BIULETYN WAT Rok XLVI, Nr 12, 1997



# Influence of ionizing radiation on SrLaGa<sub>3</sub>O<sub>7</sub> single crystals doped with rare-earth elements

SŁAWOMIR KACZMAREK IZABELLA PRACKA\* TADEUSZ ŁUKASIEWICZ\*\*\* STANISŁAW WARCHOŁ\*\*\*\*

# RYSZARD JABŁOŃSKI\* GEORGES BOULON\*\* ZBIGNIEW MOROZ\*\*\*\* KRZYSZTOF STĘPKA

 \* Instytut Optoelektroniki, WAT, 00-908 Warszawa, ul. S. Kaliskiego 2
 \* Instytut Technologii Materia<sup>3</sup>ów Elektronicznych., 01-919 Warszawa, ul. Wólczyńska 133
 \*\* Laboratoire de Phys.-Chimie des Materiaux Luminescentes, 69622 Villeurbanne cedex, France
 \*\*\* Instytut Fizyki WAT, 00-908 Warszawa, ul. S. Kaliskiego 2

\*\*\* Instytut Fizyki WAT, 00-908 Warszawa, ul. S. Kaliskiego 2
\*\*\*\* Instytut Problemów J¹drowych im. Sołtana, 05-400 Świerk
\*\*\*\*\* Instytut Chemii i Techniki Jądrowej, 02-415 Warszawa, ul. Dorodna 16

Abstract. Influence of  $\gamma$ -rays from a <sup>60</sup>Co (1,25 MeV) source and 26 MeV protons on the absorption and luminescence of SrLaGa<sub>3</sub>O<sub>7</sub> single crystals doped with Nd, Dy and Pr was studied. Color centers, which appeared after an irradiation (absorbed dose: 10<sup>5</sup> Gy), shift the absorption edge towards the longer wavelengths by a few hundreds nm (for a rod length about 36 mm). Measurements of the ESR spectra before and after gamma irradiation were also performed. They show spectra with a spin of S = 1/2, g<sub>||</sub> = 1.9838(5) and g<sub>⊥</sub> = 2.0453(5), that can be attributed to the Ga<sup>2+</sup> centers formed according to the pattern Ga<sup>3+</sup>+e<sup>-</sup>→Ga<sup>2+</sup>. Optical output measurements for Nd doped SLGO laser rods showed some improvement of laser emission at 1.06 µm for strongly defected rod. This is due to the same paramagnetic Ga<sup>2+</sup> color centers that arise in SLGO crystals after  $\gamma$ - or proton irradiation.

**Keywords:** materials engineering, color centers, ionizing radiation, luminescence **Universal Decimal Classification:** 620.1

# **1. Introduction**

The melilites (ABC<sub>3</sub>O<sub>7</sub>: A = Ca, Sr, Ba; B = La, Gd; and C = Ga, Al) are layered compounds which consist of vertex-sharing tetrahedral units linked together forming distorted planar networks with a five-membered ring pattern. Alkaline or rare-earth cations are sandwiched between these layers and located in sites with a very distorted square Archimedean antiprism configuration [1, 2]. Single crystals of SrLaGa<sub>3</sub>O<sub>7</sub> (SLGO) exhibit the highest structural homogeneity among these compounds. They appear to be promising active materials for the design of all-solid-state lasers [3, 4]. They exhibit, however, strong changes in absorption and luminescence spectra after irradiation by ionizing particles. Irradiation causes a very large additional absorption near the short-wavelength absorption edge, which depends on radiation dose and on sample thickness. These changes influence properties of lasers in which the SLGO crystals are used as the active material.

In the present work we attempted to study more detailed influence of gamma and proton radiation on optical properties of Nd, Dy and Pr ion doped SLGO crystals.

# 2. Experimental setup

The samples of SLGO crystals doped with Nd (5 at. % and 10 at. %), Pr (1 at. %, 0,5 at. %) and Dy (1 at. %, 0,5 at. %) were grown by the Czochralski method in iridium crucibles. The detailed description of the applied growth process is presented elsewhere [5-6].

### 2.1. Radiation sources

Gamma irradiation from a  $^{60}$ Co source at a dose rate of 1.5 Gy/sec up to an absorbed dose of 10<sup>6</sup> Gy was applied. For proton irradiation the beam from the cyclotron C-30 was used. The average energy of protons was about 26 MeV and fluencies varied between 10<sup>13</sup> and 10<sup>16</sup> particles/cm<sup>2</sup>.

