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Effect of increase of Ce^{3+} ions content after gamma irradiation of Ce and Ce, Nd doped YAG single crystals

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Abstract. The influence of gamma-irradiation on optical properties (absorption and luminescence) of Ce:YAG and Ce, Nd:YAG single crystals was studied. The increase of luminescence maxima at 530 nm for Ce:YAG and 548 nm for Ce, Nd:YAG crystals respectively, after gamma irradiation were observed. Also minor changes in luminescence and absorption maxima have been found after one year from gamma exposure. Luminescence peak of Ce, Nd:YAG is greater than that of Ce:YAG, but much less susceptible to gamma irradiation. In both crystals the increase of Ce^{3+} content after gamma irradiation was stated.
Keywords: optical properties, gamma-irradiation, color centers
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1. Introduction

In most cases an ionizing radiation has negative influence on material parameters and devices based on it. Nevertheless, positive influence on materials was also noticed.

That feature is due to the ability of ionizing radiation of creating not only structural defects, but also annihilating inherent defects. Especially, for creating many active media for optoelectronic devices and laser elements, it was using the rebuilding and overcharging mechanisms to create center defects in ionic crystals [1].

Color centers (CCs) arising in the crystals (additional absorption bands - AA), absorb not only pump light, but also laser light, significantly increasing laser energy losses [2]. Creating losses at the laser wavelength [3], the CCs reduce the slope efficiency.

The CCs produced by ionizing radiation or short-wave radiation of the pump lamp strongly influence the optical characteristics of yttrium-aluminium garnet (YAG) single crystals. Many publications are devoted to this problem [4-9].

The present paper considers the effects of gamma radiation on optical characteristics of Ce:YAG and Ce, Nd:YAG crystals.

2. Experimental setup

2.1. Crystal growth

The investigated crystals were pulled by the Czochralski technique from iridium crucibles at the Institute of Electronic Materials Technology. The growth was performed in the N_2 atmosphere with about 3% O_2 and 0.9 mm/h growth rate and 10-20 rpm rotation rate (crystals with the diameter of 17mm and length of 60 mm were prepared).

As the starting materials Y_2O_3, Al_2O_3, Nd_2O_3 and CeO_2 at least 4N purity were used. We assumed that Ce^{4+} ion enters in garnet particle as Ce^{3+} , that is, the next reaction takes place:

$$2CeO_2 \rightarrow Ce_2O_3 + 1/2 O_2$$

This statement is not fulfilled for each Ce^{4+} ion atom, however. The heated mixture has than the form:

$$(3-x-y)Y_2O_3 + xNd_2O_3 + 2yCeO_2 + 5Al_2O_3 \rightarrow$$
$$(3-x-y)Y_2O_3 + xNd_2O_3 + yCe_2O_3 + \frac{y}{2}O_2 + 5Al_2O_3 \rightarrow$$
$$2(Y_{3-x-y}Nd_xCe_yAl_5O_{12}) + \frac{y}{2}O_2 \uparrow$$

x and y in accordance with required Nd and Ce concentration values are choosen remembering, that $\frac{x}{3}\cdot 100\%$ *and* $\frac{y}{3}\cdot 100\%$ are atomic percentages of Nd and Ce concentration respectively.

This description do not take into account Ce ions of other valencies (e.g. Ce^{1+}). In this case a deviation from stoichometry and structure defects can appear, that change absorption and/or luminescence spectra of Ce:YAG or Ce, Nd:YAG crystal.

As the effect the Ce:YAG (0.05at.% of Ce^{3+}) and Ce, Nd:YAG (0.05 at.% of Ce^{3+} and 1 at.% of Nd^{3+}) crystals of yellow colour were obtained.

2.2. Radiation source

Gamma ray irradiation of the samples was performed with ^{60}Co source at a rate of 170 rads/sec, the absorption doses being of the order 10^2-10^5 Gy (1.25 MeV).

2.3. Spectroscopic investigations

In order to obtain the absorption coefficient in the range of 200-1100 nm, transmission spectra of the samples were measured using LAMBDA-2 Perkin-Elmer spectrometer. Samples of pure YAG, YAG doped with Ce and doped with Ce and Nd with diameter of 10 mm and thickness of 0.88-5 mm were cut out perpendicularly to the growth axis (<111> direction) from the most homogeneous parts of the crystals. After optical polishing of both ends, the crystals were examined with Mach-Zehnder interferometer system. Dispersion of the absorption coefficient $\alpha(\lambda)$ was calculated from transmission $T(\lambda)$ measurements with the consideration of multiple reflections within a sample. Additional absorption induced by radiation was assumed as:

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2} \tag{1}$$

Luminescence investigations were carried out using Perkin-Elmer LS-5B spectrofluorometer. The investigations of irradiated crystals were also performed one year after gamma exposure.

