Lanthanum-gallium tantalate: Heterogeneity and point defects

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Abstract. In this study the important factors having influence on the occurrence of color centers (crystal growth conditions and postgrowth effect on the crystal) in LGT (La$_3$Ga$_5$Ta$_{0.5}$O$_{14}$, langatate) crystals were investigated. In order to check the model of defect formation in crystals of langatate the effect of ionizing radiation on the spectral dependence of the attenuation coefficients of langatate crystals was studied. The ionizing radiation doses were $10^{11} - 10^{15}$ cm$^{-2}$. The optical homogeneity was evaluated by interferometric method on a Fizeau interferometer. The refractive indices of the crystals obtained in different atmospheres and after the isothermal annealing were measured by the prism method.

1. Introduction
Lanthanum-gallium tantalate (La$_3$Ga$_5$Ta$_{0.5}$O$_{14}$, langatate, LGT) is promising piezoelectric material [1]. It belongs to a class of symmetry 32 and is one of the isomorphic compounds of langasite (La$_3$Ga$_5$SiO$_{14}$, langasite, LGS), has a unique combination of physical properties, making it one of the most promising materials for use in pressure sensors.

Peculiarity of langatate is structure complexity of unit cell and a tendency to disordered distribution matrix ions into sites of crystal lattice [2, 3]. Irregularity and inhomogeneity of obtained crystals lead to heterogeneity of physical properties. Determination of growth conditions of homogeneous crystal allows to applying them more effective and improving the technology.

One of the major issues in the study of LGT is their color, which is determined by the presence of color centers. The important factors having influence on the occurrence of color centers are crystal growth conditions and post-growth treatment on the crystal. For this purpose methods of optical spectroscopy and electron irradiation were used.

2. Experimental procedure
In this study, we performed experiments with langatate crystals produced by the company Fomos-Materials. The crystals were grown in iridium crucibles in atmospheres of argon and in a mixture of argon and oxygen (Ar +(2%)O$_2$) and (Ar +(<2%) O$_2$) and in air, in platinum crucible. The samples represented plates of polar cut polished on both sides. To assess the quality crystal samples of langatate were studied by interferometry on a Fizeau interferometer. The samples were irradiated by different electron doses and then transmission spectra were measured. The irradiation doses were varied from $1 \cdot 10^{11}$ to $3 \cdot 10^{15}$ cm$^{-2}$. A controllable linear accelerator (LU-6) as the source of mono-energetic (6 MeV) electrons was used in experiment, where a pulse (5 - μs) electron irradiation mode was realized. The samples of 2 - mm thickness were oriented perpendicular to the electron beam. The transmission spectra were measured with a Cary – 5000 UV-VIS-NIR (Varian) spectrophotometer within the spectral range 180 – 3300 nm. The transmission spectra measurements were performed before irradiation and after each dose of irradiation.

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3. Results and discussion

Langatate crystal samples were studied by interferometry in accordance with the scheme shown in figure 1. In this case, it was observed overlapping interference patterns formed by different types of bands.

![Diagram showing interference patterns](image)

Figure 1. Scheme observation of interference patterns and interference pattern in the LGT crystal: 1 – the lower working surface of the internal wedge Fizeau plate, 2, 3 – the opposite sides of the sample.

Bands of the first type – frequent bands of different curvature – arise due to deviations from flatness of the plate surface. In this case, the interference is observed between the working surface of the wedge-shaped plate (1) and the investigated surface of the sample (2 or 3). Such patterns are different for the opposite surfaces of the plate and disappear when wedge-shaped plate removes from the interferometer. Bands of the second type form concentric circles. Their appearance depends neither on whether the observed plate surface is the upper nor the presence or absence of the wedge plate. The causes of these bands were studied. The phenomenon of interference is described by the equation (1):

$$\delta = 2 \cdot h \cdot n \cdot \cos r + \frac{\lambda}{2}$$

where $\delta$ - path-length difference, $h$ – the thickness of the plate, $n$ – refractive index, $r$ – angle of incidence, $\lambda$ - wavelength.

In accordance with the equation (1), the path-length difference depends on the plate material inhomogeneity: the thickness unevenness of the plate, change the angle of incidence of light or the refractive index. Surface morphology was complex and did not correlate with the shape of the interference pattern in the plate bulk. Consequently, the cause of this pattern is the heterogeneity of the refractive indices.

Therefore, direct measurements of the refractive indices were carried out by the prism method on a goniometer-spectrometer GS-2. The radiation source was a helium lamp. For measurements we used the langatate prism with the base surfaces perpendicular to the optical axis of the crystal. It allows to measure the main refractive indices No and Ne. The refractive indices were measured at a wavelength of $\lambda = 587.5$ nm in different areas along the prism with a step of ~ 2 mm.

Analysis of the results shows that the values of the refractive indices of the crystals grown in different atmospheres of Ar and Ar + (2%) O₂ are heterogeneous along the length of the samples and change in the third decimal place (table 1).
Table 1. The refractive indices No and Ne of the crystals grown in different atmospheres

| Growth atmosphere | No          | Ne          |
|-------------------|-------------|-------------|
| Ar                | 1.9447 ÷ 1.9468 | 1.9723 ÷ 1.9745 |
| Ar + (2%) O₂      | 1.9439 ÷ 1.9476 | 1.9715 ÷ 1.9746 |

The refractive indices decrease from the center towards the periphery of the crystal, independent of the growth atmosphere. Heterogeneity of the refractive index No for the crystal obtained in an atmosphere of Ar + (2%)O₂ is higher than in the crystals obtained in an atmosphere of Ar. This indicates a higher optical homogeneity of the crystals grown in argon atmosphere. Similar results were obtained for the refractive index Ne.