After each proton irradiation gamma lines were measured and types of nuclear reactions defined. For protons with a dose of  $10^{16}$  protons/cm<sup>2</sup>, they are presented in Table 1.

### Table 1.

protons with	a dose of 10 <sup>10</sup> protons/cm <sup>2</sup> .					
$E_{\gamma}$ (keV)	Nuclear reaction	$T_{1/2}$ (days)				
1	2	3				
165	$^{139}_{57}$ La(p,n) $^{139}_{58}$ Ce	137,7				
E <sub>x</sub> =33, 33.4, 37.8, 38.7						
	$^{88}_{58}Sr(p2n)^{87}_{39}Y$	3				
387						
484						
	$^{88}_{38}Sr(p,n) ^{88}_{39}Y$	106,6				

Energies of gamma lines and types of nuclear reactions for  $Dy^{3+}$  doped SLGO crystal (0,5at.%) irradiated by protons with a dose of  $10^{16}$  protons/cm<sup>2</sup>.

continued tab.

1	2	3
814 (1835-1022)		
898		
1325 (1836-511)		
1836		
2734 (sum peak)		
	$^{69}_{31}Ga(p\alphan)^{65}_{30}Zn$	244
1116		
	<sup>69</sup> <sub>31</sub> Ga(p2n) <sup>68</sup> <sub>32</sub> Ge	270
	$_{32}^{68}Ge _{\beta}^{68}Ga$	
1078		

### 2.2. Spectroscopic investigations

Samples of SLGO crystals doped with Nd<sup>3+</sup>, Pr<sup>3+</sup> and Dy<sup>3+</sup> diameter of 10 mm and 1-2 mm thick were cut out perpendicularly to the growth axis in the plane (111) from the most homogeneous part of crystals. After optical polishing of both ends, the crystals were examined with a Mach-Zehnder interferometer. Samples in form of a rod of 4 mm diameter and length of about 36 mm were also investigated. To obtain absorption coefficients in the range of 200-1100 nm, transmission spectra of the samples were measured before and after  $\gamma$  or proton irradiation using a LAMBDA-2 Perkin-Elmer spectrometer.

Values of additional absorption ( $\Delta K$  factors) caused by the irradiation were calculated from the formula:

$$\Delta K (\lambda) = \frac{1}{d} \cdot \ln \frac{T_1}{T_2} , \qquad (1)$$

where  $\lambda$  stands for wavelength, d for the sample thickness, T<sub>1</sub> and T<sub>2</sub> for transmission of the sample before and after gamma irradiation, respectively.

Fluorescence and excitation spectra were obtained using an ILA - 120 3 W argon ion laser. The spectra were recorded using a GDM-1000 monochromator with dispersion of 11 cm<sup>-1</sup>/mm and detected by a RCA C-31034-02 cooled AsGa photomultiplier. For data aquisition the SR 400 photon counting system, controlled with a PC computer, was used.

For the thermoluminescence studies unpolished samples were prepared, with a thickness lower than 1 mm and diameter up to 6 mm. Thermoluminescence was measured for crystals 'as grown' and gamma irradiated in the temperature range from 70 to 400 °C, by means of a " carousele " analyzer WAWA-TLD RA'95 installed in the Institute of Chemistry and Nuclear Technique in Warsaw.

#### 2.3. ESR investigations

The samples, typically of  $3,5\times3,5\times2$  mm, were measured in a BRUKER ESP-300 ESR spectrometer (X-band). The spectrometer was equipped with helium flow cryostat type ESR-900 Oxford Instruments. The ESR lines were observed before and after gamma exposure of  $10^5$  Gy dose in the temperature range from 4 to 300 K and microwave power from 0,002 to 200 mW. Moreover, the above investigations were performed for crystals annealed in air at 800 °C for three hours.

#### 2.4. Optical output measurements

Four rods cutted out from the same crystal were investigated. Measurements were made in naturally air-cooled head for the laser system pumped by xenon flash-lamp with energies from 5 to 50 J and a filter inside of the head cutting wavelength up to 350 nm. Laser rods were put into the plane-parallel laser cavity 24 cm long, made of messing covered with gold. Transmissions of output mirrors were equal to 8%, 19.5% and 36,6%, respectively, for 1,06  $\mu$ m. The rods had no AR coatings on their end faces. The laser light was detected with high-sensitive HgCdTe photoconductor and time characteristics of the lamp were observed by Si photodiode. The energy of laser pulses was measured by Gen-Tec radiometer with ED-500 gauge head.

