

# CHANGES IN LUMINESCENCE OF Ce:YAG CRYSTALS UNDER IONIZING RADIATION TREATMENT\*

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Radiation induced changes in the luminescence spectrum under influence of UV light,  $\gamma$ -rays, electrons and protons for several concentrations of  $\text{Ce}^{3+}$  ions as well as  $\text{Mg}^{2+}$  ions in yttrium-aluminum garnet crystals were investigated. To irradiate with  $\gamma$  and electron as grown crystals were used while for proton irradiations the crystals were thermally annealed. For small concentrations of cerium ions ( $\approx 0.01$  at.%) an increase in the luminescence (about 100%) was observed after gamma irradiation with a dose of  $10^5$  Gy. This increase was due to the growth in  $\text{Ce}^{3+}$  ions concentration after  $\gamma$ -irradiation ( $\approx 50\%$ ), due to the  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  recharging reaction. For highly doped Ce:YAG crystals (0.1 at.%, 0.2 at.%) also an increase, but much smaller (4%), for the Mg codoped crystals (0.1 at.%) was observed. After 1 MeV electron irradiation in the over-threshold type interaction a decrease in luminescence is observed due to the domination of the  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  ionization process. In the case of the proton irradiation, for small fluencies ( $\approx 10^{13}$  particles/cm<sup>2</sup>) an increase in luminescence is observed due to the domination of the recharging processes of  $\text{Ce}^{4+}$  ions. For larger fluencies ( $> 10^{14}$  particles/cm<sup>2</sup>) a decrease takes place due to a high level of radiation defects.

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## 1. Introduction

$\text{Ce}^{3+}$ :YAG crystals have some features highly desirable for an active material of the tuned solid state lasers [1]. The emission band from  $4f-5d$  levels has quantum efficiency close to unity and extends from 500 to about 650 nm. Broad

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pumping bands exhibit the allowed absorption of the dipole-dipole type. On the other hand, the YAG matrix has excellent thermal and optical characteristics, but a large value of the absorption from the excited state (ESA) in this material excludes a stimulated emission from the excited levels of Ce ions (states 5d) [2]. The ESA spectra of Ce<sup>3+</sup>:YAG crystal overlap with luminescence of the trivalent Ce ions, which leads to a fast decay of the luminescence (about 30 ns) and thus, the inability to get any laser action.

The Ce<sup>3+</sup>:YAG crystal is also used as a scintillator (e.g., in medical imaging, tomography, gamma-cameras) [3]. Parameters of the Ce:YAG crystal as a scintillator as well as a potential active medium, to a large extent, depend on its optical properties as well as on the kind of the structural and radiation defects. Due to local changes of the crystal field (e.g., due to additional impurities, vacancies, local distortions, etc.) various inequivalent centres arise which results in additional fluorescence of these centres [4]. They may emerge in the crystal during the growth process as well as after its annealing in high temperatures or after irradiation by ionising radiation [5-10].

The main goal of this work was the study of such structural and radiation defects in cerium doped YAG crystals which influence the crystal properties qualifying them as scintillators or active laser materials.

## 2. Experimental

### 2.1. Spectroscopic studies

From the single crystals obtained in the Institute of Electronic Materials Technology, the next parallel plate samples of 1 mm thick were cut out and both sides polished: Ce:YAG (0.1 at.% Ce) (S1), Ce:YAG (0.2 at.% Ce) (S2), Ce, Mg:YAG (0.2 at.% Ce + 0.1 at.% Mg) (S3) and Ce:YAG (0.05 at.%) (S4). Next, the optical transmission was measured before and after the thermal or radiation treatment: in UV-VIS region by means of a LAMBDA-2 Perkin-Elmer spectrophotometer and in IR region by a FTIR-1725 spectrophotometer. After measurement of the transmission, the additional absorption ( $\Delta K$  factor) was calculated according to the following formula:

$$\Delta K(\lambda) = (1/d) \ln(T_1/T_2), \quad (1)$$

where  $K$  is the absorption,  $\Delta K$  is the additional absorption,  $\lambda$  is the wavelength,  $d$  is the sample thickness,  $T_1$  and  $T_2$  are the sample transmissions before and after the treatment, respectively. The fluorescence and excitation spectra were recorded by means of a spectrofluorimeter LS-5B of Perkin-Elmer and laser excitation devices (355 nm and 442 nm).