3 Results and discussion

It is a well established fact, that Ce ions (0.02 mass.%) built in pure YAG decrease susceptibility of the crystal to gamma radiation, while appearance of the same content of Ce in Nd:YAG crystal increases it [10]. In the last case optical density in the range of UV and visible parts of the spectrum appreciably increases. As it was stated in [11], intensity of the gamma induced AA for Ce, Nd:YAG crystal, in complex manner depends on Ce ion concentration: it increases for higher mass concentrations up to 0.1% and appreciably decreases for further increasing of Ce concentration. So, in special conditions, it is possible to increase radiation stability of Nd:YAG with the use of Ce ion [12].

For Ce: YAG and Ce, Nd: YAG crystals almost another situation takes place as previous for CTH:YAG (chromium, tulium and holmium doped YAG crystal) and Er:YAG (erbium doped YAG crystal) crystals [7, 8].

In Ce:YAG crystal two absorption bands with maxima at $\lambda \approx 338$ and 458 nm (Fig. 1) are observed. After gamma exposure these maxima increase their values, and

AA bands appear (color centers) at $\lambda \approx 232$, 255, 275, 339, and 458 nm, respectively, that vanish in time dependent on the wavelength (Figs. 2 and 5). The increase of the absorption for 338 and 458nm is connected probably with increase of Ce^{3+} content in the crystals (recharging effect: $Er^{4+} \rightarrow Er^{3+}$). One can see, the vanishing of color centers is not monotonic, but is stronger for shorter wavelengths. After one year from gamma exposure, samples of Ce:YAG crystal show strong decrease of absorption values in UV, but a few one in the visible part of the spectrum, especially for wavelengths near 450nm.

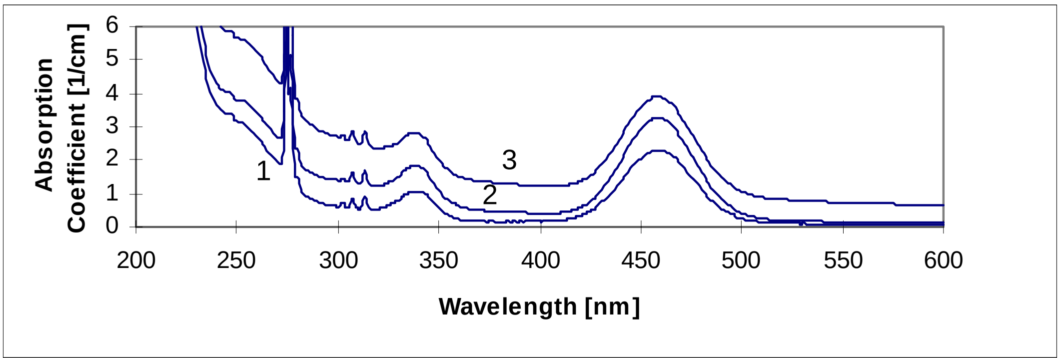

Fig.1 YAG: Ce (0.05at%) crystal after gamma exposure: 1 - before excitation, 2 - one year after gamma exposure, 3 - just after gamma exposure. One can see the two absorbtion bands: 338nm and 458nm and noncontrolled (may be Gd^{3+}) dopant band at 275 nm

It is very important, because the pumping of Ce: YAG crystal with the use of Cd-laser is possible ($\lambda_{ex} \approx 442$ nm). In table 1 values of absorption coefficient for 442 nm (Cd-laser) and 530 nm (wavelength of emisssion of YAG: Ce crystal) for YAG: Ce crystal compared with pure YAG and Nd: YAG crystals are presented. As one can see, one year after gamma irradiation absorption coefficient of Ce: YAG crystal for 530 nm is comparable with corresponding value before gamma irradiation, but absorption coefficient for 442 nm changes lower, what means greater efficiency of pumping.

