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Electrical conductivity and structural conditionality of ion transfer in langasite $La_3Ga_5SiO_{14}$: Mn

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The temperature dependence of the static electrical conductivity $\sigma_{dc}(T)$ of a single crystal of lanthanum gallium silicate (langasite) $La_3Ga_5SiO_{14}$ activated with an impurity ofMn (1000 ppm) has been studied by impedance spectroscopy. Impedance measurements of $La_3Ga_5SiO_{14}$ (sp. gr. *P321*, $Z = 1$) were carried out along crystallographic axes a (double symmetry axis) and c (triple symmetry axis). It was found that the values of $\sigma_{\|a}$ are significantly higher than the electrical conductivity $\sigma_{\|c}$, the anisotropy of the electrical conductivity is $\sigma_{\|a}/\sigma_{\|c} = 170$ at 773 K. The activation energy of electrotransport is $E_\sigma = 0.75 \pm 0.05$ and 1.09 ± 0.02 eV along the a and c axes, respectively. The electrical conductivity mechanism has an ionic nature and an impurity character; oxygen vacancies $V_O^{\bullet\bullet}$ are the most probable current carriers.

Keywords: lanthanum gallium silicate, langasite family, single crystal, electrical conductivity, anisotropy.

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1. Introduction

Crystals in the family of lanthanum gallium silicate (langasite) $La_3Ga_5SiO_{14}$ have promising piezoelectric and nonlinear optical properties and are functional materials for the dielectric physics, crystal optics, non-linear photonics, acoustoelectronics and piezo engineering. They can be used to create high-temperature piezoelectric sensors, wideband filters (including those operating with surface and bulk acoustic waves), optical media for tunable lasers etc. [1–5]. The advantages of piezoelectric $La_3Ga_5SiO_{14}$ crystals is the absence of phase transitions in the entire existence region (melting temperature $T_{fus} = 1743$ K), high values of temperature stability and absence of electronic and vibrational transition in the spectral region of $0.2{-}8\,\mu$m (the transparency window) [6].

Physical properties of $La_3Ga_5SiO_{14}$ crystals are an implicit function of defect concentration and heavily depend on growing conditions, injection of dopant impurities, external and technological impacts [6,7]. Works in the field of the making of langasite family crystals and study of their atomic structure and physical/chemical properties are being continued.

Langasite $La_3Ga_5SiO_{14}$ has the layered (in the direction of crystallographic axis c (the Z axis) structure of calcium-gallogermanate $Ca_3Ga_2Ge_4O_{14}$ (space group *P321*, $Z = 1$) [1,8,9]. The parameters of the trigonal unit cell and density for $La_3Ga_5SiO_{14}$ are $a = 8.1652(6)$, $c = 5.0958(5)$ Å, $c/a = 0.624$ [8] and $\rho = 5.75\,g/cm^3$ [6].

The chemical formula for langasite family crystals can be written as $A_3BC_3D_2O_{14}$, where cations A, B, C and D are located at four types of sites — regular systems of points of space group *P321* (Fig. 1) [4,10]. The langasite unit cell contains 23 ions. Large cations A (La^{3+}) are at sites *3e* on twofold symmetry axes. They are surrounded by eight oxygen anions, forming a coordination polyhedron (Thomson cube) $[AO_8]$. Cations B (Ga^{3+}) are located at sites *1a* on the intersection of the twofold and threefold axes, in octahedra $[BO_6]$. Cations C (Ga^{3+}) are located at sites *3f* on twofold axes, in tetrahedra $[CO_4]$. Cations D (Ga^{3+}, Si^{4+}) are located at sites $2d$ on threefold axes, in tetrahedra $[DO_4]$. Sites *3e*, *1a* and (*3f, 2d*) are characterized by octantal, hexad and quadruple coordination by oxygen and the coordination number (CN) of cations is equal to 8, 6 and 4 respectively. All sites *3e*, *1a*, *3f* and *2d* allow for wide isomorphic substitutions of cations, while their coordinates, polyhedra and CNs remain unchanged.

The four kinds of cationic polyhedra are packed in two layers (Fig. 1), which are alternately located perpendicularly to crystallographic axis c [1,9]. The first layer consists of Thomson cube $[AO_8]$ and octahedra $[BO_6]$, the second layer — of tetrahedra $[CO_4]$ and $[DO_4]$.

