Research Article

Growth and Neutron Diffraction Investigation of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ Crystals

I. A. Kaurova,¹ G. M. Kuz'micheva,² V. B. Rybakov,³ A. Cousson,⁴
O. Zaharko,⁵ and E. N. Domoroshchina²

¹ Moscow State Open University, 3 Entuziastov Street, Aleksandrov 601655, Russia

² Lomonosov Moscow University of Fine Chemical Technology, 86 Vernadskogo Prospekt, Moscow 119571, Russia

³ Lomonosov State University, Vorobyovy Gory, Moscow 119992, Russia

⁴ Laboratoire Leon Brillouin, Cea/Saclay, 91191 Gif-sur-Yvette Cedex, France

⁵ Laboratory for Neutron Scattering, ETZ Zurich & Paul Scherrer Institute (PSI), CH 5232 Villigen, Switzerland

Correspondence should be addressed to I. A. Kaurova; kaurchik@yandex.ru

Received 27 November 2012; Accepted 6 February 2013

Academic Editor: Necmettin Maraşlı

Copyright © 2013 I. A. Kaurova et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Langanite ($\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$, growth atmosphere: 99% Ar + 1% O_2) and kanigasite ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$, growth atmosphere: 100% Ar) crystals grown by the Czochralski technique in Ir crucibles along $\langle 0001 \rangle$ direction have been firstly investigated by neutron diffraction. The difference between the compositions of upper ($\text{La}_{2.935(2)}\square_{0.065}(\text{Ga}_{0.450}\text{Nb}_{0.550(3)})\text{Ga}_3(\text{Ga}_{1.965(4)}\square_{0.035})(\text{O}_{13.90(1)}\square_{0.10})$) and lower ($\text{La}_{2.940(1)}\square_{0.060}(\text{Ga}_{0.590}\text{Nb}_{0.410(2)})\text{Ga}_5(\text{O}_{13.82(1)}\square_{0.18})$) parts of orange langanite crystal was found. It was established that the colorless $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystal grown by using the single-crystal charge has the composition $(\text{Ca}_{2.95}\square_{0.05(1)})\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and is less defective in comparison to the yellow one grown by using the charge prepared by conventional solid-state reaction. For $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals the possibility of microtwin formation (two unit cells connected by the translation: $1/2 z$) was revealed for the first time. It was found that the difference between the color of crystals is attributed to the qualitative differentiation of oxygen vacancies.

1. Introduction

Kanigasite ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$, **CNGS**) and langanite ($\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$, **LGN**) crystals have langasite-type structure (sp.gr. $P321$, $Z = 1$) similar to langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$, **LGS**) and langatate ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, **LGT**) ones. Langasite family crystals possess a number of properties that ensure the successful application in piezo-, opto-, and acoustoelectronics. These properties include the absence of structural phase transitions up to the melting temperature, high thermal stability, high values of electromechanical coupling coefficients and acoustic Q , and low loss propagation of the elastic waves in the crystal. Langanite is characterized by the largest values of piezoelectric modules ($d_{11} = -7.41 \pm 0.2$ C/N; $d_{14} = 6.16 \pm 0.5$ C/N) [1] among the langasite family crystals, whereas the **CNGS** has high values of the

acoustic quality factor ($Q = 56000$) due to the fact that every atom in its structure is located in an individual position. The crystallographic orientation with a zero TCF (temperature coefficient of frequency) at room temperature was found for this crystal. The traditional Czochralski method is the primary method of obtaining large-size **LGN** [2–7] and **CNGS** [6–16] single crystals up to 200 mm in diameter.

However, the use of these compounds depends on the composition (in other words, on the type and concentration of point defects), which does not coincide with the composition of the initial charge. There are quite a few works devoted to the structural investigation of **CNGS** [6, 8, 11] and **LGN** [6, 17, 18] crystals. All of them were performed using X-ray, and the occupancies were refined only in some cases. In the literature there are no results of neutron investigation of **LGN** and **CNGS** crystals, as the most correct to identify defects in the crystallographic positions, in particular, oxygen ones.

Neutron diffraction investigations of langasite [19] and langatate [20–22] single crystals have revealed that the point defects are present in all positions of the structure. In addition, the relationship between the crystal color and the oxygen vacancies contents has been established. Probably the other crystals with langasite-type structure, in particular LGN and CNGS, will have the same relationship.