All the rods were investigated subsequently: as grown, irradiated by gamma's of  $10^3$ - $10^6$  Gy, annealed in air at 1200 °C for three hours, polished (end faces only) and again gamma-irradiated with  $10^3$  -  $10^6$  Gy.

# 3. Results

### 3.1. Thermoluminescence

The thermoluminescence measurements of the Nd: SLGO (5 at. %) crystals show, that in the crystal 'as grown' ( curve 1, Fig 1) only one defect exist with maximum at 319 °C. In the same, but gamma irradiated crystal, measured just after  $\gamma$ -irradiation with a dose of 10<sup>3</sup> Gy (see Fig. 1. curve 2), two defects are seen: at 110 °C and 260 °C, respectively. The defect at 110 °C is the new one introduced to the crystal by gamma irradiation.

As seen from Fig. 1 changes for Nd: SLGO crystals in a thermoluminescence spectrum caused by  $\gamma$ -irradiation rapidly relaxes and stays almost the same for both doses:  $10^3$  Gy (measured just after  $\gamma$ -exposure) and  $10^5$  Gy (measured after 1,5 month from  $\gamma$ -exposure, see Fig. 1. curves 2 and 3). Moreover, the maximum of the thermoluminescence shifts with time.



Fig. 1. Thermoluminescence curves of Nd: SLGO (5at.%) 'as grown' crystal before (AG -1) and after  $\gamma$ : 10<sup>3</sup>Gy (2 –just after irradiation) and 10<sup>5</sup>Gy (3 - 1,5 month later) irradiation.

## 3.2. Additional absorption and luminescence changes after ionizing radiation

Additional absorption (AA) bands observed in the Nd: SLGO (5 at. % and 10 at. %) and Pr: SLGO (1 at. %, 0.5 at. %) crystals after gamma irradiation with a dose of  $10^5$  Gy and in the Dy: SLGO (1 at. % and 0.5 at. %) crystals with a dose of  $10^6$  Gy are shown in Fig 2. As seen, in SLGO crystals doped with Dy, Nd and Pr gamma induced AA bands appear at about 290 nm and 380 nm, but the first one is much stronger than the second one. The first AA band intensity and location depend on the gamma dose and on the kind of the dopant. With the grow of the Pr or Dy concentration, the intensity of one of these bands decreases, but with the increase of the Nd concentration, it also increases. Therefore, intensity of this band as a function of dopant concentration strongly depends on the type of dopant.

Moreover, after gamma irradiation of a thin SLGO sample the shift of about 50 nm of a short-wave absorption edge was observed. The value of the shift strongly depend on gamma dose.

In Fig 2 one can see also the AA bands for the Nd: SLGO (5 at. % of  $Nd^{3+}$ ) rod (curve 3), compared with those for a 2.1 mm plate (curve 2). Shift of the short-wave absorption edge is caused by a large value of rod length (36.16 mm) and a scattering nature of absorbing centers.

Fig. 3 presents changes in transmission and absorption spectra of "as grown" Dy: SLGO crystal (1 at. %) (curve 1) after subsequent: gamma irradiation of  $10^6$  Gy (curve 2), thermal annealing in air at 1200 °C for three hours of the irradiated sample (curve 3) and gamma exposure of  $10^3$  Gy of the annealed sample (curve 4). One can see, the shift of short-wave absorption edge and two different radiation defects can be observed. First one, with a maximum at 380 nm, is connected probably with recharging effect of oxide vacancies while second one, with maximum at 290 nm, is a new radiation defect.



Fig. 2 Additional absorption bands of Dy, Pr and Nd doped SLGO crystals after gamma irradiation with doses of 10<sup>5</sup> (Pr and Nd:SLGO) and 10<sup>6</sup> Gy (Dy:SLGO).



Fig. 3. Changes in transmission and absorption spectra of 'as grown' Dy: SLGO (1at.%) crystal (1) after subseqent: gamma irradiation with a dose of 10<sup>6</sup> Gy (2), annealing in air at 1200°C for 3 h (3) and gamma exposure with a dose of 10<sup>3</sup> Gy (4).

