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Study of charge carrier mobility in superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$ by electric modulus spectroscopy

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The spectra of the complex electric modulus $M^*(\nu) = M' + iM''$ for a single crystal of the superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$ with the tysonite structure (space group $P\bar{3}c1$) were studied in the frequency ranges of $10^{-1}-10^7$ Hz and temperatures of $133-273$ K. The diagrams of the complex electric modulus $M^*(\nu)$ are characterized by a distribution of the dielectric relaxation time of charge carriers (fluorine vacancies). Relaxation peaks caused by the mobility of ion carriers are observed on the frequency dependences of the imaginary part of the electric modulus $M''(\nu)$. Based on the temperature change in the position of the relaxation maxima, the average hopping frequency, carrier mobility and activation enthalpy of ion transfer were calculated, which are $\nu_h = 3.1 \cdot 10^7$ Hz, $\mu_{mob} = 1.5 \cdot 10^{-7}$ cm^2/(sV) at room temperature (293 K, extrapolation) and $\Delta H_h = 0.37 \pm 0.02$ eV, respectively.

Keywords: dielectric spectroscopy, superionic conductor, lanthanum fluoride, strontium fluoride, tysonite structure, complex electrical module.

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1. Introduction

Nonstoichiometric phases $R_{1-y}M_yF_{3-y}$ with a tyisonite structure (type LaF_3) formed in condensed binary systems MF_2-RF_3 ($3M$ are alkaline earth elements Ca, Sr, Ba and $15R$ are rare earth elements La–Lu and Y, with the exception of Pm, Sc), are advanced fluorine-conducting superionic conductors [1–4]. The phases $R_{1-y}M_yF_{3-y}$ are heterovalent solid solutions in which the crystalline state with high ionic conductivity occurs due to heterovalent substitutions of R^{3+} cations with M^{2+}, leading to the formation of mobile defects (fluorine vacancies) in the anionic sublattice.

Various mathematical formalisms are used to describe electrophysical phenomena in superionics: complex functions of impedance $Z^*(\omega)$, addmitance $Y^*(\omega) = [Z^*(\omega)]^{-1}$, permittivity $\varepsilon^*(\omega)$ and electrical modulus $M^*(\omega) = [\varepsilon^*(\omega)]^{-1}$, where $\omega = 2\pi\nu$ — circular frequency [5,6]. These functions are interrelated, but the use of one formalism or another makes it possible to visually identify and analyze in more detail different electrophysical processes. Modular spectroscopy makes it possible to study the dielectric characteristics of ionic crystals and glasses, and to obtain information about the dielectric relaxation associated with local hops of mobile charge carriers in superionic conductors [7–9]. Nanofluorides $La_{1-y}M_yF_{3-y}$ (M = Sr, Ba) [10,11], $Ba_{0.6}La_{0.4}F_{2.4}$ [12] and glasses based on ZrF_4 [13,14].

The Shubnikov Institute of Crystallography (currently part of the Kurchatov Institute) has been conducting a program for many years to study rapid ion transfer in nonstoichiometric fluorides $R_{1-y}M_yF_{3-y}$ and materials based on them in the form of single crystals, polycrystals, ceramics and composites [15–18]. Based on the results of these studies, a tysonite solid solution of $La_{1-y}Sr_yF_{3-y}$ ($y = 0.05$) composition belongs to the most conductive fluoride superionic conductors.

The purpose of this paper is to study the spectra of the electrical module and calculate the mobility of charge carriers for a superionic conductor single crystal $La_{0.95}Sr_{0.05}F_{2.95}$.

2. Experiment

Single crystals of $La_{0.95}Sr_{0.05}F_{2.95}$ were grown from a melt by the Bridgman technique in a fluorinating atmosphere and were structurally certified at the Institute of Crystallography [19]. The experiments were performed on an undirected single crystal sample in the form of a disk with a diameter of 11.2 mm and a thickness of 1.9 mm, assuming the isotropic behavior of the ionic conductivity [20,21].