Much less changes in absorption coefficient take place for Ce, Nd: YAG crystal, as can be seen in Figs. 3 to 5. Here are two absorption bands: 250-350 nm and 350-455 nm. As a result, they correspond to two paramagnetic centers with g=2.016 and g=2.018 [1]. The temperature damage threshold for the first one is 650 K and for the second one 326-400 K, respectively. First center is relevant to O^- ion near V_k – vacancy, second – ion O- near Vk, which charge is partially compensated by the dopant ion [6]. Wavelength dependence of absorption decrease, has the same character, but changes are smaller (Fig.5). Table 2 presents corresponding values of absorption coefficients for Ce, Nd:YAG crystal compare to pure YAG and Nd:YAG crystals.

Table 1.

Absorption coefficient of YAG, Nd:YAG and Ce:YAG crystals before (1), just after (3) and one year after (2) gamma exposure for two wavelengths: 442 and 530 nm, respectively.

Wavelength [nm]	Abs.Coeff. (curve 1, Fig. 1) [1/cm]	Abs.Coeff. (curve 3, Fig. 1) [1/cm]	Abs.Coeff. (curve 2, Fig.1) [1/cm]
YAG, 442	0.02	0.88	0.70
530	0.01	0.66	0.49
YAG:Nd, 442	0.09	0.51	0.45
530	1.44	1.24	1.31
YAG:Ce, 442	1.51	2.88	2.18
530	0.1	0.79	0.18

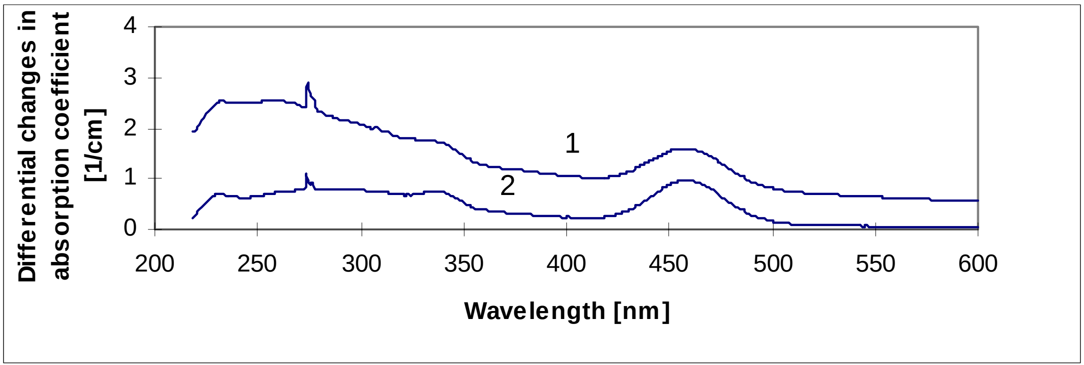

Fig.2 Differential changes in absorption coefficients of YAG:Ce (0.05at%) crystal after gamma exposure:1 - just after gamma exposure, 2 - one year after gamma exposure. AA bands are seen at: 232, 275, 338 and 458 nm

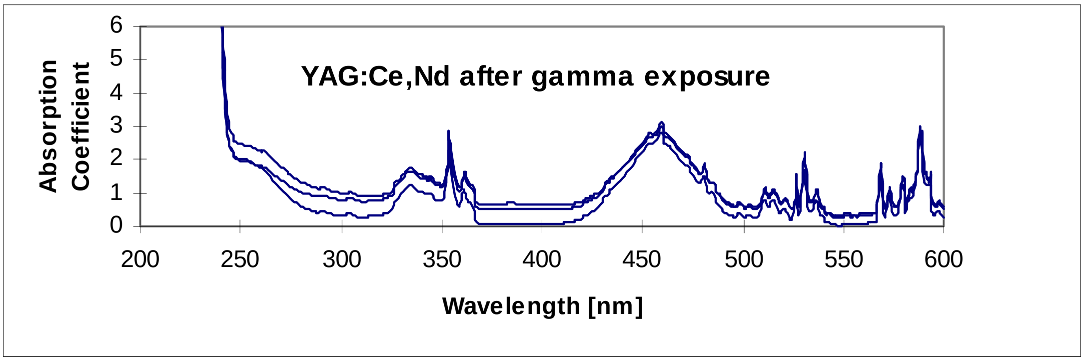

Fig. 3 Absorption coefficient of YAG:Ce, Nd (0.05at% Ce, 1at% Nd) crystal after gamma exposure: 1 - before gamma exposure, 2 - one year later, 3 - just after

Table 2.