The first of these defects (380 nm) appears mainly after previous annealing of the crystal and following  $\gamma$ -exposure. It is related to curve 5 from Fig. 2 (Pr: SLGO (0,5 at. %)) as well as to curve 4 from Fig. 3 (Dy: SLGO (1 at. %)).

The Dy: SLGO crystal (0.5 at. %, d = 2.91 mm, d - sample thickness) was also irradiated by protons ( $10^{13} - 10^{16}$  particles/cm<sup>2</sup>). The AA bands were obtained at about 270 nm and 370 nm (the first maximum on the level of 23 1/cm). The shift of the absorption edge after proton exposure was about 50 nm. This is essentially the

same picture as that related to the changes induced in the same crystal by gamma rays with a dose of  $10^6$  Gy. Therefore, we guess we are dealing with the radiation defects of the same type.



Fig. 4. Transmission spectra of gamma and proton exposure Dy: SLGO (0,5at.%) crystal for doses up to 10<sup>16</sup> protons/cm<sup>2</sup>

Shifts of the short-wave absorption edge for Dy: SLGO (0.5 at. %) crystal after gamma and proton exposures are seen together in Fig. 4. The as grown Dy: SLGO crystal (curve 1) was firstly gamma irradiated with a dose of  $10^5$  Gy (curve 2), then annealed at 1200 °C in air for three hours (curve 3) and next subsequently irradiated with protons with doses:  $3*10^{13}$ , and  $1,12*10^{16}$  protons/cm<sup>2</sup> (curves 4, and 5). One can see that the shifting due to gamma irradiation is greater than that one due to protons  $3*10^{13}$  cm<sup>-2</sup>.

Much more clearly this situation is described in Fig. 5, where for different gamma doses, changes of the transmission measured for the Nd: SLGO (5 at. %) rod of the length of 36.16 mm are shown. This rod (curve 1) was subsequently irradiated by gamma's with  $10^4$  Gy (curve 2), annealed at 400 °C for 3 hours, irradiated with  $10^5$  Gy (curve 3), annealed at 1200°C for three hours (curve 4) and, finally, irradiated with  $10^5$  Gy (curve 5). As the absorption edge, the wavelength was taken for which the transmission value reach the level of 0.001.

As seen from the figure, the short-wave absorption edge became shifted with the increase of the radiation dose towards the longer wavelengths. This shift, for the rod of about 36 mm length and  $10^6$  Gy, may even be as large as 120 nm. As seen from Fig. 5, after annealing the rod at 1200 °C, absorption edge return to position before irradiation (curves 1 and 4). Moreover, for the same values of gamma doses but different conditions of irradiation (irradiation after annealing at 400 °C and irradiation after annealing at 1200 °C with a dose of  $10^5$  Gy - curves 3 and 5) absorption edge is also the same.



Fig. 5. Transmission spectra for the Nd: SLGO (5at.%) rod of 36,16mm length for different values of  $\gamma$ -rays doses: 1-AG, 2-10<sup>4</sup> Gy, 3-10<sup>5</sup> Gy, 4-1400°C 3h in air, and 5-10<sup>5</sup> Gy



Fig. 6. Change of absorption edge position in Nd: SLGO (5at.%) crystal after  $\gamma$ -irradiation with doses from  $10^2$  to  $10^6$  Gy



Fig. 7. Luminescence spectrum for Nd: SLGO (5at.%)crystal after (1) and before (2)  $\gamma$ -irradiation with dose of  $10^5$  Gy

Gamma irradiation with different doses of 4 different rods but of the same length and thickness, cut from the same crystal was performed. The change of the short-wave absorption edge as a function of gamma dose is shown in Fig. 6. It is seen from the Fig. 6., that this change is linear as a function of the dose. Similar dependence was observed for plates cut from 2 mm Nd: SLGO and Dy: SLGO crystals, but the shifts were smaller (a maximum about 50 nm). This suggest that the color centers responsible for this shifting are of a scattering type. Similar investigations performed for Pr: SLGO rod with  $\phi = 4$  mm and 1 = 39.12 mm gave the shift of about 200 nm, for  $10^6$  Gy gamma's.

Fig. 7 shows relative changes in a luminescence of the Nd: SLGO (5 at. %) crystal before and after the  $10^5$  Gy gamma exposure. Small decrease in relative values of a luminescence close to  $\lambda = 910$  nm can be noticed.

