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RADIATION-INDUCED DEFECTS AND DICHROISM IN $La_3Ga_{5,5}Ta_{0,5}O_{14}$ CRYSTALS*

Nina Kozlova[1], Oleg Buzanov[2], Anna Kozlova[1], Evgeniia Zabelina[1], Vladimir Shayapov[1,3], Nikita Siminel[1], Dmitry Spassky[1,4]**

[1] National University of Science and Technology "MISiS", Moscow, Russia
[2] "Fomos-Materials" Company Limited, Moscow, Russia
[3] Nikolaev Institute of inorganic chemistry SB RAS, Novosibirsk, Russia
[4] D.V. Skobeltsyn Institute of Nuclear Physics, M.V. Lomonosov Moscow State University, Moscow, Russia

Abstract. *We investigated the transmission spectra of the langatate (LGT, $La_3Ga_{5,5}Ta_{0,5}O_{14}$) crystals grown in different conditions (crucible – Ir or Pt, growth atmosphere – air, pure Ar, Ar with addition of oxygen 2% or less then 2%), in the initial state and after electron irradiation. We observed dichroism in these crystals. Dichroism indicates the anisotropy of defect centers. We obtained the dependence of transmission on the irradiation dose and found that electron irradiation causes a decrease of transmission in the wavelength range 250-700 nm. On the transmission spectra in the infrared region, we observed oscillations, which can presumably refer to the formation of a layered structure as a result of irradiation. We have calculated the thickness of the formed layer. Luminescent characteristics of LGT crystals depend on growth conditions. Intensity of luminescence in LGT (Ar+(2%)O_2) is lower than in LGT (Ar). Electron irradiation leads to the reduction of intensity. The observed luminescence in langatate crystals is provided by different luminescent centers.*

***Key words*:** *Langatate, radiation-induced defects, electron irradiation, dichroism, transmission spectra, luminescence*

1. INTRODUCTION

The study of structure and defects in multicomponent oxide single-crystal dielectric materials is a nontrivial task.

Crystal structure is anisotropic – it determines the presence of various phenomena, for example dichroism. In crystals, there are some defective centers, for example, Frenkel defects, Schottky, V-centers, etc. or groups of centers (clusters). These centers can also possess their own symmetry, which complicates the definition of their origin.

Another question is whether the results of the definition of the composition of materials obtained for the powders, even with high accuracy, may be projected to the single-crystal materials.

In addition, the composition of modern perspective crystals includes chemical elements, for example, lanthanides, with non-exhaustively studied practical characteristics.

Thus, the investigation of the Ca-gallogermanate crystals' defect structure, in particular, langasite (LGS, $La_3Ga_5SiO_{14}$) and langatate (LGT, $La_3Ga_{5,5}Ta_{0,5}O_{14}$) continues for over 20 years. However, a clear and consistent model of the structure and origin of the defects has not been presented yet. [1]

Though different groups of authors offer their own assumptions, sometimes directly contradictory, about the origin of color centers in these crystals, for example oxygen vacancies in [2] and incorporated oxygen in [3], the fact that the color of the crystals depends on the growth atmosphere has not been challenged, to our knowledge.

Therefore, new methods are required for the study of the defect structure in these crystals, for example luminescence spectroscopy methods. Also, it is well-known that characteristics of materials significantly change after irradiation. Studying irradiation effects on ion structures is a productive method for understanding the origin of the defect structure and mechanisms of its formation [4, 5].

Here we present the results of our studies of the optical characteristics of LGT crystals, grown in different atmospheres, as-grown and after electron irradiation, taking dichroism into account.