Electrophysical measurements were performed by impedance spectroscopy (Solartron 1260) in the frequency ranges of $10^{-1}-10^7$ Hz and resistance ranges of $1-10^{10}$ Ω with a voltage of 30 mV. Silver paste Leitsilber was used as electrodes. The area of the electrodes was 75 mm^2. The measurements were performed in vacuum ($\sim 10^{-3}$ Pa) in the temperature range of $133-273$ K. The experimental setup is described in Ref. [22].

The relationship between the integrated electrical module $M^*(\omega) = M' + iM''$ and the impedance $Z^*(\omega) = Z' + iZ''$

is given by the following expression

$$M^*(\omega) = i\omega C_0 Z^*(\omega), \qquad (1)$$

where C_0 is the capacity of an empty open cell. The calculations used experimental data for the bulk impedance of the measuring electrochemical cell Ag/$La_{0.95}Sr_{0.05}F_{2.95}$/Ag (impedance data related to the interface Ag/$La_{0.95}Sr_{0.05}F_{2.95}$, excluded from consideration).

The electrical module can be represented as follows [5,7]

$$M^*(\omega) = M_s \int\limits_0^{\infty} \left[i\omega\tau_0/(1 + i\omega\tau_0)\right] g(\tau) d\tau, \qquad (2)$$

where $M_s = 1/\varepsilon_s$, ε_s is the static (at zero frequency) dielectric constant, $g(\tau)$ is the distribution function of dielectric relaxation times, τ_0 is the average time of dielectric relaxation. The hodographs of the electrical module $M^*(\nu)$ in the complex plane M', M'' and the frequency dependence graphs of its real $M'(\nu)$ and imaginary $M''(\nu)$ components were processed using the FIRDAC program [23].

3. Results and discussion

Figure 1 shows the examples of the hodograph of an electrical module in the complex plane $M^*(\nu) = M'(\nu) + iM''(\nu)$ and the frequency dependences $M'(\nu)$ and $M''(\nu)$ for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$ at temperature 152.6 K. The spectra of the electrical module have a similar appearance at other temperatures. The obtained spectra $M^*(\nu)$ correspond to the dielectric processes of polarization (charge accumulation) in the bulk of the crystal. The study of the electrical module of crystals provides important information about the microscopic characteristics of the dielectric relaxation of an electric charge.

The hodograph $M^*(\nu)$ is a part of a semicircle with the center shifted from the axis of the abscissa by the angle of depression θ. This type of hodograph $M^*(\nu)$ can be described by the Cole-Cole type relaxation time distribution [24]:

$$M^* = M_\infty - (M_\infty - M_s)/[1 + (i\omega\tau_0)^{1-\alpha}], \qquad (3)$$

where the parameter $\alpha = 2\theta/\pi$ characterizes the deviation from the Debye behavior, M_s and M_∞ correspond to the values of the electrical module at zero and infinite frequency, respectively. The values of the parameter α for the crystal $La_{0.95}Sr_{0.05}F_{2.95}$ are equal to 0.1−0.25 in the range of measured temperatures.

The low-frequency cutoff of the hodograph $M^*(\nu)$ on the abscissa axis M_s makes it possible to determine the static dielectric constant:

$$\varepsilon_s = 1/M_s. \qquad (4)$$

The values of static permeability ε_s in the temperature range of 133−210 K are 17 ± 1. It can be seen that they are typical for crystals with an ionic chemical bond.