### 3.3. ESR investigations

ESR measurements revealed that after  $10^5$  Gy gamma exposure of SLGO undoped and Nd doped (5 at. %) crystal an anisotropic spectrum is observed. This spectrum has two lines with linewidth  $\Delta H_{pp} = 3$ mT, designed as G1 in Fig. 8.



Fig.8 . ESR spectrum for SLGO crystal before and after  $\gamma$ -irradiation with the dose of  $10^5$  Gy. 8a). ESR spectra before and after  $\gamma$ -exposure, 8b). G1 defect in SLGO crystal and 8c). Time quenching of G1 defect. Fitting was performed for the curve:  $y=y_0+A_1*exp(-(x-x_0)/\tau)$ , where: $x_0=0$ ,  $y_0=0.06245$ , t=264h,  $A_1=0.86$  and  $\chi_{sqr}=7.516*10^{-5}$ 

Its angular dependence for (001) plane is depicted in Fig. 9. The g-factor varies in the range of 2,0045 - 2,044. The same type of angular dependences for (100) plane was also observed.

These lines are observed at temperatures from 4 to 300 K but above 227 K due to line broadening, only isotropic single line is observed. The above mentioned lines appear in SLGO crystal after gamma irradiation independently on the kind of impurity, also in the undoped SLGO crystal.

After annealing the crystal in air at 800 °C for three hours these lines disappear. Moreover, after 1 month of storage the sample at room temperature the intensity of ESR lines generated after irradiation decreases about 10 times (Fig.8. - curve: ESR intensity as a function of a time) which gives the life-time of the observed center of 264 hours.



Fig. 9. Angular dependences of irradiation defect G1 in (001) plane of SLGO crystal. Small picture inside the figure show ESR spectrum for [110] direction. P denotes phosphorus lines (signal lines)

#### 3.4. Optical output measurements

For three of four Nd: SLGO rods, ('good rods' with a low value of laser emission threshold at 1.06  $\mu$ m), a decrease of optical output after  $\gamma$ -exposure and further after thermal annealing was observed as it is shown in Fig. 10. Values of slope efficiencies of Nd: SLGO lasers are described also as a number near each optical output curve. The results of the investigations of all the rods before and after  $\gamma$ -irradiation of 'as grown' crystals are presented in Ref. [7].

The results for the fourth rod ('bad rod' with a high value of laser emission threshold at  $1.06 \mu m$ ) are presented in Fig. 11., which shows an increase of output energy after gammas exposure and again a decrease after thermal annealing.



Fig. 10. Optical output of a 'good' Nd: SLGO (5 at. %) laser emitting at 1.06 μm, for different kinds of processing: 1-'as grown', 2-γ-10<sup>5</sup> Gy of 'as grown' rod and 3-annealing the rod in air at 1200 °C for 3h. Numbers near curves denote slope efficiencies of the laser



Fig. 11. Optical output of a 'bad' Nd: SLGO (5 at .%) laser emitting at 1.06 μm, for different kinds of processing: 1 - 'as grown', 2 - γ-10<sup>5</sup> Gy of 'as grown' rod, 3 - annealing the rod in air at 1200 °C for 3h and 4 - γ-10<sup>5</sup> Gy - irradiation of previously annealed the rod

# 4. Discussion

It was stated in Ref. [7] that in Nd: SLGO (5 at. %) lasers after gamma irradiation one can obtain an improvement of their optical output, provided that these crystals had been strongly defected.

Probably, the output energy of a laser increases as a result of appearance of color center (CC), shifting the absorption edge and, in this way, lowering the absorption in the UV region (lowering the optical losses) and also changing the amplitude relations of the luminescence.

In Fig. 1. one can see this CC having its maximum at 110  $^{\circ}$ C and relaxing (curves 2 and 3) with time. Second CC with a maximum at 260  $^{\circ}$ C that arises also for unirradiated crystal is connected probably with an oxide vacancy in SLGO

structure and arises also in undoped crystal. The same behavior show also Nd:BaLaGa<sub>3</sub>O<sub>7</sub> [8], Cr:SrGdGa<sub>3</sub>O<sub>7</sub> and also SLGO crystals doped with Dy and Pr ions. In Figs 2. and 3. two the same CC's are seen in absorption spectra. The first one, with a maximum at about 290 nm, is connected with a paramagnetic defect generated in SLGO crystal by  $\gamma$ -irradiation and causes a strong absorption (tens of 1/cm) in the region of the absorption edge. The second one, with a maximum at about 380 nm, is connected probably with a recharging effect of oxide vacancy. It is observed especially after  $\gamma$ - or proton irradiation of the crystal previously thermally annealed.