Absorption coefficient of YAG, Nd: YAG and Ce, Nd:YAG crystals before (1), just after (3) and one year after (2) gamma exposure for four wavelengths: 442 (Cd-laser), 507, 524 and 548 nm

Wavelength [nm]	Abs.Coeff. (curve 1, Fig. 3) [1/cm]	Abs.Coeff. (curve 3, Fig. 3) [1/cm]	Abs.Coeff. (curve 2, Fig. 3) [1/cm]
YAG, 442	0.02	0.88	0.70
507	0.01	0.73	0.54
524	0.01	0.68	0.50
548	0.01	0.61	0.45
YAG:Nd, 442	0.09	0.51	0.45
507	0.24	0.51	0.47
524	0.22	0.49	0.43
548	0.06	0.28	0.27
YAG:Ce, 442	1.61	1.89	1.90
507	0.29	0.6	0.55
524	0.23	0.55	0.49
548	0.03	0.32	0.27

As one can see from Fig. 6, AA bands are higher for pure YAG than for Ce:Nd:YAG and Nd:YAG, but lower than for Ce:YAG crystal. To determine the lasing features of these materials, we have measured luminescence spectra in the range of 475-800 nm. From Fig. 7 it is evident that for Ce:YAG crystal after one year from gamma exposure, the ratio of luminescence (areas under curves 1 and 2) is of order 2.11. The luminescence corresponds to $4f^05d^1 \rightarrow 4f^1$ transitions of Ce^{3+} ions [13]. The same parameter for Ce, Nd:YAG crystal is equal to 1.17 (Fig. 8). This means that Ce, Nd:YAG crystal is less susceptible to gamma irradiation (concentrations of Ce^{3+} - 0.05at.% - are the same).

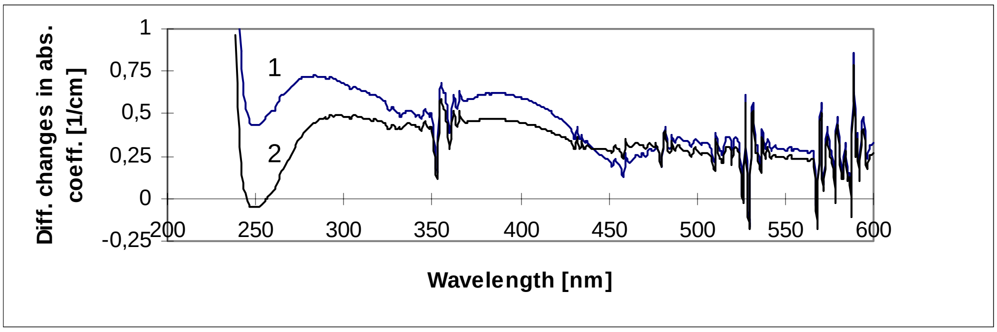

Fig. 4 Differential changes in absorption coefficient of YAG:Ce,Nd (0.05at% Ce, 1at% Nd) crystal: 1 - just after gamma exposure, 2 - one year later

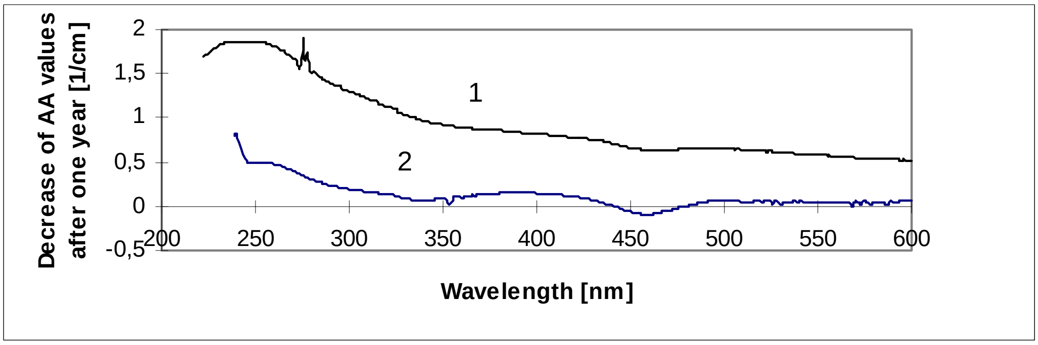

Fig. 5 Decrease of additional absorption values v.s. wavelength for YAG:Ce (1) and YAG:Ce,Nd (2) crystals. It is seen that a character of AA vanishing values is unmonotonic