The aim of this work is to determine the compositions of CNGS and LGN crystals grown by the Czochralski technique using neutron diffraction.

2. Experimental Technique

$\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals were grown by the Czochralski technique along $\langle 0001 \rangle$ direction in a Kristal-3M growth system in Ir crucible ($h = 120$ mm, $d = 120$ mm, the thickness of wall and the bottom $s = 2$ mm) using a pure Ar (CNGS) or 99-98% Ar + 1-2% O_2 (LGN) growth atmospheres. The pulling rate was 1–3 mm/h, and the crystal rotation rate was 1–10 rpm. The CNGS and LGS seeds were used for $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystals growth, respectively. Either crushed CNGS single crystal (crystal 1) or polycrystalline material prepared by conventional solid-state reaction (Al_2O_3 crucible, $T \sim 1300^\circ\text{C}$, 6 hours) (crystal 2) was used for growth of two CNGS crystals. Starting materials were prepared by mixing of 99.99% pure La_2O_3 , Ga_2O_3 , Nb_2O_5 , SiO_2 , and CaCO_3 powders at the stoichiometric ratio. A single-crystal charge was used for $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystal growth.

The colorless (crystal 1) and yellow (crystal 2) $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystals 50 mm in diameter with 80 mm long cylindrical portion [23], as well as the orange $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal 30 mm in diameter with 100 mm long cylindrical portion [24], were grown by the Czochralski technique. All the crystals were transparent. The faceting of the crystals was represented by poorly pronounced faces of the hexagonal prism.

The CNGS samples under investigation represent the upper parts of colorless (CNGS-1) and yellow (CNGS-2) single crystals (Figures 1(a) and 1(b)). Orange LGN samples were cut from the top (LGN-1, LGN-1') and bottom (LGN-2) of the crystal (Figures 2(a) and 2(b)). It should be noted that the upper parts (LGN-1, LGN-1') had a more intense orange color.

The neutron diffraction analysis (NDA) of LGN-1 (size: $\sim 4.3 \times 4 \times 5$ mm) and CNGS-2 (size: $\sim 4 \times 4 \times 4$ mm) samples was carried out at room temperature on the four-circle diffractometer installed at the hot source (5C2) of the Orphee reactor (LLB, France; $\lambda = 0.83$ Å, ω -scan mode), and investigation of CNGS-1 (size: $\sim 3 \times 4 \times 4$ mm), LGN-1' (size: $\sim 4 \times 4 \times 4$ mm), and LGN-2 (size: $\sim 4 \times 4 \times 4.5$ mm) samples was performed at room temperature on the four-circle single-crystal TriCS diffractometer (Paul Scherrer Institute, Switzerland; $\lambda = 1.18$ Å, ω -scan mode).

The X-ray diffraction analysis (XRD) of CNGS-2 microregion $\sim 0.3 \times 0.3 \times 0.3$ mm was carried out on a CAD-4 four-circle diffractometer at room temperature (MoK $_{\alpha}$ radiation, graphite monochromator, ω -scan mode).

The crystal structure (atomic coordinates, occupancies of all positions) was refined using the full-matrix least squares procedure in the anisotropic approximation for all atoms with SHELXL-97 program package [25].

3. Results and Discussions

In the $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ structure each atom is located in the individual position: Ca in the dodecahedral (position 3e), Nb in the octahedral (position 1a), Ga in the tetrahedral (position 3f), and Si in a trigonal-pyramidal (position 2d) [8]. While in the $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})(1)\text{Ga}_3(2)\text{Ga}_2(3)\text{O}_{14}$ crystals lanthanum atoms are in the dodecahedral position of the structure, and gallium atoms occupy octahedral (Ga, Nb)(1) position, half replaced by the niobium atoms, tetrahedral Ga(2) and trigonal-pyramidal Ga(3) ones [17].