### 2.2. Annealing conditions

After each irradiation in order to remove radiation defects, annealing of Ce:YAG and Ce, Mg:YAG crystals was performed in air at 400°C for 3 hours. Also, annealing of these crystals in oxidising and reducing atmospheres was done; the first one at 1400°C in air during 4 h, performed immediately after growth, to get rid of the growth defects; the second one, at 1200°C in the gas mixture of N<sub>2</sub> + H<sub>2</sub>, during 1 hour, in order to change the defect structure of these crystals.

### 2.3. Irradiation conditions

The crystals were irradiated: by UV light and  $\gamma$ -quanta, immediately after the growth was accomplished (as grown) both, at room and liquid nitrogen temperatures; by protons, after annealing at 1400°C and, by electrons, after annealing at 800°C.

The UV source of pulsed linear xenon flushlamp was used. The gamma source of  $^{60}\text{Co}$  with a strength of 1.5 Gy/s was used. The samples were irradiated with gamma doses up to  $10^5$  Gy.

For proton irradiation the beam from a C-30 cyclotron of the Sołtan Institute of Nuclear Studies in Świerk was used. The proton energy was about 20 MeV, and the beam current at the sample was about 0.2 mA. The proton fluency was varied from  $10^{13}$  to  $10^{16}$  particles/cm $^2$ .

For electron irradiation the electron beam from Van de Graaf accelerator was used. The electron energy was 1 MeV and electron fluency was  $10^{16}$  particles/cm $^2$ .

### 3. Results and discussion

Absorption spectra of the S1, ..., S4 crystals in the UV-VIS range are presented in Fig. 1. In this figure  $4f-5d$  transitions are seen for Ce ions for the wavelengths: 227 nm, 266 nm, 340 nm, and 455 nm. The fifth  $4f-5d$  transition, at 211 nm, was earlier described in Ref. [1]. As seen, the presence of Mg in YAG crystals manifests itself by a shift of the fundamental absorption edge towards the longer wavelengths by about 100 nm.

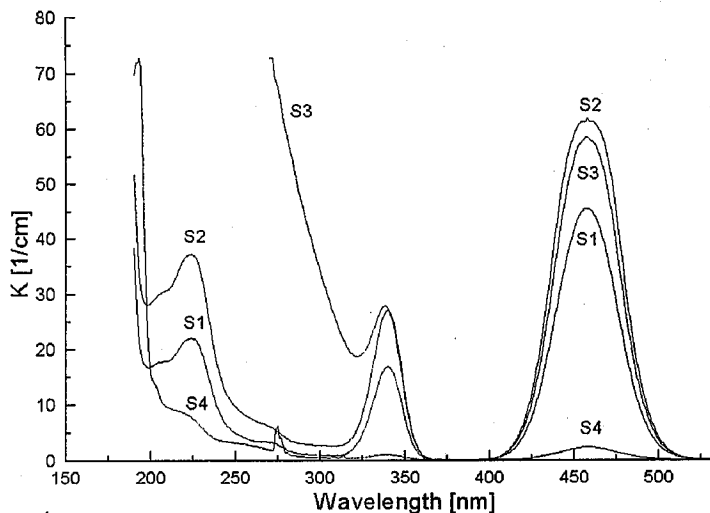


Fig. 1. Absorption of S1, ..., S4 crystals in the UV-VIS range at room temperature.

Figure 2 shows the excitation and the luminescence spectra for Ce, Mg:YAG crystal. A broad, intense luminescence band between 450 and 700 nm is seen. The  $\lambda_{\text{em}} \approx 530$  nm and various  $5d$  excitation bands are observed in the spectral range of 200–500 nm peaked at  $\lambda_{\text{ex}} \approx 455$  nm at room temperature.