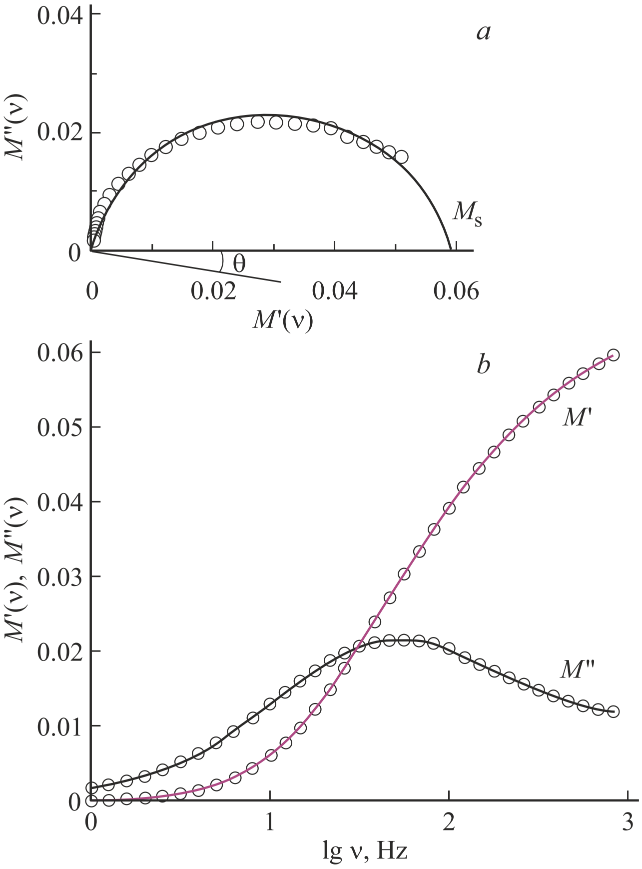

Figure 1. *a*) Diagram of the electrical module $M^*(\nu)$ in the complex plane M', M'' and *b*) frequency dependences $M'(\nu)$, $M''(\nu)$ for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$ in frequency range of $1-1 \cdot 10^3$ Hz at 152.6 K. The depression angle θ for the hodograph of the electrical module is equal to 14°.

Figure 2 shows the frequency dependences of the imaginary part of the complex module $M''(\nu)$ of the $La_{0.95}Sr_{0.05}F_{2.95}$ crystal. Relaxation peaks are observed on dependencies $M''(\nu)$ at $\nu = \nu_{M''}$ due to ionic mobility.

The values of relaxation maxima $\nu_{M''}(T)$ in the temperature range of 133−255 K for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$ are given in the table, and their temperature dependence is shown in Figure 3.

It can be seen that the characteristic frequency $\nu_{M''}$ has an activation character. The average frequency of hopping attempts and activation enthalpy for mobile ions can be calculated based on the temperature change in the position of the relaxation maxima, provided that the following condition is met $\nu_h \approx \nu_{M''}$ [9].

The temperature dependence of the hopping frequency ν_h of charge carriers for the $La_{0.95}Sr_{0.05}F_{2.95}$ crystal corresponds to the Arrhenius equation:

$$\nu_h = \nu_0 \cdot \exp[-\Delta H_h/k_B T], \qquad (5)$$

where ν_0 is the pre-exponential multiplier of the hopping frequency and ΔH_h is the activation enthalpy of the anion

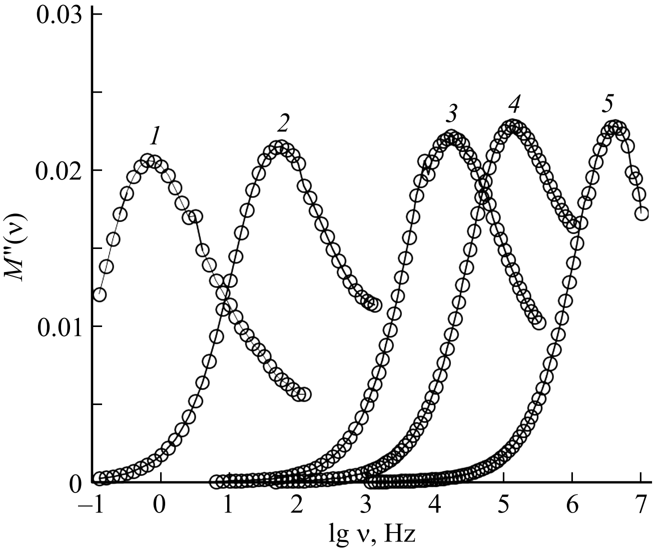

Figure 2. Frequency dependences of the imaginary part $M''(\nu)$ for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$: curve *1* — 132.8 K, *2* — 152.6 K, *3* — 191.2 K, *4* — 210.5 K, *5* — 254.6 K.