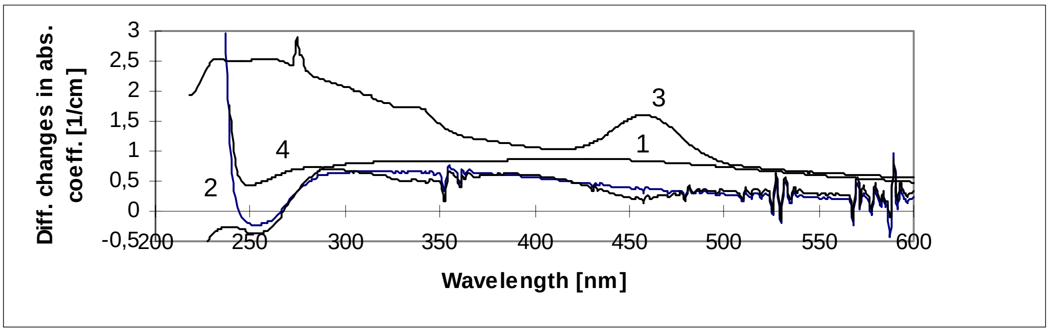

Fig. 6 Differential changes of absorption coefficient of YAG (1), YAG:Nd (2), YAG:Ce (3) and YAG:Ce,Nd (4) crystals after gamma exposure. One can see that maximum values of AA bands appear for: YAG - 254, 318 and 423 nm, YAG:Nd - 253, 318 and 380 nm, Ce:YAG - 217, 233, 333 and 458 nm, YAG:Nd,Ce - 249, 284, 386 and 482 nm

Fig. 9 shows a comparison (in the same conditions of the excitation) of luminescence phenomenon for Ce, Nd:YAG and Ce:YAG crystals. Corresponding ratio is equal to 2.61, what means that Ce, Nd:YAG crystal gives stronger emission than Ce:YAG one. Moreover, for Ce:YAG crystal one maximum of luminescence in the range of 475-800 nm at 530 nm appear; for Ce:Nd:YAG there are 5 maxima, at λ~507, λ~524, λ~546, λ~576 and λ~604 nm, respectively, what is the result of re-absorption process due to Nd^{3+} ions. These maxima correspond to absorption spectrum of the crystal, what is seen from Fig. 10. It is also seen sensibilization process of Ce^{3+} ions by Nd^{3+} ions (greater values of the luminescence for Ce:YAG crystal than for Ce, Nd:YAG one) (see Fig. 9). From Fig. 11 it is obvious, that for Ce, Nd:YAG crystal, the shape of the luminescence in the range of 470-800nm, is not influenced by other, noncontrolled impurities. Figs 12 and 13 show luminescence of Ce, Nd:YAG crystal for different values of excitation and emission wavelengths. Fig. 14 shows the same effect as in Fig. 11 except for Ce:YAG crystal.

4. Conclusion

After gamma irradiation of Ce: YAG, at least two AA bands appeared at 338 and 458 nm. Where absorption by Ce^{3+} ions take place [13]. These bands are connected with gamma-induced increase of Ce^{3+} ions content (recharge effect: $Ce^{4+} \rightarrow Ce^{3+}$). The increase of Ce^{3+} ions content is obvious after analysis of the luminescence curves before and after gamma irradiation. The increase of luminescence value after gamma irradiation for 530 nm means increase of concentration of active centers emitting at this wavelength, i.e., Ce^{3+} ions. Other bands are: 275 nm – connected with uncontrolled impurity of gadolinium and 250 nm, connected with uncontrolled impurities of Fe ions.