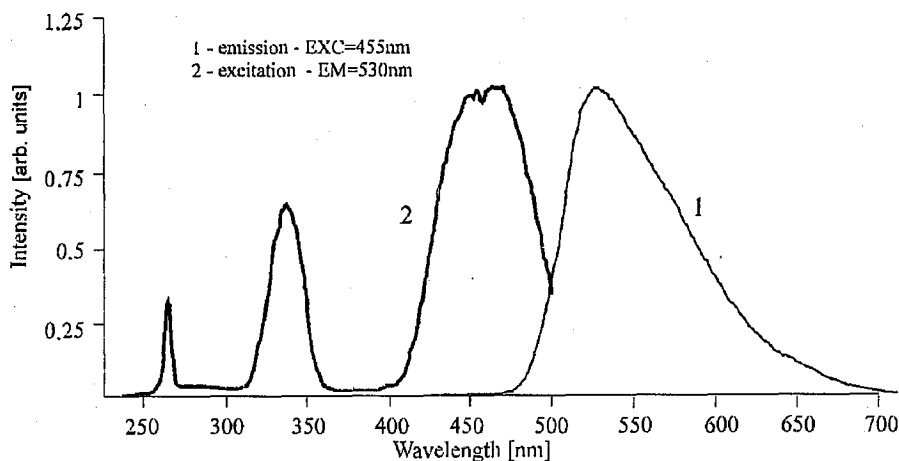


Fig. 2. Emission (1) and excitation (2) spectra of Ce, Mg:YAG (S3) crystal at room temperature.

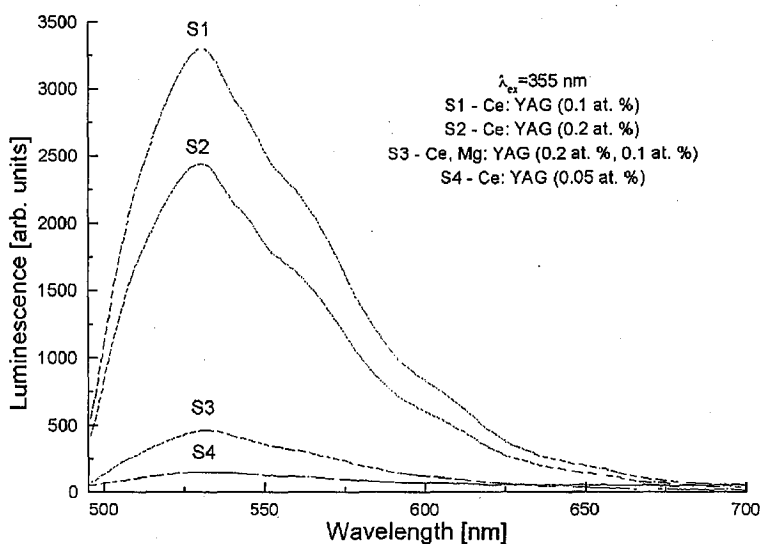


Fig. 3. Uncorrected luminescence spectra of S1, ..., S4 samples detected at  $\lambda_{exc} = 355 \text{ nm}$  (laser).

Figure 3 illustrates the luminescence measurements for as grown S1, ..., S4 samples. At the excitation wavelength of 355 nm the competition from the Mg-related absorption strongly reduces the efficiency of Ce excitation and, consequently, the height of the spectrum shown by trace (S3).

Figure 4 compares intensities of the luminescence obtained for S4 crystal (curve 1) before and (curve 2) one year after  $\gamma$  exposure with a dose of  $10^5 \text{ Gy}$ .

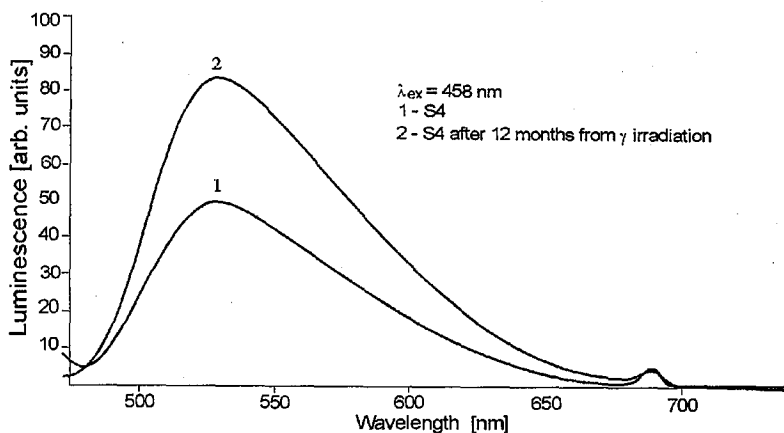


Fig. 4. Comparison of the luminescence obtained for S4 crystal before (1) and one year (2) after  $\gamma$ -irradiation with a dose of  $10^5$  Gy.