3.1. $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ Crystals. According to the neutron diffraction data obtained (Table 1), CNGS-1 cut from the colorless crystal has a composition $(\text{Ca}_{2.95}\square_{0.05(1)})\text{NbGa}_3\text{Si}_2\text{O}_{14}$ with vacancies ($\square$) located in the Ca position- V_{Ca} ". The deficiency of other positions, as well as their occupation by the other atoms (antistructural defects), was not detected. Due to the fact that the electroneutrality condition for the refined composition is not satisfied, we assumed that a certain number of Ca^{2+} ions in the structure are interstitial ones, as for the $(\text{La}_{2.964}\square_{0.036})\text{La}_{(0.036)}\text{Zr}_{0.5}\text{Ga}_5\text{Si}_{0.5}\text{O}_{14}$ [26]. The analysis of the residual nuclear density does not exclude such possibility. The peak with the coordinates $x = 0.464$, $y = 0.069$, and $z = 0.136$ close to the interstitial La_i atom coordinates ($x = 0.418$, $y = 0.009$, and $z = 0.139$) [26] was found. Interstitial Ca_i atoms (like La_i atoms) are displaced from the dodecahedral positions approaching one of four oxygen atoms, thus forming two reduced Ca–O (~ 2.06 Å) and two increased distances. According to Bokiy [27] "the apparent size of the interstitial atoms depends on their relative quantity: the smaller relative quantity of dissolved non-metal, the smaller the apparent size of its atoms."

Thereby, it allow us to rewrite the CNGS-1 crystal composition as $(\text{Ca}_{2.95}\square_{0.05(1)})\text{Ca}_{i(0.05)}\text{NbGa}_3\text{Si}_2\text{O}_{14}$.

Refining the structure of CNGS-2 cut from the yellow crystal by direct methods allows revealing both atomic coordinates similar to CNGS-1 ones (the unit cell 1) and atomic coordinates associated with the previous ones by the transition matrix $/100/010/00z+0.5/$ (the unit cell 2). Both these unit cells are present in structure of CNGS-2 crystal in the ratio of unit cell 1: unit cell 2 $\sim 4:1$ (Table 2). For the structure determination the atomic coordinates of CNGS-1 were taken as the initial ones. However, as a result of the calculation, fairly strong peaks of the residual nuclear density were found. The coordinates of peaks correspond to a crystal model with a shift $1/2 z$. The refinement of the structure using the second model (the initial coordinates are shifted by $1/2$ along the z -axis) based on electron density maps led to the appearance of strong peaks of the residual nuclear density with the coordinates of the initial model (without shift). These experimental results suggest the existence of the translation twin (like racemic twins) at the level of elementary cells. In

FIGURE 1: Photo of the samples CNGS1 (a) and CNGS2 (b).

FIGURE 2: Photo of the samples LGN1 (a) and LGN2 (b).

other words, in CNGS-2 structure there are two unit cells which can be connected with the transition: $1/2 z$. Thereby, the volume defect of the crystal structure (translation twin) is present in some regions of the CNGS-2 sample. Such a defect has not been previously met for langasite family crystals.

According to our results of X-ray diffraction analysis (XRD) which were used for the refinement of the crystal structure of CNGS-2 sample a microregion has a composition $\text{Ca}_3\text{NbGa}_3(\text{Si}_{1.985}\square_{0.015(10)})(\text{O}_{13.97(3)}\square_{0.03})$ ($R_1 = 5.23\%$) with vacancies in trigonal-pyramidal (V_{Si}'''') and oxygen (V_{O}'') positions.

Takeda et al. [5] and Kimura et al. [28] have suggested that the color of langasite family crystals depends on material of the crucible, in particular, Ir. However, the orange LGN and colorless CNGS have been grown using both Pt and Ir crucibles under the same growth conditions. It should be noted that, according to [29], the crystal color cannot be associated with the presence of iridium in the composition of the crystal, because, according to the inductively coupled plasma atomic emission spectroscopy data, the iridium content in the colored crystals is lower than 1 ppm. It can be assumed that the Ir content less than 1 ppm can cause the yellow color of

CNGS crystal. However the crystal growth in Pt crucibles at the same growth conditions as growth in the Ir crucible leads to the orange color of the crystals too. Thus, the influence of crucible material on color of LGN and CNGS is quite controversial.

Kuz'micheva et. al. [20, 22], Kaurova et. al. [21], and Domoroshchina et. al. [29] have reported using X-ray or neutron diffraction analysis that the LGS and LGT crystals color depends on the presence of oxygen vacancies in the structure of crystals; that is, the absence of color for this crystals is due either to the absence of oxygen vacancies or to their large content. Thus, the light yellow and yellow crystals, as well as the colorless ones, are characterized by different compositions of oxygen positions [21, 22].