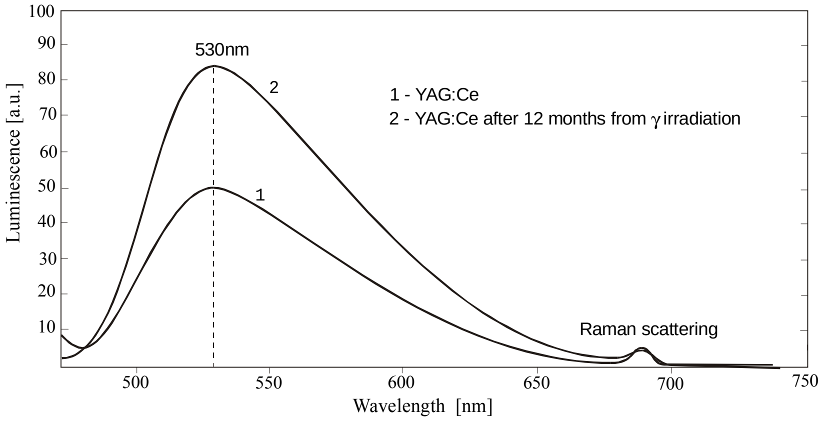

Fig. 7 Intensity of luminescence (green color for 530 nm) for YAG:Ce crystal one year after gamma exposure (2) and before gamma exposure (1). Intensity ratios after integrating of curves 1 and 2 in the range of 470-800nm are: 2.11:1

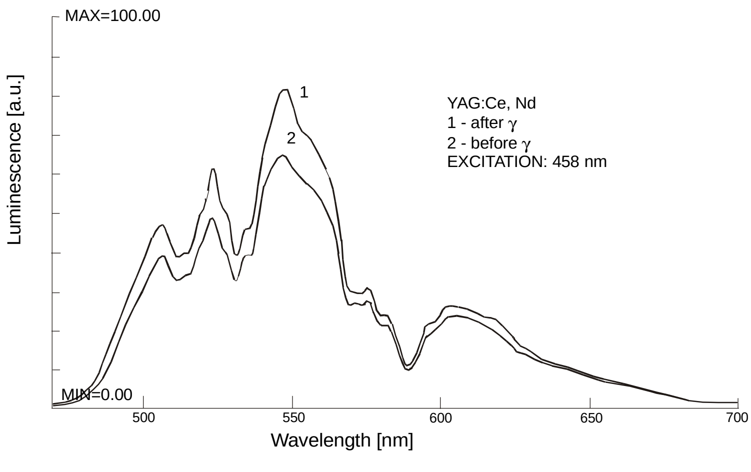

Fig. 8 Intensity of luminescence (green colour also) for YAG:Ce, Nd crystal one year after gamma exposure (1) and before gamma exposure (2). Intensity ratios after integrating of curves 1 and 2 in the range of 470-700 nm are: 1.17:1

After gamma irradiation of Ce, Nd: YAG crystal, two absorption bands: 250-350 nm and 350-455 nm appear, which corresponds to two paramagnetic centers. Also the band at 250 nm appears, which is connected with uncontrolled impurity of Fe ions. As one can see, the increase (but lower then for Ce:YAG crystal) of Ce^{3+} ions content after gamma irradiation of the crystal takes place.

It is possible to obtain the emission from coherently pumped Ce:YAG and/or Ce,Nd: YAG crystals for 530 nm or 548 nm, respectively.

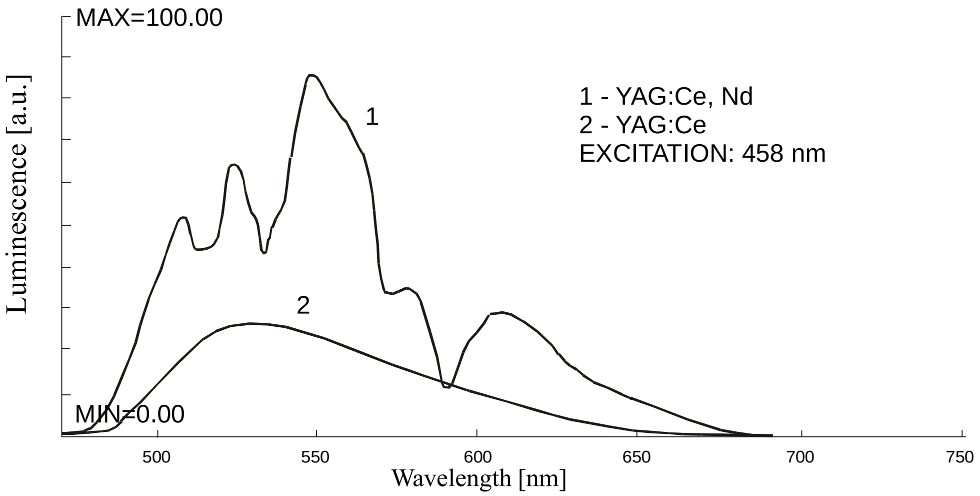

Fig.9 Comparison of YAG:Ce,Nd (1) and YAG:Ce (2) crystal luminescence one year after gamma exposure. Intensity ratios after integrating of curves 1 and 2 in the range of 470-800 nm are: 2.61:1

