (2019). (in Russian).
- [25] E.A. Sulyanova, D.N. Karimov, S.N. Sulyanov, B.P. Sobolev. *Kristallografiya* **59**, 19 (2014). (in Russian).
- [26] B.P. Sobolev, K.B. Seiranian. *J. Solid State Chem.* **39**, 17 (1981).
- [27] L.A. Muradyan, B.A. Maksimov, B.F. Mamin, N.N. Bydanov, V.A. Sarin, B.P. Sobolev, V.I. Simonov. *Kristallografiya* **31**, 248 (1986). (in Russian).
- [28] A.A. Loshmanov, B.A. Maksimov, B.P. Sobolev, N.I. Sorokin, V.I. Simonov. *Koordinatsionnaya khimiya* **15**, 1133 (1989). (in Russian).
- [29] B. Trnovtsova, P.P. Fedorov, I.I. Buchinskaya, M. Kublika. *Elektrokhimiya* **47**, 683 (2011). (in Russian).
- [30] D.N. Karimov, I.I. Buchinskaya, A.G. Ivanova, O.N. Ilyina, N.A. Ivanovskaya, N.I. Sorokin, B.P. Sobolev, T.M. Glushkova, D.A. Ksenofontov. *Kristallografiya* **63**, 972 (2018). (in Russian).

- [31] D.N. Karimov, I.I. Buchinskaya, N.I. Sorokin, T.M. Glushkova, S.P. Chernov, P.A. Popov. *Kristallografiya* **64**, 818 (2019). (in Russian).
- [32] N.I. Sorokin, D.N. Karimov, E.A. Krivandina, Z.I. Zhmurova, O.N. Komarkova. *Kristallografiya* **53**, 297 (2008). (in Russian).
- [33] N.I. Sorokin. *ZhNKh* **66**, 885 (2021). (in Russian).
- [34] P.P. Fedorov, B.P. Sobolev. *Kristallografiya* **37**, 1210 (1992). (in Russian).
- [35] N.I. Sorokin, E.A. Krivandina, Z.I. Zhmurova. *Kristallografiya* **58**, 952 (2013). (in Russian).
- [36] N.I. Sorokin, M.V. Fominykh, E.A. Krivandina, Z.I. Zhmurova, B.P. Sobolev. *FTT*, **41**, 310 (1996). (in Russian).
- [37] B.P. Sobolev, K.B. Seiranian, L.S. Garashina, P.P. Fedorov. *J. Solid State Chem.* **28**, 51 (1979).
- [38] A. Duvel, J. Bednarcik, V. Sepelak, P. Heitjans. *J. Phys. Chem. C* **118**, 7117 (2014).
- [39] A.N. Matsulev, B.M. Buznik, A.I. Livshits, P.P. Fedorov, B.P. Sobolev. *FTT*, **30**, 3554 (1988). (in Russian).
- [40] F.A. Kroger. *The chemistry of inperfect crystals*. North-Holland, Amsterdam (1964). 1039 p.
- [41] B.P. Sobolev, A.M. Golubev, P. Herrero. *Kristallografiya* **48**, 148 (2003). (in Russian).
- [42] W. Bollmann. *Kristall und Technik* **15**, 197 (1980).