2. MATERIALS AND METHODS

Samples of $La_3Ga_{5,5}Ta_{0,5}O_{14}$ crystals were provided by "Fomos-Materials" Company Ltd. Crystals were grown by the Czochralski method in a modified "Crystal-3m" apparatus with inductively heated Ir or Pt crucible in a protective atmosphere of argon with the addition of oxygen (<2% or 2%), in pure argon or in the air. The difficulty of growth in pure argon was that this type of protective atmosphere did not suppress the evaporation of gallium oxides from the melted surface. This process leads to the loss of the melt stoichiometry. But crystals grown in pure argon possess properties very useful for further applications, for example, they have at least 10-15 times higher electrical resistivity in the range of 350-600 °C. It is very important for high

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**zabev@mail.ru

temperature devices based on LGT. The color of the crystals varies, depending on the oxygen content in the protective atmosphere, from colorless (at 0% of O_2) to amber (at 2% of O_2). But this dependence is not linear in relation to the percentage of oxygen – the intensity of the color of LGT grown in the air (20% of oxygen) is in between those grown in pure argon and those grown in Ar+(2%)O_2. [1]

The studied samples were in the form of polished plates with a thickness of ~2 mm with faces oriented perpendicular to the crystallographic X-axis (the axis of order 2).

The samples were irradiated by electron doses from $1 \cdot 10^{13}$ to $5 \cdot 10^{15}$ cm^{-2}. We used a controllable linear accelerator (LU-6) as the source of monoenergetic (6 MeV) electrons, with a pulse (5 μs) electron irradiation mode.

The luminescence was excited by the second and third harmonic of YAG:Nd^{3+} (λ_{ex}=350 nm, W=0.5 mJ; λ_{ex}=355 nm, W=2 mJ; λ_{ex}=532 nm, W=2 mJ;) at T=95 K and 300 K.

The optical absorption spectra of as-grown samples and samples after irradiation were measured in the wave-range of 200-2500 nm using UV-Vis-NIR spectrophotometer «Cary-5000» (Agilent Technologies) in the Accredited Interdepartmental Educational-Testing Laboratory of Semiconductor and Dielectric Materials "Single Crystals and Stock on their Base" (NUST "MISIS").

2. Results and discussion

2.1. Initial state

In the absorption spectra of LGT, we usually observed the foregoing absorption bands: in the UV region of 290 and 360 nm, in the visible region of 480 nm and in the IR of 1850 and 2920 nm. If the crystal was colored in the UV-Vis region, we observed three absorption bands (290, 360 and 480 nm) and if it was colorless - only one band (290 nm) [1].

In LGT in directions perpendicular to the optical axis, the dichroism phenomenon is observed [1]. Dichroism refers to the difference between the absorption of light rays with different polarization due to two refractive indices of the crystal. Dichroism is most pronounced when studied in the linearly polarized light with two mutually perpendicular polarizations. However, studies in circular or non-polarized light, as here, are preferred since such spectra can give information about defects in crystals [6].

In the dichroism study, we install the sample into the sample holder in a way so that the light will propagate along the crystallographic axis X (position (1)), and then we turn the sample by 90° around the axis of the propagation of light (position (2)). For each position, we record transmission spectra (Fig. 1).

We use a usual mathematical formula to gain contrast obtained at the variations of transmission in two rotary positions when light propagates along X direction to calculate the degree of dichroism Δ [7]:

$$\Delta = \frac{D_1 - D_2}{D_1 + D_2} \qquad (1)$$

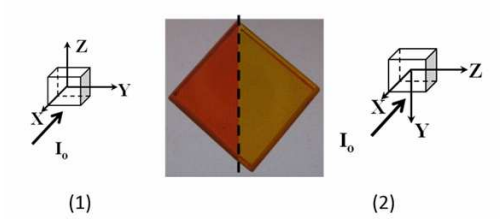


Figure 1. Dichroism in as-grown LGT (Ar+(2%)O2): left – position 1; right – position 2.

where D1 is the optical density of the light transmitted through the sample in the sample position (1); D2 - in the position (2).