Intensities ratio after integrating of the curves 1 and 2 in the range of 470–800 nm is 2.11:1. One can conclude that even one year after  $\gamma$ -irradiation 100% change in luminescence intensity is observed. This phenomenon was explained earlier by an increase in the  $\text{Ce}^{3+}$  concentration due to the reaction  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ , stimulated by the  $\gamma$  radiation [10]. Irradiation of the cerium and magnesium doped YAG crystals with the initial concentrations of 0.1 and 0.2 at.% Ce and 0.1 at.% Mg (S1, ..., S3 samples) did not show any significant changes in the luminescence. Only a small (a few nm) shift of the luminescence maximum was observed. It is so because we treated our crystals with different types of ionising radiation with the aim of recording the changes in the Ce valency.

Figure 5 presents additional absorption recorded for S3 sample after subsequent treatments. As seen, in all the cases the largest changes in the absorption arise near 340 and 455 nm, that is during all these treatments the changes in  $\text{Ce}^{3+}$  concentration take place. A positive value of additional absorption for S3 as grown sample irradiated by  $\gamma$ -rays indicate that in this crystal  $\text{Ce}^{4+}$  ions, compensated by  $\text{Mg}^{2+}$  were present just after growth and due to, e.g., Compton effect they stayed  $\text{Ce}^{3+}$  ( $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ ). So, Mg doping changes the  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  balance in the sample [7]. After  $\gamma$ -irradiation an increase in  $\text{Ce}^{3+}$  content is seen as positive additional absorption in the range of  $\text{Ce}^{3+}$  ions transitions. Each subsequent treatment leads to an appropriate reaction of the type  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  (similar changes were observed in IR region for  $f-f$  transitions).

Similar behaviour exhibits S4 sample. S1 and S2 samples do not show the above-described features. It is seen in Fig. 6. As seen from Fig. 6 the S1 and S2 samples show opposite changes after  $\gamma$ -irradiation with respect to S3 and S4 samples. These changes are almost equal in amplitude. However, in the case of S1 and S2 samples they include  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  ionisation process which takes place after  $\gamma$ -irradiation. Thus, S4 and S3 and, S1 and S2 crystals exhibit opposite behaviour in additional absorption after  $\gamma$ -irradiation. It is possible that in the S4 low doped with Ce crystal, similarly as in the S3 crystal,  $\text{Ce}^{4+}$  ions arise after

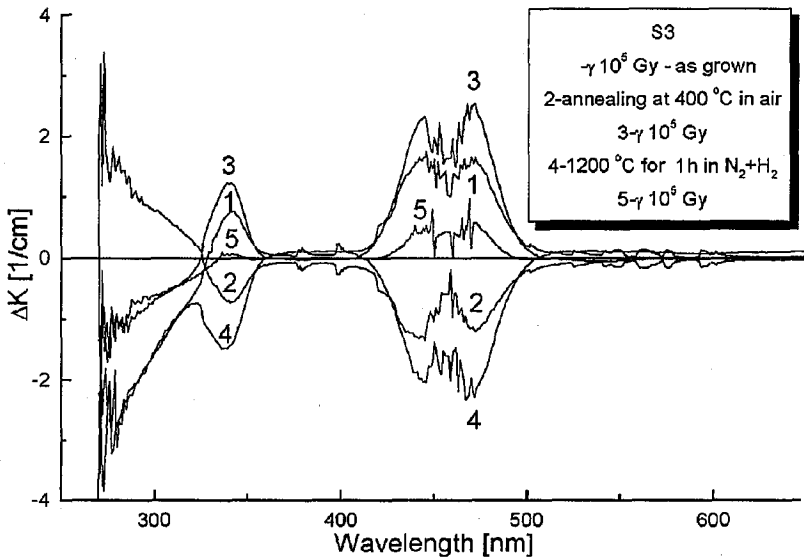


Fig. 5. Additional absorption for S3 crystal after:  $\gamma$ -irradiation with a dose of  $10^5$  Gy (1); annealing at  $400^\circ\text{C}$  in air for 3 h (2);  $\gamma$ -irradiation,  $10^5$  Gy (3); annealing at  $1200^\circ\text{C}$  in the  $\text{N}_2 + \text{H}_2$  gas mixture for 1 h (4); and  $\gamma$ -irradiation,  $10^5$  Gy (5).