According to our data [21, 22] and the literature data [30], the annealing in vacuum of the orange crystal causes its discoloring. It is accompanied by oxygen vacancies content increasing in the crystal structure [21, 22]. Annealing in air of the same crystal leads to more saturated color tones [21, 22, 30]. It is accompanied by decreasing the content of oxygen vacancies [21, 22]. In turn, colorless crystals grown in argon and treated in vacuum do not change their color [30].

TABLE 1: Refined compositions of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystals according to the results of the neutron diffraction analysis (NDA).

Crystal	Unit cell parameters, Å a, c	Refined composition (NDA)
<i>CNGS-1</i>	8.0911 (2) 4.9811 (1)	$(\text{Ca}_{2.95}\square_{0.05(1)})\text{NbGa}_3\text{Si}_2\text{O}_{14}$ $R = 4.15\%$
<i>LGN-1</i>	8.2283 (4) 5.1268 (3)	$(\text{La}_{2.935(2)}\square_{0.065})(\text{Ga}_{0.450}\text{Nb}_{0.550(3)})\text{Ga}_3(\text{Ga}_{1.965(4)}\square_{0.035})(\text{O}_{13.90(1)}\square_{0.10})$ $R = 8.10\%$
<i>LGN-2</i>	8.2293 (3) 5.1272 (2)	$(\text{La}_{2.940(1)}\square_{0.060})(\text{Ga}_{0.590}\text{Nb}_{0.410(2)})\text{Ga}_5(\text{O}_{13.82(1)}\square_{0.18})$ $R = 7.24\%$

TABLE 2: The atom coordinates in two-twinned unit cell of *CNGS-2* crystal.

Parameter		<i>CNGS-2</i>	
		Unit cell 1	Unit cell 2
Ca	x	0	0
	y	0.5724	0.5936
	z	0	0.5
Nb	x	0	0
	y	0	0
	z	0	0.5
Ga	x	0	0
	y	0.2334	0.2501
	z	0.5	0
Si	x	1/3	1/3
	y	2/3	2/3
	z	0.4710	0.9700
O(1)	x	1/3	1/3
	y	2/3	2/3
	z	0.1853	0.7245
O(2)	x	0.1352	0.1553
	y	0.4529	0.4489
	z	0.3069	0.7638
O(3)	x	0.2255	0.2553
	y	0.1566	0.1511
	z	0.2404	0.7638

The results of NDA and XRD investigations of the *CNGS* crystals confirm these conclusions. The color of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ is also caused by the oxygen vacancies, which are absent in the structure of the colorless crystal 1. It is not excluded that the annealing of crystals in the air will weaken their color, will reduce the quantity of point defects, and will improve their optical properties, as it was observed for langasite crystals [31]. According to our results, only oxygen vacancies which depend on growth and treatment conditions take part in color centers formation.

Thus, the colorless $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystal (crystal 1) grown by using the single-crystal charge is structurally more perfect in comparison with the yellow one (crystal 2) grown by the charge prepared by conventional solid-state

reaction. In this way, colorless $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystal is more preferred for the practical application in piezoelectric and acoustic-electronic devices. The results of the dielectric properties investigations of *CNGS* crystals are the confirmation of this conclusion. For the colorless crystals the values of relative dielectric constants are higher compared with the ones for the yellow crystals [16, 32].

The same (upper) parts of crystals 1 and 2 were investigated by the diffraction methods. The compositions of the upper part of the crystal growing from polycrystalline charge differ from those of the lower part [19]. If this crystal will be crushed and regrown the composition will probably be averaged and oxygen content will be increased.