An essential factor for stability of the $A_3BC_3D_2O_{14}$ structure is the fact that the crystalline frame, composed of octahedra $[BO_6]$ and tetrahedra $[CO_4]$ and $[DO_4]$, is stabilized by large cations (La^{3+}) in the octantal coordination. On the contrary, large cations at octahedral and tetrahedral sites destabilize the structure, therefore sites B, C and D are occupied by cations of a smaller radius. Thereat, the size of tetrahedron D is smaller than that of tetrahedron C, so that smaller cations will be located at site D, and larger ones — at site C.

Electrical conductivity of dielectric ionic crystals, which include langasite family crystals, usually is of the ionic

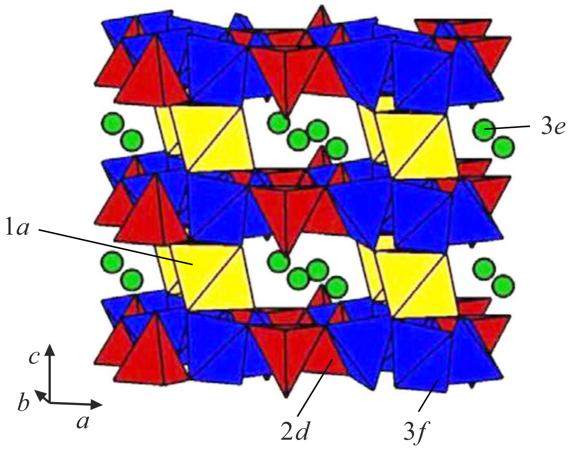

Figure 1. Structure of langasite crystal $La_3Ga_5SiO_{14}$ consisting of alternating layers of two types: the first layer contains 1a-octahedra [GaO_6] and large cations La (3e); the second one contains two varieties of tetrahedra [GaO_4] and [$(Ga,Si)O_4$].

nature. Ionic conductivity in dielectrics has an activation nature: thermal activation of ionic crystals causes the formation of mobile point defects [11]. The smaller the electrical conductivity value (the higher the electrical resistance), the more perfect the dielectric crystal is structurally. Ionic electrical conductivity is one of the reasons for electrical aging of dielectrics [12].

The main intrinsic defects in $La_3Ga_5SiO_{14}$ crystals, according to [13,14], are vacancies of oxygen $V_O^{\bullet\bullet}$, gallium V_{Ga}''' and lanthanum V_{La}''' (the defect designations are given in the Kröger–Vink notation [15]). In addition to them, $La_3Ga_5SiO_{14}$ crystals can contain significant concentrations of non-intrinsic defects due to impurities.

As distinct from the studies of optical, mechanical and thermal properties [7,13,16–21], so far there is insufficient data about the electrical conductivity and anisotropy mechanism for langasite crystals. Electrical conductivity of lanthanum gallium silicate is low and its value limits the operation reliability of piezoelectric element in different devices. Studies of Electrical conductivity of $La_3Ga_5SiO_{14}$ crystals by the direct current method along axes a and c [22,23] and the alternating current method (impedance spectroscopy) along axis c have been performed comparative recently [24]. However, the data about electrical conductivity in $La_3Ga_5SiO_{14}$ crystals in these papers is contradictory.

The direct current measurements [22,23] revealed a strong change (by several orders) of the electrical conductivity value of $La_3Ga_5SiO_{14}$ along axis c in the temperature range of 293–723 K. It was shown that electrical conductivity of the langasite crystal is of ionic nature and the impurity pattern. The ionic conductivity value is equal to $\sigma \sim 10^{-8}$ S/cm at 673 K [22,23], which is significantly lower than the electrical conductivity of a superionic conductor —stabilized zirconium oxide $Zr_{1-x}Y_xO_{2-x}$ with the fluorite structure ($\sigma \sim 2 \cdot 10^{-5}$ S/cm [25–27]).

The electrical conductivity value of the $La_3Ga_5SiO_{14}$ crystal along axis c in the impedance measurements [24] in the same temperature range (293–723 K) changed only in 2 times and heavily depended on electrode material type. Therefore it is interesting to continue studying the langasite ionic crystals by the impedance spectroscopy method.

The paper presents the results of measurements of the temperature dependence of static electrical conductivity $\sigma_{dc}(T)$ along crystallographic axes c and a and discusses the structural mechanism of electron transfer in crystals of langasite $La_3Ga_5SiO_{14}:Mn$.