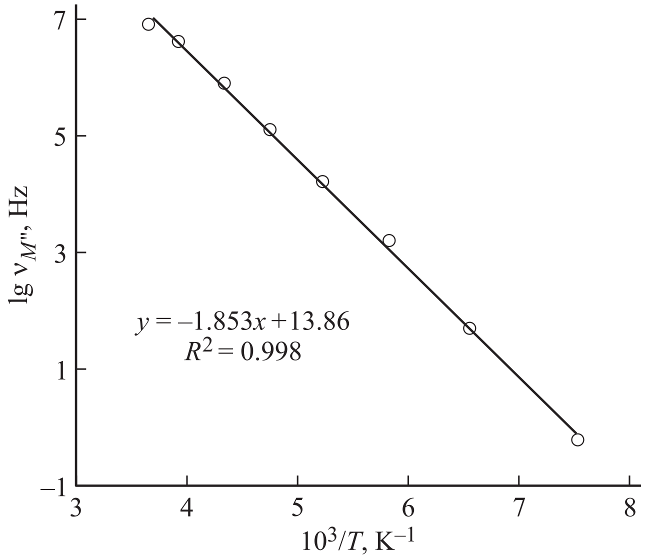

Figure 3. Temperature dependence of relaxation maxima $\nu_{M''}(T)$ for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$.

carrier hopping. Calculated parameters of the equation (5) are $\nu_0 = 7.2 \cdot 10^{13}$ Hz and $\Delta H_h = 0.37 \pm 0.02$ eV.

The results obtained are in satisfactory agreement with the data for the hopping motion of charge carriers calculated using the Almond-West method for the alternating current conductivity $\sigma_{ac}(\nu)$of this crystal [20]: $\nu_0 = 1.9 \cdot 10^{14}$ Hz and $\Delta H_h = 0.37 \pm 0.03$ eV. The values of enthalpies ΔH_h completely coincide for two approaches and the difference in the estimates of the multiplier ν_0 is 2.6 times.

Bulk resistance R_b and relaxation peak frequency $\nu_{M''}$ on dependence $M''(\nu)$ for superionic conductor single crystal $La_{0.95}Sr_{0.05}F_{2.95}$

T, K	R_b, Ω	lg $\nu_{M''}$, Hz
273.5	$1.93 \cdot 10^3$	6.9
254.6	$6.2 \cdot 10^3$	6.6
230.4	$3.74 \cdot 10^4$	5.9
210.5	$2.3 \cdot 10^5$	5.1
191.2	$1.82 \cdot 10^6$	4.2
171.7	$2.52 \cdot 10^7$	3.2
152.6	$6.14 \cdot 10^8$	1.7
132.8	$4.3 \cdot 10^{10}$	−0.2

Figure 4 shows the temperature dependence of the ionic conductivity $\sigma_{dc}(T)$ for the studied single crystal. The dependence $\sigma_{dc}(T)$ satisfies the Frenkel-Arrhenius equation:

$$\sigma_{dc} = (\sigma_0/T)\exp[-\Delta H_\sigma/k_B T], \tag{6}$$

where the pre-exponential factor of electrical conductivity $\sigma_0 = 4.6 \cdot 10^5$ SK/cm and the enthalpy of activation of ionic conductivity $\Delta H_\sigma = 0.39 \pm 0.01$ eV.

As noted in Ref. [22], within the limits of experimental accuracy, the enthalpy of activation of the hopping frequency and ionic conductivity coincide for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$: $\Delta H_h = \Delta H_\sigma$. Therefore, the processes of hopping dielectric relaxation and ionic conduction are interrelated and are determined by the same charge carriers — „impurity“ fluorine vacancies $V_F^{\bullet}$, formed as a result of heterovalent substitutions of La^{3+} cations on Sr^{2+} in the crystal lattice of tisonite:

$$La_{La}^{\times} \to Sr_{La}' + V_F^{\bullet}. \tag{7}$$

Here, the designations of defects are given in the Kröger-Wink system [25].