3.2. $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ Crystals. According to the neutron diffraction data obtained (Table 1), the composition of the upper part *LGN-1* of $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal can be written as $(\text{La}_{2.935(2)}\square_{0.065})(\text{Ga}_{0.450}\text{Nb}_{0.550(3)})\text{Ga}_3(\text{Ga}_{1.965(4)}\square_{0.035})(\text{O}_{13.90(1)}\square_{0.10})$, that is, with Nb > Ga in the octahedral position (Ga,Nb)(1) and with vacancies in the dodecahedral (V_{La}''') and trigonal-pyramidal (V_{Ga}''') positions and in the oxygen (V_{O}'') one. The atomic coordinates which were used for the *LGN-1* calculation was also used for the refinement of the crystal structure and composition of the *LGN-1* sample cut from the top of the crystal. The refined composition of *LGN-1'* can be written as $(\text{La}_{2.940(2)}\square_{0.060})(\text{Ga}_{0.485}\text{Nb}_{0.515(6)})(\text{Ga}_{2.940(2)}\square_{0.060})\text{Ga}_2(\text{O}_{13.84(1)}\square_{0.16})$ ($R = 10.02\%$). The compositions of the *LGN-1* and *LGN-1'* samples are in good agreement with each other. However, for the *LGN-1'* sample as well as for the *CNGS-2* sample sufficiently strong peaks of the residual electron density with coordinates associated with the found ones by the transition matrix $/100/010/00z+0.5/$ were revealed. It also indicates the defect structure of the upper part of the $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal what can be connected with the using of *LGS* as a seed.

The lower part of the crystal (*LGN-2*) has a composition $(\text{La}_{2.940(1)}\square_{0.060})(\text{Ga}_{0.590}\text{Nb}_{0.410(2)})\text{Ga}_5(\text{O}_{13.82(1)}\square_{0.18})$ with vacancies located in the dodecahedral (V_{La}''') and the oxygen (V_{O}'') positions and with Ga > Nb in the octahedral position (Ga, Nb)(1).

Thus, according to the neutron diffraction data obtained, there are the same types of point defects (the vacancies in the lanthanum and oxygen positions) in the compositions of the top and the bottom of the $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal.

Different ratios of Ga/Nb and of oxygen vacancies concentrations (Table 1) indicate the composition and properties inhomogeneity over the volume of the crystal. It is not excluded that the LGN crystal color is also attributed to the qualitative differentiation of oxygen vacancies present in the structures. In orange crystals (LGN-I, LGN-I') a higher oxygen content was found. In our opinion, the relationship between color and oxygen content for LGN must be the same as for LGT [21, 22] and LGS [29]. For example, the color of the crystals of composition $\text{La}_3(\text{Ga,Ta}^{5+})\text{Ga}_5\text{O}_y$ varies depending on oxygen content (the neutron diffraction results): $y = 13.872(6)$ is colorless crystal, $y = 13.918(7)$ yellow crystal, $y = 13.969(8)$ orange crystal, $y = 13.975(6)$ light yellow crystal, and $y = 14.0$ colorless crystal; that is, the colorless crystals may be characterized either by the absence of oxygen vacancies or by their large content [21, 22]. The reason of crystal color is believed to be the color center formation: $(V_{\text{O}}^{n*}, ne')^{\times}$: $V_{\text{O}}^{n*} > (V_{\text{O}}^{n*}, ne')^{\times}$ colorless crystals and $V_{\text{O}}^{n*} < (V_{\text{O}}^{n*}, ne')^{\times}$ colored crystals.

4. Conclusions

The colorless and yellow $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystals (growth atmosphere: 100% Ar) and orange $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystal (growth atmosphere: 99%Ar + 1% O_2) were grown by the Czochralski technique in the Ir crucible along $\langle 0001 \rangle$ growth direction. The results of the neutron diffraction investigations of this crystals are reported.

It was established that the using of single-crystal charge is necessary for the growth of structural quality crystals.

The difference between the compositions of top and bottom of $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal was found. The poor structural quality of $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ crystal upper part is due to the using of $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystal as a seed.

The possibility of microtwins formation (two unit cells connected by the translation: $1/2 z$) was revealed for $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystals.

It was found that the color of the $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystals is caused by oxygen vacancies present in the structures like the $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$ and $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ crystals.