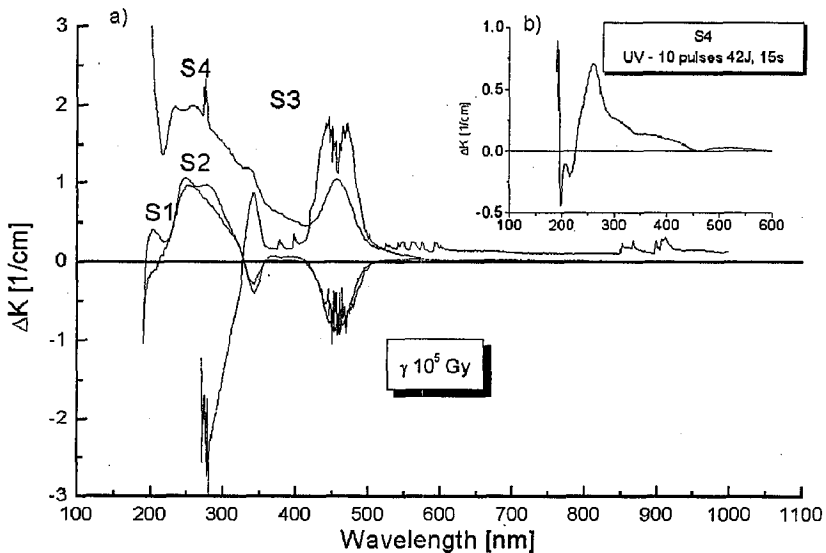


Fig. 6. Additional absorption (a) for S1, ..., S4 crystals after  $\gamma$ -irradiation with a dose of  $10^5$  Gy and (b) for S4 crystal after UV-irradiation with a xenon pump lamp.

the growth. In this figure changes in the absorption measured for S4 crystal after UV-irradiation are also seen. On the base of the changes taking place near 340 and 455 nm one can conclude that UV-irradiation leads to the ionisation of Ce ( $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ ).

An analogous effect (a change in the concentration of  $Ce^{3+}$  ions after irradiation) is observed after an irradiation of the Ce:YAG (S4 sample) by electrons with over-threshold energy (1 MeV, fluency  $5 \times 10^{16}$  particles/cm<sup>2</sup>). It is illustrated in Fig. 7, curve 7. This effect is similar to that observed after the UV-irradiation (Fig. 6b), where the ionisation process of  $Ce^{3+}$  ions is observed. In Fig. 7 the influence of all applied kinds of radiation on Ce:YAG crystals is seen. A comparison of curves 1, 2 and 7 shows that the influence of each type of irradiation on Ce:YAG crystal is different, although they exhibit common features. Namely, recharging effects are seen after each kind of radiation (Ce-bands centred at 340 and 455 nm and Fe-band at 275 nm ions and, the appearing of F-centres-bands centred at about 300 nm [11]). Curves 2–6 in Fig. 7a and curves 1–5 in Fig. 7b describe additional absorption for S4 sample after proton irradiation with fluencies from  $10^{13}$  to  $10^{16}$  particles/cm<sup>2</sup> as (Fig. 7a) relative changes and (Fig. 7b) absolute changes in absorption, respectively. As seen, in the sense of additional absorption as a function of dose, curves 4 (Fig. 7a) and 3 (Fig. 7b) are the critical ones.

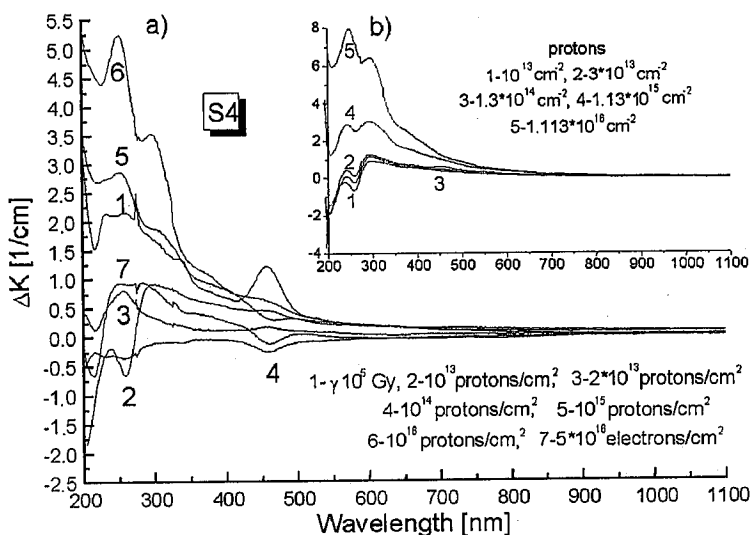


Fig. 7. Additional absorption bands for S4 sample (a) after  $\gamma$ , electron and proton (relative fluencies) and (b) after proton (absolute fluencies) irradiations.