In the transmission spectra of the crystals, dichroism is observed around the absorption bands so, in the crystals obtained in pure argon, this effect is nearly invisible, but in the case of the crystals grown in the oxygen-containing atmosphere, dichroism is detected more clearly. The effect is the clearest in the case of crystals grown in the atmosphere with 2% of oxygen and is most pronounced around the absorption band at 380-500 nm. (Fig. 2).

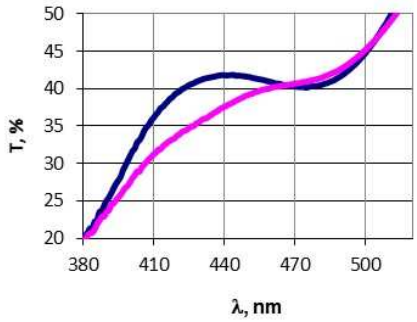


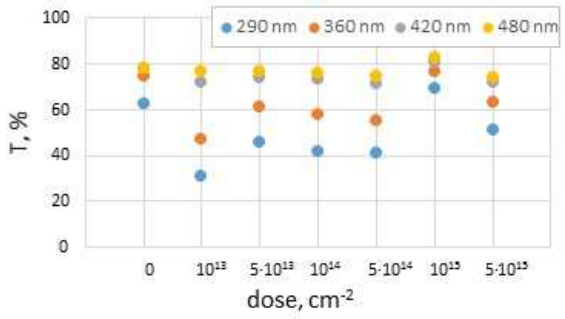
Figure 2. Dichroism in as-grown LGT (Ar+(2%)O2), wave region 380-500 nm: blue – initial position, pink – with rotation by 90° around the beam of incident light

1.2. Influence of irradiation

The experiment on the influence of electron irradiation on the langatate crystals was organized as follows: we exposed the samples to several stages of irradiation with the accumulation of the dose, and after each irradiation dose we obtained transmission spectra.

First of all, on the transmission spectra of the irradiated samples, except for the three above-mentioned bands, we observed the fourth band - at 420 nm.

Then we plotted dose dependences on each absorption band (Fig. 3). In the **wavelength range of 250 -700 nm** in all investigated crystals, irradiation by electrons leads to a decrease of transmission. This effect is a consequence of significant changes of the defect structure in crystals.



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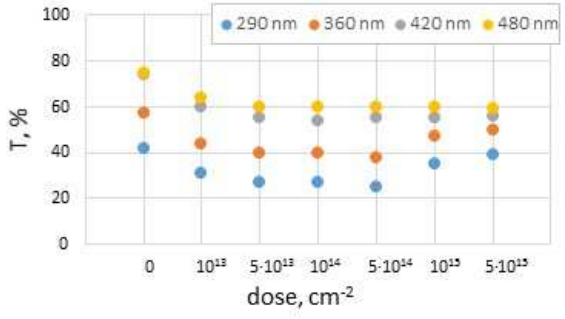

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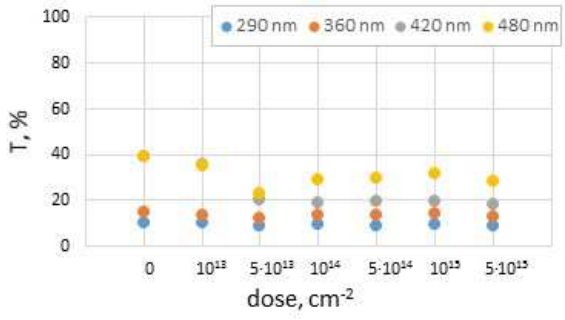

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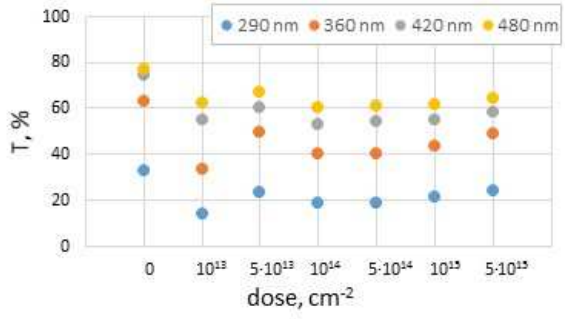