References

- [1] J. Bohm, E. Chilla, C. Flannery et al., "Czochralski growth and characterization of piezoelectric single crystals with langasite structure: $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS), $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ (LGN) and $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGT). II. Piezoelectric and elastic properties," *Journal of Crystal Growth*, vol. 216, no. 1, pp. 293–298, 2000.
- [2] B. V. Mill and Y. V. Pisarevsky, "Langasite-type materials: from discovery to present state," in *Proceedings of IEEE International Frequency Control Symposium and Exhibition*, pp. 133–144, June 2000.
- [3] T. Fukuda, H. Takeda, K. Shimamura et al., "Growth of new langasite single crystals for piezoelectric applications," in *Proceedings of the 11th IEEE International Symposium on Applications of Ferroelectrics (ISAF-XI)*, pp. 315–319, August 1998.
- [4] J. Bohm, R. B. Heimann, M. Hengst, R. Roewer, and J. Schindler, "Czochralski growth and characterization of piezoelectric single crystals with langasite structure: $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS), $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ (LGN), and $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGT). Part I," *Journal of Crystal Growth*, vol. 204, no. 1, pp. 128–136, 1999.
- [5] H. Takeda, K. Shimamura, T. Kohno, and T. Fukuda, "Growth and characterization of $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ single crystals," *Journal of Crystal Growth*, vol. 169, no. 3, pp. 503–508, 1996.
- [6] G. M. Kuzmicheva, E. N. Domoroschina, V. B. Rybakov, A. B. Dubovsky, and E. A. Tyunina, "A family of langasite: growth and structure," *Journal of Crystal Growth*, vol. 275, no. 1-2, pp. e715–e719, 2005.
- [7] B. H. T. Chai, A. N. P. Bustamante, and M. C. Chou, "A new class of ordered langasite structure compounds," in *Proceedings of IEEE International Frequency Control Symposium and Exhibition*, pp. 163–168, June 2000.
- [8] B. V. Mill, E. L. Belokoneva, and T. Fukuda, "New compounds with a $\text{Ca}_3\text{Ga}_2\text{Ge}_2\text{O}_{14}$ -type structure: $\text{A}_3\text{XY}_3\text{Z}_2\text{O}_{14}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $\text{X} = \text{Sb}, \text{Nb}, \text{Ta}$; $\text{Y} = \text{Ga}, \text{Al}, \text{Fe}, \text{In}$; $\text{Z} = \text{Si}, \text{Ge}$)," *Russian Journal of Inorganic Chemistry*, vol. 43, no. 8, pp. 1168–1175, 1998.
- [9] M. M. C. Chou, S. Jen, and B. H. T. Chai, "New ordered langasite structure compounds—crystal growth and preliminary investigation of the material properties," in *Proceedings of IEEE Ultrasonics Symposium*, pp. 225–230, October 2001.
- [10] T. Karaki, R. Sato, M. Adachi, J. I. Kushibiki, and M. Arakawa, "Piezoelectric properties of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ single crystal," *Japanese Journal of Applied Physics B*, vol. 43, no. 9, pp. 6721–6724, 2004.
- [11] I. H. Jung, A. Yoshikawa, T. Fukuda, and K. H. Auh, "Growth and structure of $\text{A}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ ($\text{A} = \text{Sr}, \text{Ca}$) compounds," *Journal of Alloys and Compounds*, vol. 339, no. 1-2, pp. 149–155, 2002.
- [12] I. H. Jung, Y. H. Kang, K. B. Shim, A. Yoshikawa, T. Fukuda, and K. H. Auh, "Single crystal growth and characterizations of $\text{A}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ -type compounds for piezoelectric applications," *Japanese Journal of Applied Physics B*, vol. 40, no. 9, part 1, pp. 5706–5709, 2001.
- [13] Z. Wang, D. Yuan, D. Xu et al., "Growth and dielectric properties of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystals," *Journal of Alloys and Compounds*, vol. 370, no. 1-2, pp. 291–295, 2004.
- [14] Z. Wang, X. Cheng, D. Yuan et al., "Crystal growth and properties of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ single crystals," *Journal of Crystal Growth*, vol. 249, no. 1-2, pp. 240–244, 2003.
- [15] Z. Wang, D. Yuan, A. Wei et al., "Growth and optical activity of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ single crystal," *Applied Physics A*, vol. 78, no. 4, pp. 561–563, 2004.
- [16] X. Shi, D. Yuan, X. Yin, S. Guo, X. Zhang, and Z. Li, "Crystal growth and dielectric, piezoelectric and elastic properties of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ single crystal," *Journal of Crystal Growth*, vol. 293, no. 2, pp. 485–488, 2006.
- [17] A. A. Kaminskii, B. V. Mill, E. L. Belokoneva, C. E. Sarkisov, T. Y. Pastukhova, and G. G. Khogzhabagyan, "Crystal structure and stimulated emission $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}-\text{Nd}^{3+}$," *Journal of Inorganic Materials*, vol. 20, pp. 2058–2061, 1984 (Russian).
- [18] T. S. Chernaya, S. S. Kazantsev, V. N. Molchanov et al., "Crystal structure of $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ at 20 K," *Crystallography Reports*, vol. 51, no. 1, pp. 23–28, 2006.
- [19] G. M. Kuz'micheva, O. Zakharko, E. A. Tyunina, V. B. Rybakov, E. N. Domoroshchina, and A. B. Dubovski, "Neutron diffraction and X-ray diffraction investigations of langasite crystals," *Crystallography Reports*, vol. 53, no. 6, pp. 989–994, 2008.
- [20] G. M. Kuz'micheva, O. Zaharko, E. A. Tyunina et al., "Point defects in langatate crystals," *Crystallography Reports*, vol. 54, no. 2, pp. 279–282, 2009.