As was shown elsewhere [12], an increase in  $\gamma$ -dose leads to saturation of changes in the absorption spectrum due to recharging of all point defects existing before irradiation in the crystal. Changes in absorption spectrum introduced into the crystal by electron or proton irradiation do not show such saturation effect. It is because Frenkel defects are formed in a crystal when fluency of ionising particles exceed some critical value. From Fig. 7 one can see that this critical value for protons is equal to about  $10^{14}$  particles/cm<sup>2</sup>.

The formation of Frenkel defects is clearly seen in Fig. 8, where dose dependences of additional absorption after proton irradiation of Ce:YAG (S4) crys-

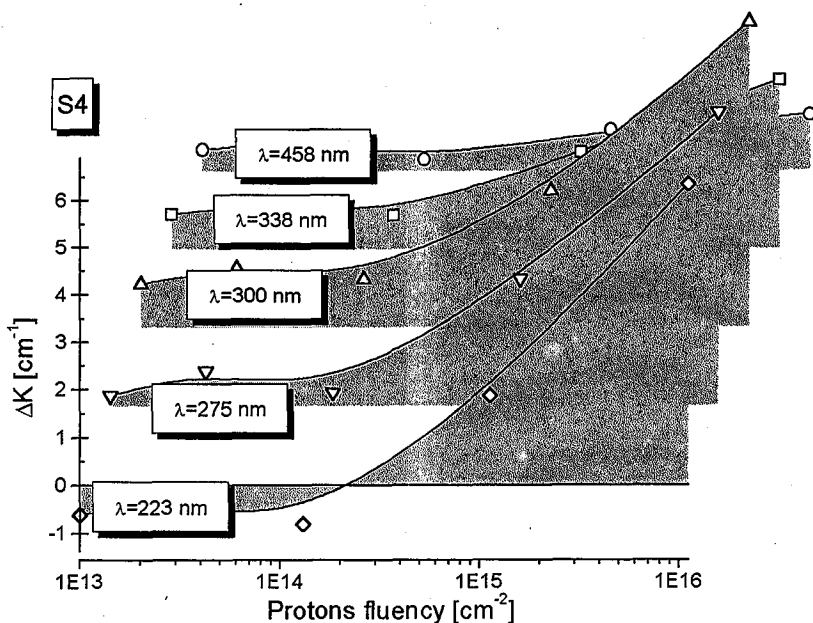


Fig. 8. Fluency dependences of Ce:YAG (S4 sample) crystal after proton irradiation for several wavelengths.

tal for several wavelengths are presented. As seen, when the fluency is small ( $< 10^{14}$  particles/cm<sup>2</sup>) then recharging effects dominate in the interaction of protons with the crystal (ionisation and delta electrons). When the fluency exceeds a value of  $10^{14}$  particles/cm<sup>2</sup>, a linear increase starts in fluency dependence of additional absorption which means the presence of Frenkel defects. Irradiation with protons of other samples, (S1, ..., S3), leads to the same changes as in  $\gamma$  case (for example, for S3 sample we obtained the additional absorption of the same type as curve 1 in Fig. 5).

Figure 9 compares changes in the luminescence recorded for S1, ..., S4 samples after proton irradiation and S1, ..., S3 after  $\gamma$ -irradiation. As seen from the figure, changes in the luminescence are only quantitative and relatively much larger for low doping S4 sample than for S1, ..., S3 crystals. For S4 sample an increase in intensity of the luminescence is observed after irradiation with  $10^{13}$  protons/cm<sup>2</sup> (curve 2), while after  $3 \times 10^{13}$  protons/cm<sup>2</sup> (curve 3) a decrease is observed (Fig. 9a). This increase is due to recharging processes during the proton interaction with the crystal while a decrease is associated with the forming of Frenkel defects. S3 sample shows a decrease in the luminescence after  $\gamma$ -irradiation with a dose of  $10^6$  Gy, while S1 and S2 samples show an increase after both types of the irradiation.