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Figure 3. Dose dependences of transmission of the LGT crystals grown in different atmospheres and crucibles: a) Ar, Ir, b) Ar+(<2%)O2, Ir, c) Ar+(2%)O2, Ir, d) air, Pt; light blue – 290 nm; orange – 360 nm; grey – 420 nm; yellow – 480 nm

In the case of Ar crystals, irradiation leads to the appearance of absorption bands at 290 nm, and at 360 nm they appeared even at the minimum dose of irradiation. The absorption intensity increases more than twice and then, with the increase of the dose, the intensity reduces. This means that color centers at these wavelengths are unstable. Increasing the 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.

The influence of the doses of irradiation on the color centers of the crystal obtained in (Ar+O2) atmosphere is insignificant. This means that defect centers generated in the process of growth are stable enough. The effect of irradiation on the transmission spectra, for the crystals obtained in the air and with oxygen concentration of less than 2%, is close: the most notable influence is on the bands in the UV region of the spectrum.

Judging by the UV absorption bands intensity changes, these bands may presumably be associated with defects by Frenkel: the occurrence of interstitial ion and vacancy [5]. On the basis of the radii of the ions forming the structure, and the sizes of voids in it [1], these interstitial ions are most likely the ions of gallium or tantalum.

We repeated the measurements of langatate crystals transmission after electron irradiation when dichroism was observed (Fig. 4). First of all, the defects caused by electron irradiation were unstable and eventually the transmission spectrum of the crystal returned to its original state.

Nevertheless, we can see dichroism - the difference in the transmission between absorption bands for 2 positions (ΔT) of the sample relative to the incident light beam, Table 1.

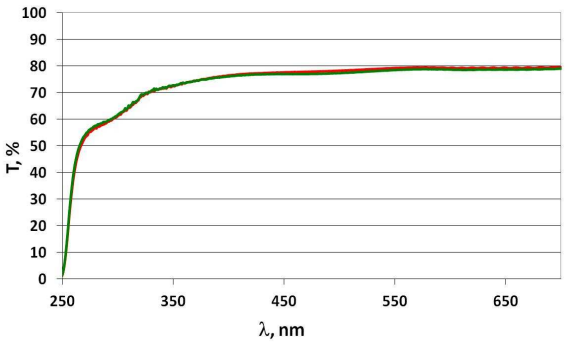
Table 1. Dichroism in the maxima of the absorption bands in the UV-Vis region of wavelength (after last dose or irradiation $5 \cdot 10^{15}$ cm^{-2}).

Growth conditions	Approximate T, %		
	290 nm	360 nm	480 nm
Ar, Ir,	-	-	-
Ar+(<2%)O2, Ir	-	3	7
Ar+(2%)O2, Ir	-	4	11
air, Pt	-	4	4

Dichroism in crystals depends on both the symmetry of the structure and the symmetry of the absorbing centers [8]. It seems that the defect centers observed in the visible range of wavelengths were anisotropic.

In the IR of the transmission spectra up to 2500 nm on the crystals grown in air and with the concentration of oxygen <2%, we observed the absorption band in the region of 1700-2000 nm (Fig. 5).

This absorption band is complex and consists of at least two absorption sub-bands with maxima approximately at 1830 and 1880 nm.