2. Experiment

A single crystal of manganese-activated langasite, $La_3Ga_5SiO_{14}:Mn$, was used in the experiments; in [13] it was studied by optical spectroscopy methods. Manganese-activated langasite of optical quality was grown by B.V. Mill (MSU) from the melt by the Czochralski method; the crystal growing procedure is given in [9]. The crystal is pink, the manganese impurity content is 0.1 mass.% (1000 ppm) Mn.

The sample for electrophysical measurements was a rectangular parallelepiped $3.1 \times 5.9 \times 7.1$ mm with edges parallel to the crystallographic directions of the trigonal system [0001] (axis c) and $[2\overline{11}0]$ (axis a).

Static electrical conductivity σ_{dc} was determined from the impedance spectra in the frequency range of $5-5 \cdot 10^5$ Hz and resistance range of $1-10^7\,\Omega$ (Tesla BM-507 device). Temperature measurements of impedance were performed from room temperature to 827 (along axis c) and 785 K (along axis a). Given the low electrical conductivity of the $La_3Ga_5SiO_{14}:Mn$ crystal, values of σ_{dc} were determined from the impedance spectra only in the narrow temperature ranges of 767–827 K (along axis c) and 736–785 K (along axis a). Graphite paste DAG-580 was used as an electrode material. The experimental setup and the electrophysical measurement procedure are described in [28]. The relative measurement error σ_{dc} is equal to 5%.

3. Discussion of results

The temperature dependences of electrical conductivity $\sigma_{dc}(T)$ of the $La_3Ga_5SiO_{14}:Mn$ crystal along axes a and c are shown in Fig. 2. The conductometric data was processed in compliance with the Arrhenius–Frenkel equation

$$\sigma_{dc} T = \sigma_0 \exp(-E_\sigma/kT), \tag{1}$$

where σ_0 is the pre-exponential multiplier of electrical conductivity and E_σ is the energy of electron transport activation. The values of σ_{dc} in impedance measurements along axis c at 767 and 827 K are equal to $3.5 \cdot 10^{-7}$ and $10.6 \cdot 10^{-7}$ S/cm respectively. Energy of electron transport activation $E_\sigma = 1.09 \pm 0.02$ eV, multiplier $\sigma_0 = 3.75 \cdot 10^3$ SK/cm and conductivity $\sigma_{dc} = 3.8 \cdot 10^{-7}$ S/cm at 773 K, calculated

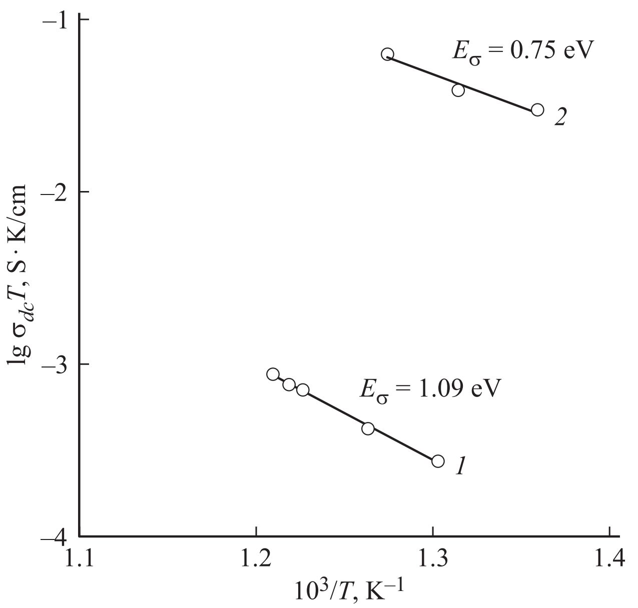

Figure 2. Temperature dependences of electrical conductivity of the $La_3Ga_5SiO_{14}$ crystal: Mn along different crystallographic directions: *1* — along axis *c* (direction [0001]) and *2* — along axis *a* (direction [2110]).

from processing of the temperature dependence $\sigma_{dc}(T)$ (the coefficient of correlation of the experimental data to theoretical equation (1) is $R^2 = 0.995$).