The important condition in technology of growth of langatate is the choice of growth atmosphere. The color intensity decreases from the crystal obtained in argon with 2% of oxygen (it is bright orange) to the crystal obtained in argon or in air (it is almost transparent and colorless) [3]. Transmission spectra of crystals obtained under the different conditions in initial state (before irradiation) are presented in figure 2.

![Figure 2](image)

Figure 2. Transmission spectra of crystals obtained under the different conditions (atmospheres 1 - in (Ar), 2 - (Ar +(＜2%) O₂), 3 – air, 4 - (Ar +(2%)O₂)) in initial state [3].

As the most changes of transmission spectra of the crystals are observed in the visible range transmission spectra are shown in wavelengths from 230 to 590 nm. Absorption bands are observed in all examined crystals regardless of growth atmosphere at wavelengths 290, 360, 480 nm. The absorption bands indicate presence of several point defects or their complexes in the form of color centers.

It is obvious, that the reason of crystal coloration is the presence of color centers. But a pattern of defect formation in langatate remains unknown. Some authors attribute [5 – 7] langatate coloration to different concentration of oxygen vacancies. Combination oxygen vacancy (V_o^{++}) and two electrons corresponds to F-center. It is logical that maximum concentration of oxygen vacancies is observed in crystal obtained in Ar, minimum concentration in the air (as shown in equation (2)). In this case according to the offered pattern crystal obtained in atmosphere of Ar must be most colored. So it is contrary to real coloration and spectra (Figure 2).

\[
\left[ V_{o}^{++} \right]_{(Ar)} < \left[ V_{o}^{++} \right]_{(Ar+(2\%O_{2})} < \left[ V_{o}^{++} \right]_{(Ar+(＜2\%)O_{2})} < \left[ V_{o}^{++} \right]_{(Ar)}
\]  

(2)
Considerable changes of defect structure were the result of irradiation in crystal obtained in Ar atmosphere (Figure 3a). The absorption bands at 290 and 360 nm appeared even at the minimum dose irradiation. Absorption intensity increases more than twice. It means color centers at these wavelengths are unstable. Increasing of irradiation dose leads to intensity changes from 5 to 10% for absorption bands at 420 - 480 nm and from 15 to 35% for absorption bands at 290 - 360 nm.

Quite the contrary influence of irradiation on color centers of crystal obtained in (Ar+((\sim2\%)O_2)) atmosphere is insignificant (Figure 3b). Color centers generated in process of growth are stable enough.

\[\text{Figure 3. Transmission spectra of crystals obtained in Ar (a) and Ar+((2\%)O_2) (b) after different irradiation doses (1-initial state, 2-8 – increasing electron doses)}\]

Increase of irradiation dose has an essential effect on absorption intensity at 420-480 nm for langatate obtained in Ar atmosphere and at 290-360 nm for langatate obtained in atmosphere (Ar+((\sim2\%)O_2)), see figures 4. Strong changes are observed at dose 1\times10^{12} \text{cm}^{-2}.

\[\text{Figure 4. Dose dependence for langatate samples grown in Ar (a) and Ar+((2\%)O_2) (b) atmospheres at different wavelength: 1 - 480 nm, 2 - 420 nm, 3 - 360 nm, 4 - 290 nm.}\]

These crystals were additionally investigated by X-ray diffraction analysis before and after irradiation. The results are evidence of vacancy mechanism of defect formation in langatate crystals. Vacancy concentration increases after irradiation. Lattice distortion takes place. Values of the spacing parameter “a” is shown in the table 2. Spacing parameter in crystal obtained in Ar+((2\%)O_2) is much less than in crystal grown in Ar and both differ from tabulated value 8.2345 Å. Irradiation leads to
decrease of value of spacing parameter for langatate obtained in Ar atmosphere. Difference between tabulated value and value for crystal obtained in Ar+O₂ is small.

Table 2. Value of spacing parameter (a), before and after irradiation

| Sample                  | Spacing parameter a, Å | Sample                  | Spacing parameter a, Å |
|-------------------------|------------------------|-------------------------|------------------------|
| Ar (initial)            | 8.23453                | Ar+(2%)O₂ (initial)     | 8.23407                |
| Ar (irradiated)         | 8.23411                | Ar+(2%)O₂ (irradiated)  | 8.23405                |

Preliminary model of defect formation was proposed. It’s supposed that gallium and oxygen vacancies are appearing in process of irradiation, further they form F- and V-centers and their complexes. Possible processes in langatate crystals under electron irradiation are shown in equations 3-8:

\[ \text{Ga}^{+++} + e^- \rightarrow \text{Ga}^{++} \]  \hspace{1cm} (3)
\[ \text{O}^- - 4e^- \rightarrow \text{O}_2 \uparrow + 2V_{o}^{++} \]  \hspace{1cm} (6)
\[ \text{Ga}^{+++} + 2e^- \rightarrow \text{Ga}^+ \]  \hspace{1cm} (4)
\[ V_{Ga}^{---} + 3p^+ \rightarrow V^0 \]  \hspace{1cm} (7)
\[ 2\text{Ga}^+ + \text{O}^- \rightarrow \text{Ga}_2\text{O} \uparrow + 2V_{Ga}^{---} \]  \hspace{1cm} (5)
\[ V_{o}^{++} + 2e^- \rightarrow F^0 \]  \hspace{1cm} (8)

4. Conclusions
In this study significant influence of electron irradiation on optical transmission spectra of LGT crystals were shown. Dependence of transmission intensity of all absorption bands on the electron irradiation dose value was observed. Also growth atmosphere of LGT crystals influences on susceptibility to electron irradiation. In process of growth and irradiation vacancies defects are generated.

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