The intensity and location of the first center strongly depend on the kind and concentration of a dopant. For the neodymium increase of the intensity is observed with an increase of Nd concentration in SLGO crystal, while for Pr and Dy a decrease of intensity is observed.

The intensity depends also on radiation dose. With the growth of dose the value of the intensity also increases.

A great value of the AA arising after  $\gamma$ - or proton-irradiation near short-wave absorption edge causes shifting of the edge, which for a gamma dose of 10<sup>6</sup> Gy can have value of 50 nm. This shifting depends on gammas or protons dose and on thickness of investigated sample. This suggests that the CC responsible for this shifting is of a scattering type.

The dependence of the shifting on gamma absorbed dose for Nd: SLGO crystal is presented in Fig. 6. As one can see, it have linear character as a dose function and for rods with a length of 36 mm can have a value of 200 nm.

Arising of this CC in Nd: SLGO crystal causes small changes in luminescence spectrum seen at a wavelength of 910 nm in Fig. 7.

Improvement of the laser emission in a 'bad' Nd: SLGO rod at 1,06  $\mu$ m which is seen in Fig. 11 is probably due to characteristic radiation defect, that is connected with a greater than in Nd: YAG increase of AA value in the range of absorption pump spectrum. For Nd: YAG rod we have obtained  $\Delta k_{max} = 0.7$  [1/cm], while for Nd: SLGO  $\Delta k_{max} = 2$  [1/cm] both in UV range of absorption spectrum for a gamma dose of 10<sup>5</sup> Gy.

Growth of the laser emission threshold after thermal annealing, which is seen also in figures 10 and 11, is due to the fact that for the temperature of 1200 °C some dopants contained in the crystal are oxidized. In this way transparency for both end faces of a rod, as well as its side surface, changes essentially. End faces were polished after annealing process in contrary to side surface. The decrease of the laser slope efficiency after thermal annealing process of the laser rod can be explained by arising in the crystal CC with a maximum at 380 nm after  $\gamma$ - or proton irradiation.

b)



Fig. 12. a) Crystallographic positions of  $Sr^{3+}$ ,  $La^+$ ,  $Ga^{3+}$  and  $O^{2-}$  ions in SLGO lattice; b) Complexes of  $(Ga-O)^{1-}$  arising in SLGO structure (T1 tetrahedron) after  $\gamma$ - or proton irradiation.

Fig.12a. illustrates crystallographic positions of La<sup>+</sup>, Ga<sup>3+</sup>, Sr<sup>3+</sup> and O<sup>2-</sup> ions in the SLGO lattice (c-axis projection). In this figure one can see six T1, T2...T6 tetrahedra of  $GaO_4^{2-}$  type.

Fig. 12b. shows complexes of  $(Ga-O)^{1-}$  arising in SLGO structure (T1 tetrahedron) after  $\gamma$ - or proton irradiation.

The obtained results can be explained by means of the following process:  $Ga^{3+}$  ion captures the electron which was knocked out from  $O^{2-}$  ion by  $\gamma$  or proton irradiation and in a consequence,  $Ga^{2+}$  paramagnetic center is formed with a spin value equal to S = 1/2. The process can be illustrated by the following reactions:  $O^{2-}+\gamma \rightarrow O^{1-} + e^{-}$ ;  $Ga^{3+}+e^{-} \rightarrow Ga^{2+}$ . The measured angular dependences of ESR lines

show that this process inside T1 tetrahedron takes place and suggest that T1 configuration is energetically the most favorable for this kind of process. Favorable position of T1 tetrahedra with respect to irradiation process is connected with local symmetry of the crystal field. In this situation the spin Hamiltonian can be written in the following form:

$$\mathbf{H} = \mathbf{g} \cdot \boldsymbol{\beta} \cdot \mathbf{H} \cdot \mathbf{S} \tag{2}$$

where: S = 1/2,  $H_{rez} = v/(g \cdot \beta/h)$ ,  $g^2 = g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta$ ,  $\beta$  - Bohr magneton,  $\theta$  - angle between magnetic field and axis of a centers, h - Planck constant, g - Lande factor and  $H_{rez}$  - magnetic field.