One can conclude that in Ce, Mg:YAG crystal after annealing process some quantity of Ce<sup>4+</sup> ions was formed (negative values of additional absorption bands in the range of Ce<sup>3+</sup> ions transitions, peaked at 340 and 458 nm, after annealing — curves 2 and 4 in Fig. 5). Proton irradiation leads to the change of valency of Ce<sup>4+</sup> ions (positive values of the additional absorption bands) to Ce<sup>3+</sup>. This



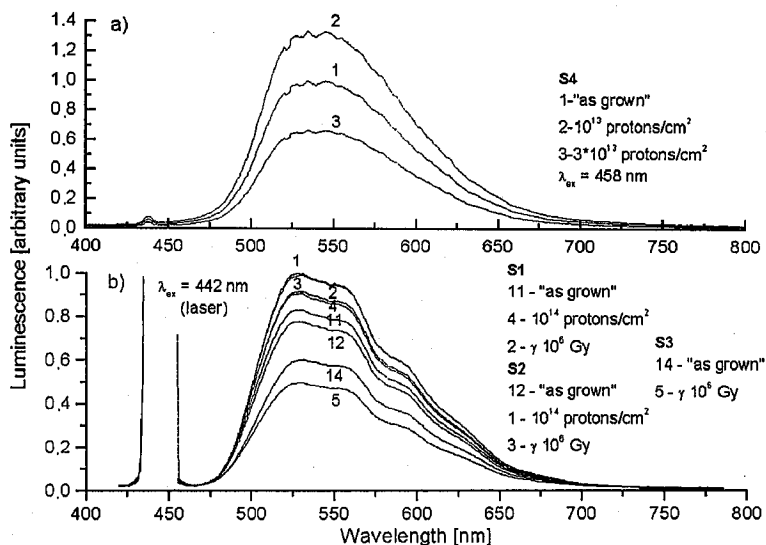


Fig. 9. Changes in a luminescence spectrum for S4 (a) and S1, ..., S3 (b) samples after proton and  $\gamma$ -irradiation with fluencies between  $10^{13}$  and  $10^{14}$  particles/cm<sup>2</sup> and doses of  $\gamma$ -quanta  $10^6$  Gy (laser).

is probably due to the capture of electrons emitted in large quantities along the proton trajectory due to the Coulomb interaction of the projectile with atoms of medium (delta electrons). The magnitude of the changes suggests that in the Ce, Mg:YAG crystal before the annealing process there existed  $\text{Ce}^{4+}$  ions compensated by  $\text{Mg}^{2+}$ . Thus, we go to the same conclusion as before for  $\gamma$ -rays.

Why the changes in the luminescence spectrum of the Ce:YAG crystals in some cases are small (S1, ..., S3) and in other cases are large (S4)?

These changes are associated with the changes in absorption spectrum. It is known that there exists an unambiguous relation between the concentration of the absorption centres and parameters of the absorption band, which is expressed by the formula of Smakula, modified in Ref. [2] for the cases when the shape of the absorption line is Gaussian or Lorentzian. Using this formula, total concentrations of  $\text{Ce}^{3+}$  were calculated in the samples ( $N$ ) and, also relative changes of  $\text{Ce}^{3+}$  concentrations due to the radiation ( $\Delta N$ ).

For the calculations the lowest absorption band for transitions  $4f-5d$  in  $\text{Ce}^{3+}$  ion with a maximum at  $\lambda = 458$  nm was chosen which, according to [1], has a Gaussian shape. In this case  $\text{Ce}^{3+}$  concentration can be calculated using the following formula:

$$N_{\text{Ce}} = 0.87 \times 10^{17} [\text{cm}^{-3}] KW [n / (n^2 + 2)^2] / f_0, \quad (2)$$

where  $K$  is the value of the absorption coefficient at the band maximum [ $\text{cm}^{-1}$ ],  $W$  is the FWHM of absorption band [eV],  $n$  is the refractive index at the wavelength in the maximum of absorption,  $f_0$  is the oscillator strength for given transition. The value of the refractive index,  $n = 1.847$ , was calculated from the formula

$$n^2 - 1 = A\lambda^2 / (\lambda^2 - B), \quad (3)$$

where the coefficients  $A = 2.283$  and  $B = 0.01261$  were obtained from the experimental data of Ref. [9].