The conductivity value extrapolated by equation (1) to the temperature of 573 K, which is equal to $1.7 \cdot 10^{-9}$ S/cm, and the energy of electron transport activation of 1.09 eV agree well with the data obtained by the direct current electrical conductivity method for crystal of complex oxides $La_3Ga_5SiO_{14}$ ($\sigma_{dc} \sim 10^{-9}$ S/cm and $E_\sigma = 1.0 \pm 0.1$ eV [23,24]) $Sr_{0.75}Ba_{0.25}Nb_2O_6$ ($\sigma_{dc} \sim 10^{-9}$–10^{-8} S/cm and $E_\sigma = 1.1$ eV [29]).

Values of σ_{dc} are considerably higher in the measurements along axis *a*. At 736 and 785 K they are equal to $4.1 \cdot 10^{-5}$ and $8.1 \cdot 10^{-5}$ S/cm respectively. Energy of electron transport activation $E_a = 0.75 \pm 0.05$ eV and multiplier $\sigma_0 = 3.86 \cdot 10^3$ SK/cm (correlation coefficient $R^2 = 0.945$); conductivity $\sigma_{dc} = 6.5 \cdot 10^{-5}$ S/cm at 773 K.

Transfer of electric charges in a trigonal crystal of lanthanum gallium silicate is anisotropic. The value of electrical conductivity anisotropy is equal to $\sigma_{\|a}/\sigma_{\|c} = 170$ at 773 K, where $\sigma_{\|a}$ and $\sigma_{\|c}$ are the measurements along crystallographic axes *a* and *c* respectively. This fact is confirmed by the results of the studies [23,30], which revealed an anisotropic behavior of electrical resistance of langasite family crystals $La_3Ga_5SiO_{14}$ and $La_3Ga_{5.5}M_{0.5}O_{14}$ ($M =$ Nd, Ta).

A crystal chemical analysis indicates the possibility of high-temperature O^{2-}-ion transfer according to the vacansion mechanism in the structure of the $La_3Ga_5SiO_{14}$ complex oxide. The band gap in the $La_3Ga_5SiO_{14}$ crystal is equal to $E_g \approx 5$ eV [31,32]. $La_3Ga_5SiO_{14}$ crystals have the ionic type of chemical bonding (Coulomb interaction between cations and anions). It facilitates mobility of O^{2-} anions in the lanthanum gallium silicate structure and a lower absolute charge value as compared to La^{3+}, Ga^{3+} and Si^{4+} cations. Ion transfer of high-charge La^{3+}, Ga^{3+} and Si^{4+} cations is unlikely.

The radius of O^{2-} oxygen anion (1.35–1.42 Å for CN = 2–8 [33]) is rather large as compared to the ionic radii of La^{3+} cations (1.16 Å for CN = 8), Ga^{3+} (0.62 and 0.47 — for CN = 6 and 4 respectively) and Si^{4+} (0.26 for CN = 4), which make up the langasite crystal structure, that's why the probability of oxygen embedding into interstitial sites is low.

The vacansion mechanism of ion transfer, as the most probable one, in $La_3Ga_5SiO_{14}$ crystals, where mobile ion defects are oxygen vacancies $V_O^{\bullet\bullet}$, is indicated in [30]. The existence of defects $V_O^{\bullet\bullet}$ is the basis of all models of the defect structure of crystals in complex oxides of the langasite family [7,14,17]. It should be noted that the formation of vacancies $V_O^{\bullet\bullet}$ is the preferred method for creating a disordered subsystem of mobile conductivity anions in oxygen-conducting solid electrolytes [34]. The formation of anionic vacancies $V_O^{\bullet\bullet}$ causes an increase of mobility of O^{2-} anions without a change of the spatial location of conductivity channels.

The authors of [13] used the optical spectroscopy and EPR methods to demonstrate that manganese ions are in the valent state Mn^{2+} (electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$) and they embed into octahedral sites *1a* space group *P321*, substituting the Ga^{3+} cations. Mn^{2+} cations are characterized by octahedral coordination in inorganic oxides (MnO) and fluorides (MnF_2).

Impurity defects (vacancies $V_O^{\bullet\bullet}$) form by substitution of Ga^{3+} cations (0.62 Å) at octahedral sites by Mn^{2+} cations (0.67 Å). The crystal-chemical mechanism of oxygen vacancy formation in the matrix of langasite doped with manganese cations is as follows

$$2\mathrm{Ga}_{\mathrm{Ga}}^{\times} + 3\mathrm{O}_{\mathrm{O}}^{\times} \rightarrow 2\mathrm{Mn}'_{\mathrm{Ga}} + V_{\mathrm{O}}^{\bullet\bullet} + 2\mathrm{O}_{\mathrm{O}}^{\times}. \qquad (2)$$

One oxygen vacancy forms in the structure after two manganese cations are implanted.