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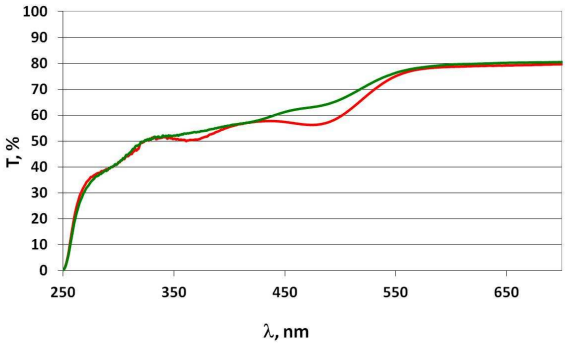

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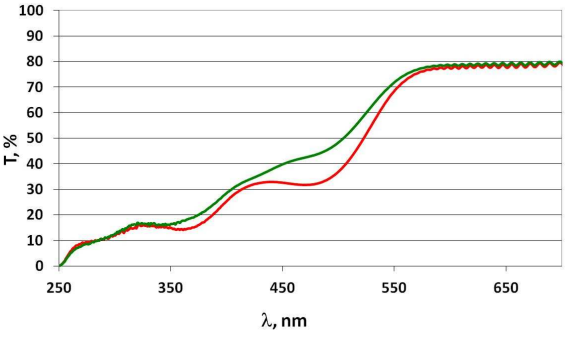

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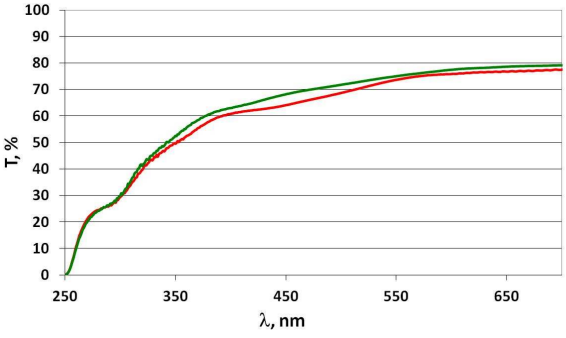

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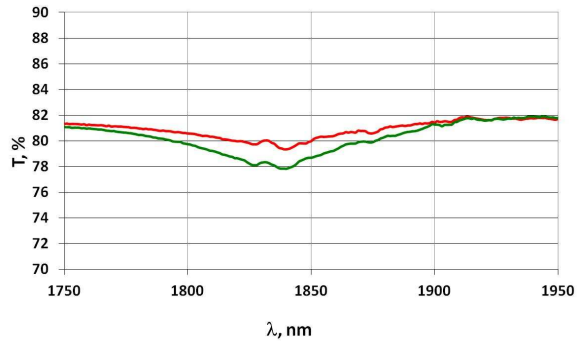
Figure 4. Dichroism in the transmission spectra of the irradiated LGT ($5 \cdot 10^{15}$ cm^{-2}), grown in different atmospheres and crucibles: a) Ar, Ir, b) Ar+(<2%)O2, Ir, c) Ar+(2%)O2, Ir, d) air, Pt; red – initial position, green – with rotation by 90°



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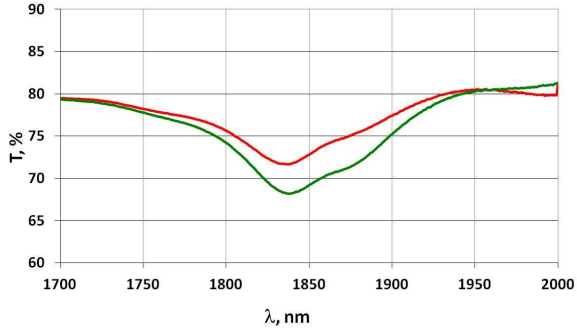

b)

Figure 5. Absorption bands in the transmission spectra of the irradiated samples in the wavelength region 1700-2000 nm: a) Ar+(<2%)O2, Ir, b) Ar+(2%)O2, Ir; red – initial position, green – with rotation by 90°

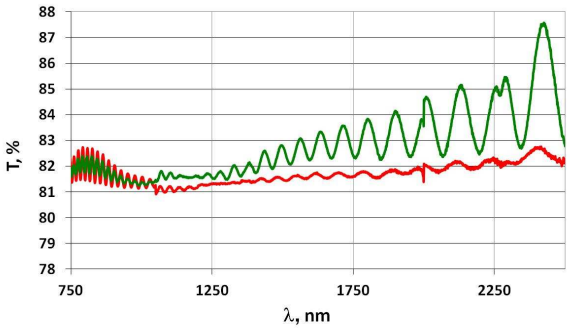

Figure 6. Example of oscillations in transmission spectra of the irradiated sample (LGT, Ar) in IR region: red – basic position, green – with rotation by 90°

In the transmission spectra of all irradiated samples, except from those grown with <2% O_2, we observed oscillations in IR (Fig. 6). Oscillations in one position are larger than in another due to dichroism.