- [21] I. A. Kaurova, G. M. Kuz'micheva, V. B. Rybakov, A. B. Dubovskii, and A. Cousson, "Composition, structural parameters, and color of langatate," *Inorganic Materials*, vol. 46, no. 9, pp. 988–993, 2010.
- [22] G. M. Kuz'micheva, I. A. Kaurova, V. B. Rybakov et al., "The color of langatate crystals and its relationship with composition and optical properties," *Crystal Research and Technology*, vol. 47, no. 2, pp. 131–138, 2012.
- [23] I. A. Kaurova, G. M. Kuz'micheva, V. B. Rybakov, A. B. Dubovsky, A. Cousson, and O. Zaharko, "Growth and structural investigations of $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystals," *Khimicheskaya Tekhnologiya*, vol. 11, no. 10, pp. 585–591, 2010 (Russian).
- [24] G. M. Kuz'micheva, E. A. Tyunina, E. N. Domoroshchina, V. B. Rybakov, and A. B. Dubovskii, "X-ray diffraction study of $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ langasite-type single crystals," *Inorganic Materials*, vol. 41, no. 4, pp. 412–419, 2005.
- [25] G. M. Sheldrick, "A short history of SHELX," *Acta Crystallographica A*, vol. 64, no. 1, pp. 112–122, 2007.
- [26] A. A. Pugacheva, B. A. Maksimov, B. V. Mill' et al., "Growth and structure of $\text{La}_3\text{Zr}_{0.5}\text{Ga}_5\text{Si}_{0.5}\text{O}_{14}$ crystals," *Crystallography Reports*, vol. 49, no. 1, pp. 53–59, 2004.
- [27] G. B. Bokiy, *Introduction to Crystal Chemistry*, MGU, Moscow, Russia, 1954.
- [28] H. Kimura, S. Uda, O. Buzanov, X. Huang, and S. Koh, "The effect of growth atmosphere and Ir contamination on electric properties of $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ single crystal grown by the floating zone and Czochralski method," *Journal of Electroceramics*, vol. 20, no. 2, pp. 73–80, 2008.
- [29] E. N. Domoroshchina, G. M. Kuz'micheva, V. B. Rybakov, A. B. Dubovsky, E. A. Tyunina, and S. Y. Stepanov, "Relationship between growth conditions, structure and optical properties of langasite crystals $\text{La}_3\text{Ga}_5\text{SiO}_{14}$," *Perspective Materials*, vol. 4, pp. 17–30, 2004 (Russian).
- [30] O. A. Buzanov, E. V. Zabelina, and N. S. Kozlova, "Optical properties of lanthanum-gallium tantalate at different growth and post-growth treatment conditions," *Crystallography Reports*, vol. 52, no. 4, pp. 691–696, 2007.
- [31] E. A. Tyunina, G. M. Kuz'micheva, O. Zaharko, and A. B. Dubovsky, "Effect of growth and post-growth treatment conditions on langasite crystals optical properties," *Vestnik MITHT*, vol. 5, no. 5, pp. 27–35, 2010 (Russian).
- [32] M. Adachi, T. Funakawa, and T. Karaki, "Growth of substituted langasite-type $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ single crystals, and their dielectric, elastic and piezoelectric properties," in *Proceedings of the 13th IEEE International Symposium on Applications of Ferroelectronics (ISAF '02)*, pp. 411–414, June 2002.