The values of activation energy $E_\sigma = 0.8$–1.1 eV in $La_3Ga_5SiO_{14}$: Mn are close to the energy of ion transfer activation ($E_\sigma = 1$–1.2 eV [25–27,35]) of oxygen-containing superionic conductor $Zr_{1-x}Y_xO_{2-x}$ ($x = 0.12$), where the charge carriers are mobile oxygen vacancies $V_O^{\bullet\bullet}$. This fact indicates the oxygen vacancies $V_O^{\bullet\bullet}$ as the most probable current carriers.

In addition to electrophysical properties, anisotropy was found in trigonal $La_3Ga_5SiO_{14}$ crystals in the measurements of mechanical (microhardness, thermal expansion coefficient, elastic coefficients) and thermal (thermal conductivity) properties [16–20].

The mechanism of ionic conductivity in the $La_3Ga_5SiO_{14}$: Mn crystal is non-intrinsic (due to the Mn^{2+}) impurity, the mobile charge carriers are impurity vacancies $V_O^{\bullet\bullet}$. Vacancies $V_O^{\bullet\bullet}$ can go from one oxygen coordination polyhedron to another. Apparently, the layered structure in the direction of axis c hinders the ion transfer through the layers of closest packing as compared to the ion transfer in the direction of axis a in the layer plane. As a result, the enthalpy of activation for motion of mobile vacancies decreases in the layer plane $V_O^{\bullet\bullet}$.

Given the considered mechanism of oxygen vacancy formation (2), the structural formula of the $La_3Ga_5SiO_{14}:Mn$ crystal can be written as

$$La_3Ga_{5-x}Mn_xSiO_{14-x/2}\square_{x/2}, \quad (3)$$

where $\square_{x/2}$ are oxygen vacancies. While taking the parameters of a trigonal unit cell from [8] and assuming the manganese impurity concentration in the crystal equal to $x = 10^{-3}$ (1000 ppm) in the first approximation, the concentration and mobility of oxygen vacancies were estimated within the framework of a crystal-chemical model. The concentration of oxygen impurity vacancies is equal to

$$n = x/(2 \times 0.866 \times a^2 \times c) = 1.7 \cdot 10^{18}\,\text{cm}^{-3}. \quad (4)$$

Their mobility at 573 K (the contribution of thermal own vacancies of oxygen to electrical conductivity $\sigma_{\parallel c}$ at this temperature is not yet significant) is

$$\mu = \sigma_{dc}/qn = 6 \cdot 10^{-9}\,\text{cm}^2/\text{V}\cdot\text{s}, \quad (5)$$

where q is the elementary charge.

4. Conclusion

Measurements of electrical conductivity $\sigma_{dc}(T)$ of dielectric ionic oxide crystals of the langasite family are difficult due to their small value. Electrical conductivity of $La_3Ga_5SiO_{14}$ is sensitive to the formation of manganese cations (1000 ppm) in the crystal structure, is of the ionic nature and impurity pattern. Ionic conductivity of the $La_3Ga_5SiO_{14}:Mn$ crystal is due to migration of oxygen vacancies $V_O^{\bullet\bullet}$ across the crystal lattice; these vacancies form upon heterovalent substitution of Ga^{3+} cations by Mn^{2+} at octahedral sites *1a* space group *P321*.

The obtained temperature dependences of langasite electrical conductivity made it possible to determine the energy of migration of crystal lattice defects — oxygen vacancies $V_O^{\bullet\bullet}$. We have analyzed the parameters of electron transfer in different crystallographic directions of the $La_3Ga_5SiO_{14}:Mn$ crystal and revealed anisotropy of ionic conduction and energy of ion transfer activation. A decrease of the enthalpy of activation for motion of O^{2-} anions across vacant crystallographic sites along axis a (as compared to axis c) results in an increase of the ionic conductivity value by ~ 2 orders.

The concentration and mobility of impurity oxygen vacancies were estimated based on a crystal-chemical model.

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Conflict of interest

The authors declare that they have no conflict of interest.

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