The presence of oscillations in the transmission spectra may presumably indicate the occurrence of the altered layer; its thickness can be calculated by the following equation [9]:

$$2dn\cos\varphi_0 = \frac{m\lambda}{2} \qquad (2)$$

where d and n are the appropriate thickness and refractive index [10] of the layer, respectively; φ_0 - is the angle of the incidence of light on the sample; λ – wavelength of incident light; m – order of interference.

Thus, if you know the values of wavelengths λ_1 and λ_2 in extremes, you can determine the optical path by the formula for two adjacent maximum or minimum values [9]:

$$dn = \frac{\lambda_1 \lambda_2}{2(\lambda_1 - \lambda_2)} \qquad (3)$$

or for adjacent minimum and maximum values

$$dn = \frac{\lambda_1 \lambda_2}{4(\lambda_1 - \lambda_2)} \qquad (4)$$

Calculated by these formulae, the values of the altered layer are above 12±3 μm for all the samples where they were presumably observed.

The electron path inside the material is determined by Kanaya-Okayama's formula [11]:

$$R_e = \frac{0{,}0276 \cdot A}{\rho \cdot Z^{0{,}889}} \cdot E^{1{,}67} \qquad (5)$$

where Z - the average atomic number, A - the average atomic weight, ρ – density (ρ=6,15 g/m^3 [12]), E energy of electrons (E=6 MeV).

The depth of the electron penetration calculated according to the formula (5) is 18 μm, this result corresponds well with the value obtained by the formulae (3-4).

For the calculations of the altered layer thickness according to the formulae (3-4) we used the refractive index and the density of the langatate. Thicknesses calculated according to the formulae (3-4) and to the formula (5) differ probably as a result of a mismatch of the refractive index and density of the altered layer and LGT.

The composition and nature of the altered layer will be investigated in further works.

2.3. Luminescence

Since we observed the most pronounced differences between the optical properties of crystals grown in argon and with 2% oxygen, luminescence was studied only in the samples obtained from these crystals (Fig. 7) after the last electron doze of 5·10^{15} cm^{-2}.

First of all, independently from the temperature for the samples in the initial state, we revealed a significant effect of the growth atmosphere on the intensity of luminescence: luminescence, in the case of Ar langatate samples, is more intensive than in crystals obtained with 2% of oxygen in the growth atmosphere.

This difference of intensity is probably caused by the reabsorption of emission from the bulk of crystal by the absorption band at 480 nm. The band strongly depends on the oxygen concentration in the growth atmosphere.

The electron irradiation leads to the increase of intensity of luminescence upon the excitation of samples at 95 K, and the decrease upon excitation at 300 K for all samples and each growth atmosphere.

Luminescence bands (Fig. 7) are not elementary; this indicates that different mechanisms are involved in the luminescence process.

At low temperatures, the complicated character of the luminescence band is revealed more clearly: we can see at least 5 peaks.