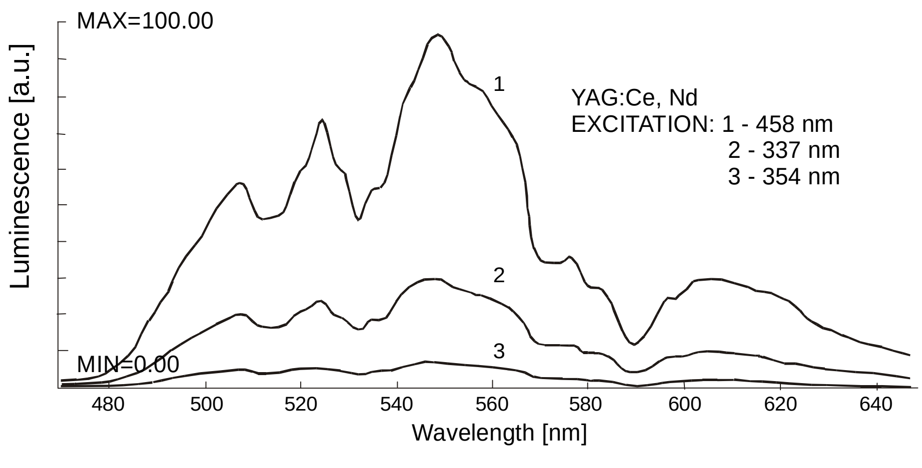

Fig. 10 Comparison of luminescence spectra for YAG:Ce, Nd crystal before gamma exposure, for different types of excitations: 1 - 458 nm, 2 - 337 nm and 3 - 354 nm. Intensity ratios after integrating of curves 1, 2 and 3 in the range of 470-660 nm are: 10.69:4.19:1

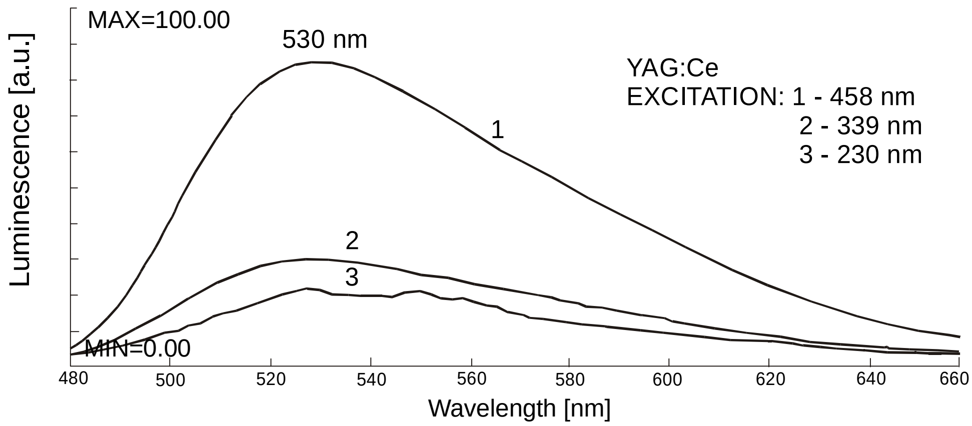

Fig. 11 Comparison of luminescence spectra for gamma exposured (5.10^4 Gy) YAG:Ce crystal and for different types of excitations: 1 - 458nm, 2 - 339 nm and 3 - 230 nm. Intensity ratios after integrating of curves 1, 2 and 3 in the range of 480-660 nm are: 4.56:1.53:1