Because the direction of an axis each of 4-th (Ga-O)<sup>1-</sup> complexes inside T1 tetrahedron is of [111] type and maximum  $H_{res}$  is directed along [110], that is  $\varphi = 45^{\circ}$  in (001) plane, we have obtained:

$$g_{\parallel}^2 = 2g_{\lceil 110 \rceil}^2 - g_{\lceil 100 \rceil}^2$$
 and  $g_{\perp}^2 = 2g_{\lceil 100 \rceil}^2 - g_{\lceil 110 \rceil}^2$  (3)

For angular dependence (Fig.7)  $g_{[100]} = 2.025$  and  $g_{[110]} = 2.0045$  or 2.044 are obtained, and for individual complex we have obtained  $g_{\parallel} = 1.9838(5)$  and  $g_{\perp} = 2.0453(5)$ .

As can be seen in Fig. 8. the time constant of relaxation process for G1 paramagnetic defect (part of month - 264 hours) is of the order of a time constant of relaxation process for the defect seen in Fig. 1. So, these defects are of the same type and nature.

# **5.** Conclusions

After  $\gamma$  or proton irradiation of the SLGO crystal doped with Pr, Dy and Nd, as well as undoped ones, AA bands appear in the absorption spectra, with maxima at about 270 nm and 370 nm.

The first band shifts the absorption edge of the crystal towards the longer wavelengths. This shifting depends on the radiation dose and has similar character for gammas and protons for doses up to  $10^6$  Gy and fluences up to  $10^{14}$  protons/cm<sup>2</sup>. It also depends on the crystal thickness, which indicates the scattering nature of the produced color centers.

Moreover, intensity and location of the first maximum, depend on the gamma dose and on the kind and concentration of a dopant. With the growth of the Pr or Dy concentration, a maximum of this band decreases, but with the increase of the Nd concentration, it also increases. The growth of the Pr concentration shift this maximum towards the shorter wavelengths.

The second band appears mainly after previous annealing the SLGO crystal in air and is probably connected with recharging effect of oxygen vacancies that arises in the crystal during growth process. It leads to decrease of the laser slope efficiency after thermal annealing process of the laser rod. Annealing of the gammas and protons irradiated crystal with doses up to  $10^6$  Gy and  $10^{13}$ - $10^{14}$  particles/cm<sup>2</sup>, respectively, at 400 °C for three hours, causes disappearance of the produced color centers.

The shift of the absorption edge of the irradiated Nd: SLGO crystal can have a positive influence on its laser properties [7]. Improvement of the laser emission in a 'bad' Nd: SLGO rod at 1,06  $\mu$ m is probably due to characteristic radiation defect, that is connected with a greater than in Nd: YAG increase of AA value in the range of absorption pump spectrum.

Investigations of ESR spectra show that the centers shifting the absorption edge are of the paramagnetic origin. Probably, as result of ionizing radiation, paramagnetic centers are formed according to the reaction  $Ga^{3+} + e^{-} \rightarrow Ga^{2+}$ .

### **ACKNOWLEDGEMENTS**

Authors would like to thank MSc. R. Piramidowicz from IMIO of Warsaw University of Technology for his help in obtaining the luminescence curves of Nd: SLGO samples before and after  $\gamma$ -exposure, MSc. K. Kopczyński from IO WAT for his help in obtaining the optical output curves of Nd: SLGO lasers and Prof. A. Jeleński from ITME for useful discussion.

Received July 4, 1997; revised October 25, 1997.