The relationship between the mobility μ_{mob} of charge carriers and the frequency of their hops ν_h is given by the

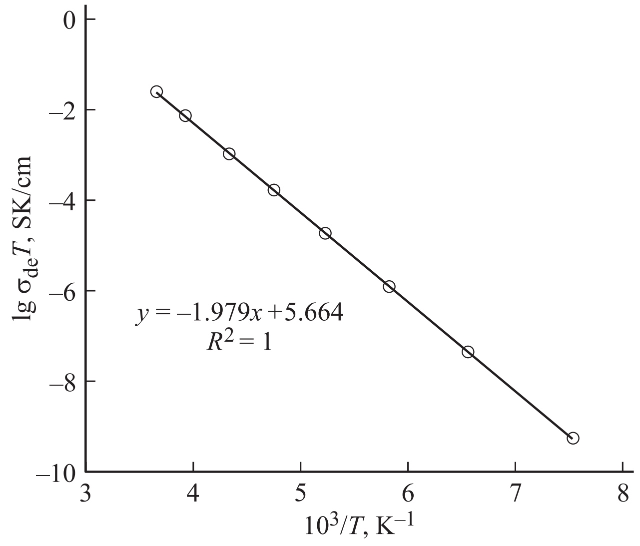

Figure 4. Temperature dependence of electrical conductivity $\sigma_{dc}(T)$ for superionic conductor $La_{0.95}Sr_{0.05}F_{2.95}$.

Nernst-Einstein equation

$$\mu_{\mathrm{mob}} = q\nu_{\mathrm{h}}d^2/6k_{\mathrm{B}}T, \tag{8}$$

where d is the hopping distance of charge carriers.

In the tysonite structure, fluorine ions are distributed in three_ crystallographic positions of the spatial group $P\bar{3}c1$ with the ratio $\mathrm{F}_1 : \mathrm{F}_2 : \mathrm{F}_3 = 12 : 4 : 2$ [26–28]. The coordination number of fluorine anions by cations is 4 for F_1 and 3 for F_2, F_3. The crystallochemical difference between positions F_2 and F_3 is small, therefore, when interpreting physical properties, they are often grouped into the general group $\mathrm{F}_{2,3}$. It is generally assumed [29–31] that the ion transfer below 420 K is mainly associated with the migration of fluorine vacancies $V_{\mathrm{F}}^{\bullet}$ along structural positions F_1.

Taking the average value between the nearest ion positions F_1 in the crystal LaF_3, equal to 0.27 nm, it is possible to calculate by extrapolation the values of the frequency of hops and mobility of charge carriers at room temperature (293 K). Then, according to equations (5) and (6), their values are $\nu_{\mathrm{h}} = 3.1 \cdot 10^7$ Hz and $\mu_{\mathrm{mob}} = 1.5 \cdot 10^{-7}\,\mathrm{cm}^2/(\mathrm{sV})$.

4. Conclusion

The spectra of the complex electrical module $M^*(\nu) = M' + iM''$ for the superionic conductor $\mathrm{La}_{0.95}\mathrm{Sr}_{0.05}\mathrm{F}_{2.95}$ are studied. $M'(\nu)$, $M''(\nu)$ diagrams are characterized by the presence of a relaxation time distribution of charge carriers. Relaxation peaks due to the mobility of ion charge carriers are observed on the frequency dependence of the imaginary part of the electrical module $M''(\nu)$. The enthalpy of activation of charge carrier hopping $\Delta H_{\mathrm{h}} = 0.37 \pm 0.02$ eV, and the frequency of hopping attempts $\nu_0 = 7.4 \cdot 10^{13}$ Hz were calculated from the temperature change in the position of relaxation maxima. The average frequency of hops and mobility of charge carriers at room temperature (293 K, extrapolation) are $\nu_{\mathrm{h}} = 3.1 \cdot 10^7$ Hz, $\mu_{\mathrm{mob}} = 1.5 \cdot 10^{-7}\,\mathrm{cm}^2/(\mathrm{sV})$, respectively.

It was found that the dielectric characteristics of the superionic conductor $\mathrm{La}_{0.95}\mathrm{Sr}_{0.05}\mathrm{F}_{2.95}$ obtained by modular spectroscopy and using the Almond-West approach are in satisfactory agreement with each other.

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Conflict of interest

The author declares no conflict of interest.

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