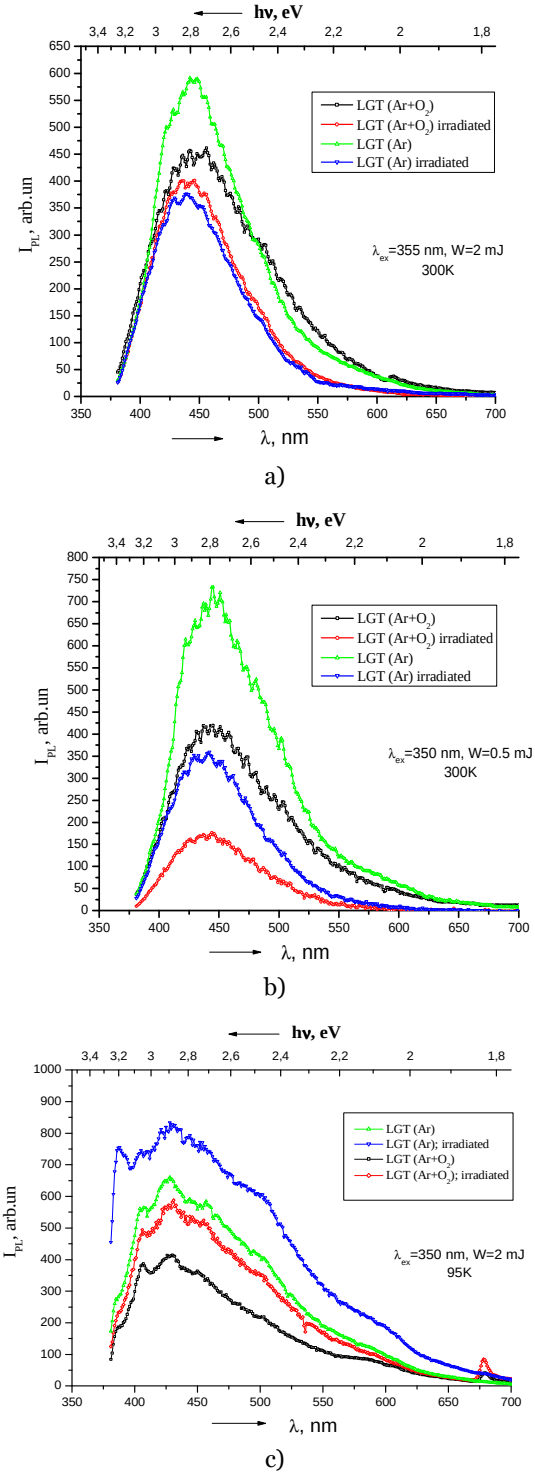

Figure 7. Luminescence of LGT crystals, grown in Ar or Ar+(2%)O_2 in the initial state and after irradiation (electron dose of 5·10^{15} cm^{-2}).

The origin of the peaks observed in luminescent spectra and nontrivial character of luminescence intensity at different temperatures are objectives of further works.

3. CONCLUSIONS

We investigated the influence of electron irradiation on the transmission spectra of langatate crystals grown in different conditions (crucible – Ir or Pt, growth atmosphere – air, pure Ar, Ar with addition of 2% oxygen or less then 2%).

We obtained dose dependences and revealed that electron irradiation:

- causes a decrease of transmission in the wavelength range between 250-700 nm,

- differently influences defects depending on the growth atmosphere: in all crystals except $(2\%)O_2$ it mostly influences defects responsible for the bands in the UV region; in $(2\%)O_2$ crystal, it influences defects responsible for the absorption bands in 400-500 nm.

Defects induced by the electron flow are unstable and they disintegrate over time.

We observed dichroism in these crystals. This effect is most clearly pronounced in the bands in the visible region, especially in the crystals obtained in the atmosphere with 2% oxygen. Dichroism indicates the anisotropy of defect centers.

On the transmission spectra in the infrared region, we observed oscillations, which can presumably be referred to the formation of a layered structure as a result of irradiation. The thickness of the formed layer was approximately 12 μm.

The luminescent characteristics of LGT crystals depend on growth conditions. The intensity of luminescence in LGT $(At+(2\%)O_2)$ is lower than in LGT (Ar). The electron irradiation leads to the increase of intensity of luminescence upon excitation of samples at 95 K, and the decrease upon excitation at 300 K for all samples and each growth atmosphere. The observed luminescence in langatate crystals is provided by different luminescent centers.

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