#### REFERENCES

- [1.] A. A. Kaminskii, E. L. Belokoneva, B. V. Mill, S. E. Sarkisov and K. Kurbanov, *Phys. Stat. Sol. (a)*, 97 (1986) 279
- [2.] L. R. Black, D. M. Andrauskas, G. F. de la Fuente, and H. R. Verdun, Proc. SPIE, 1104 (1989) 175
- [3.] W. Ryba-Romanowski, S. Gołąb, G. Dominiak-Dzik, M. Berkowski, *Materials Science and Engineering B*, 15(3) (1992) 217
- [4.] S. Kaczmarek, Z. Mierczyk, K. Kopczyński, Opto-electronics Review, 2 (1993) 54
- [5.] I. Pracka, W. Giersz, M. Świrkowicz, A. Pajączkowska, S. Kaczmarek, Z. Mierczyk, K. Kopczyński, Materials Science and Engineering B, 26(2-3) 1994, 201
- [6.] I. Pracka, M. Malinowski, K. Kopczyński, S. Kaczmarek, Z. Mierczyk, M. Świrkowicz, J. Kisielewski, T. Łukasiewicz, Proc. SPIE, 3178, 42-44
- [7.] S. Kaczmarek, K. Kopczyński, A. Pajączkowska, I. Pracka, A. O. Matkovskii, Proc. SPIE, 3179, 268-273
- [8.] R. Jabłoński, S. M. Kaczmarek, M. Berkowski, 'Radiation defects in BaLaGa<sub>3</sub>O<sub>7</sub> crystals', Spectrochimica Acta Part:A, in print.

s.	KACZMAREK	R.	JABŁÓŃSKI	I.	PRACKA	G.H	BOULON
т.	ŁUKASIEWICZ	Ζ.	MOROZ	s.	WARCHOŁ	к.	STĘPKA

Wlijanije ionizirujuszczewo izluczenija na monokristally SrLaGa307 legirowannyje redkozemelnymi elementami **REBIONO. ИССЛЕДОВАН**О wliqnie opromenenią kristallow SrLaGa<sub>3</sub>O<sub>7</sub> legirowannyh Nd, Dy i Pr kwantami gamma (<sup>60</sup>Co, 1,25 MeV) i protonami (26 MeV) na ih opti\$eskie harakteristiki. Prowedeno issledowanią &PR pered i posle g-izlu\$eniq (doza g-izlu\$eniq 10<sup>5</sup> Gy). Centry okraski woznika@]ie posle izlu\$eniq kristalla SLGO wblizi korotkowolnowogo kraq absorpcii, perenosąt !tot kraj w dlinnowolnowu@ storonu na neskol%ko sotok nm. &to, po na[emu mneni@, swqzano s paramagnitnym ionom Ga<sup>2+</sup> so spinom S = 1/2, woznika@]im posle opromeneniq kristalla SLGO kwantami gamma ili protonami.

s.	KACZMAREK	R.	JABŁÓŃSKI	I.	PRACKA	G.J	BOULON
т.	ŁUKASIEWICZ	Ζ.	MOROZ	s.	WARCHOŁ	ĸ.	STĘPKA

### Wpływ promieniowania jonizującego na monokryształy SrLaGa307 domieszkowane jonami ziem rzadkich

**Streszczenie.** Przedstawiono wyniki badań wpływu kwantów gamma ze źródła <sup>60</sup>Co (1,25 MeV) oraz protonów z akceleratora C30 o energii 26 MeV na absorpcję i luminescencję monokryształów SrLaGa<sub>3</sub>O<sub>7</sub> domieszkowanych jonami Nd<sup>3+</sup>, Dy<sup>3+</sup> oraz Pr<sup>3+</sup>. Centra barwne powstające po naświetlaniu tych kryształów (dawką 10<sup>5</sup> Gy oraz 10<sup>14</sup> protonów/cm<sup>2</sup>, odpowiednio), przesuwają krawędź absorpcji w stronę fal długich o kilkaset nm (dla pręta o długości ok. 36mm). Pokazano również wyniki badań widm ESR przed i po naświetleniu kwantami gamma. Otrzymano widma odpowiadające spinowi S=1/2 oraz wartościom:  $g_{\parallel} = 1.9838(5)$  i  $g_{\perp} = 2.0453(5)$ , które mogą być związane z centrami Ga<sup>2+</sup> powstałymi w wyniku reakcji przeładowania: Ga<sup>3+</sup>+e<sup>-</sup>→Ga<sup>2+</sup>. Przedstawiono również wyniki badań właściwości generacyjnych kryształów Nd: SrLaGa<sub>3</sub>O<sub>7</sub>, uzyskując poprawę tych właściwości dla emisji na długości fali 1,06 µm w przypadku silnie zdefektowanego pręta. Wynika to z obecności w tym kryształe tych samych centrów barwnych, które otrzymano wcześniej w wyniku naświetlania tego kryształu kwantami gamma lub protonami (centra Ga<sup>2+</sup>).