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REFERENCES

1. Szvarc K.K., Ekmanis J.A., (in Russion) Dielectric materials: radiation process and
susceptibility to radiation, Zinatne, Riga, 1989.
2. Malov N.A., Riabov A.I., Nasielski S.P., Tormkin T.N., Svom E.M., Usolcev I.F., (in Russion) "Mechanism of influence of γ-quanta on energetic characteristics of Nd:YAG crystals", Kvantovaja Elektronika, vol. 10 (1983), No. 5, pp.1067-1069.
3. Rose T.S., Hopkins M.S., Fields R.A., "Characterization and Control of Gamma and Proton Radiation Effects on the Performance of Nd:YAG and Nd:YLF Lasers", IEEE, J. of Quantum Electronics, vol. 31 (1995), No.9, pp. 1593-1602.
4. Karaseva L.G., Konstantinov L.J., Gromov V.V., (in Russion) "Nature of radiation colour centers in single crystals of yttrium aluminium garnet", *Radiat.Phys.Chem.*, vol.26, (1985) No6, pp.723-730.
5. Habibulajev P.K., Biedilov I.R., Bejsemdajeva H.B., (in Russion) "Radiationally activated process in solid-state lasers", FIAN , Taszkient, 1988, p.316.
6. Matkovskii A.O., Sugak D.Yu., Ubizskii S.B., Shpotiuk O.I., Chernyj E.A., Vakiv N.M., Mokshyckii V.A., (in Russion) "Influence of ionizing radiation on optoelectronic materials Svit, Lviv, 1994, p.212
7. Kaczmarek S., Matkowski A.O., Mierczyk Z., Kopczyñski K., Sugak D.Yu., Frukacz Z., "Influence of UV and γ-radiation on optical properties of YAG crystals doped with: Ce, Pr, Nd, Er, Ho, Tm, Cr and Mg", Opto-electronics Review, vol. 3 (1995), No. 3/4, pp. 74-79

8. Kaczmarek S., Mierczyk Z., Kopczyñski K., Matkowski A.O., Sugak D.Yu., Frukacz Z., "Interaction of ionizing radiation with rare-earth doped YAG crystals", Proceedings of the International Conference on Intermolecular Interactions in Matter, Eds. K.Sangwal, E.Jartych and J.M.Olchowik, Lublin, 1995, pp.134-141.
9. Biedilov M.R., Bejsembajeva H.B., Sabitov M.S., (in Russion) "Low-dose irradiation of ruby and Nd^{3+}:YAG lasers", Kvantovaja Elektronika, vol.21 (1994), No12, pp.1145-1147.
10. Pirogova G.N., Krickaja V.E., Anisimov N.A., Demashkina L.G., Influence of a radiation on optical features of yttrium-aluminium garnets, Izv. AN SSSR, Ser. Neorg. Mater., vol. 11 (1975), No. 10, pp. 1812-1817.
11. N.S.Kovaleva, A.O.Ivanov, E.P.Dubrovina, A relevance of the creating of radiation color centers to growth defects in Nd: YAG crystals, Kvantovaya Elektronika, vol.8 (1981), No. 11, pp. 2433-2438.
12. M.R.Biedilov, H.B.Bejsembajeva, P.K.Habibulajev, R.P.Saidov, Influence of an electron beam on performance of Nd: YAG laser, Ukr. Fiz. Journ., vol. 31 (1986), No. 1, pp. 59-65
13. J.Mares, Energy transfer in YAlG:Nd codoped with Ce, Czechoslovak Jornal of Physics, vol.B35 (1985), pp. 883-891

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Wpływ promieniowania gamma na kryształy YAG domieszkowane Ce i Ce, Nd

Streszczenie. Zbadano wpływ promieniowania gamma na własności optyczne krzsztełów Ce:YAG oraz Ce, Nd:YAG. Zaobserwowano wzrost luminescencji w obu kryształach w obszarze 470-800 nm (maksimum dla 530 nm) po naœwietleniu ich kwantami gamma. Silniej wzrasta luminescencja kryształu Ce:YAG. Wzrost ten po upływie roku od naœwietlenia był jeszcze ponad dwukrotny. Wzrost ten związany jest ze wzrostem koncentracji Ce^{3+} po naświetleniu kryształu kwantami gamma (reakcja $Ce^{4+} \rightarrow Ce^{3+}$).

REZIUME

Issledowano wlijanie gamma izlucenija na opticeskie swojstwa kristallow ittrij-aljuminewogo granata legirowannogo ceriem i odnowremenno ceriem i nieodimom. Posle izluceniq etih kristallow gamma kwantami widno powyszenie luminescencii w oblasti 470-800 nm (maximum w 530 nm). Silnee wozrastaet luminescenciq kristalla Ce:YAG. Luminescenciq etogo kristalla posle goda ot obluceniq w dwa raza bolsze cem luminescenciq dla kristalla neoblucennogo. Eto powyszenie swjazano s rostom koncentracii Ce^{3+} posle gamma obluceniq (reakcija: $Ce^{4+} \rightarrow Ce^{3+}$).