Parameters  $K$  and  $W$  were obtained experimentally and are shown in Table. Also the values of  $Ce^{3+}$  concentrations in the samples S1, ..., S4 before and after a given kind of radiation, calculated from the relation (4), are shown. The first part of Table presents the above parameters for  $\gamma$ -irradiation of all investigated samples (S1, ..., S4). In the second part similar calculations are presented for the S4 crystal only, irradiated by 10 pulses of 42 J energy from the xenon lamp, next annealed in air at 1700 K for 4 hours and irradiated by protons with a fluency from  $10^{13}$  to  $10^{16}$  particles/cm<sup>2</sup> and by electrons with a fluency of  $10^{16}$  particles/cm<sup>2</sup> (another sample of the same crystal).

During calculations it was assumed that the oscillator strength of the chosen transition equals  $f_0 = 3 \times 10^{-3}$ . This assumption is based on the results of Ref. [4], in which oscillator strengths of  $Ce^{3+}$  ions were calculated for various oxides.

From Table it is seen that  $Ce^{3+}$  concentration increases by about 50% after  $\gamma$  and proton irradiations of YAG crystals (S4) with a low incident  $Ce^{3+}$  concentration (about 0.01 at.%). The irradiation of the crystals with the UV and over-threshold electrons leads to a decrease in  $Ce^{3+}$  concentration (about 5%).

TABLE

Parameters of the  $Ce^{3+}$  absorption band with a maximum at  $\lambda = 458$  nm and calculated values of  $Ce^{3+}$  concentrations ( $N_{Ce}$ ) in the samples S1, ..., S4: before and after gamma irradiation with  $10^5$  Gy; before and after irradiation by protons, electrons and UV light and, changes of this concentration ( $\Delta N_{Ce} = [(N_{after} - N_{before})/N_{before}]$ ).

Type of interaction	No.	$K$ [cm <sup>-1</sup> ]	$W$ [eV]	$N_{Ce}$ [at.%] before irradiation	$N_{Ce}$ [at.%] after irradiation	$\Delta N_{Ce}$ × 100%
Gamma rays dose $10^5$ Gy						
	S1	45.33	0.237	0.1412	0.1387	-1.75
	S2	61.74	0.235	0.1923	0.1903	-1.05
	S3	58.4	0.238	0.1819	0.1855	1.96
	S4	2.3	0.236	0.0072	0.0102	41.77
Protons						
$10^{13}$ cm <sup>-2</sup>	S4	2.18	0.233	0.0068	0.0082	20.37
$3 \times 10^{13}$ cm <sup>-2</sup>	S4	2.18	0.238	0.0068	0.0087	28.12
$10^{14}$ cm <sup>-2</sup>	S4	2.18	0.235	0.0068	0.079	16.33
$10^{15}$ cm <sup>-2</sup>	S4	2.18	0.234	0.0068	0.0096	41.68
Electrons						
$5 \times 10^{16}$ cm <sup>-2</sup>	S4	3.52	0.230	0.0110	0.0104	-5.02
UV light						
10 pulses, 42 J, 15 s	S4	2.36	0.234	0.0073	0.0070	-4.92

The  $Ce^{3+}$  concentration of high doped Ce:YAG crystals decreases after  $\gamma$  and proton irradiations (about 2%) except the S4 sample in which, due to  $Mg^{2+}$  ions,  $Ce^{4+}$  ions are also present (an increase about 2%).

#### 4. Conclusions

A change in the concentration of trivalent Ce and associated with it the change in the luminescence spectrum after UV light,  $\gamma$ , proton and electron irradiation in both kinds of crystals (low- and highly doped) is connected with the presence of, except  $Ce^{3+}$  ions, also  $Ce^{4+}$  ions. The UV light and over-threshold electrons ionise  $Ce^{3+}$  ions (also other active ions, e.g. uncontrolled Fe ions) increasing  $Ce^{4+}$  concentration in the crystal. Gamma-rays and protons, beside an increase in  $Ce^{4+}$  concentration by ionisation, can also decrease  $Ce^{4+}$  concentration due to, e.g., Compton or delta electrons. In the case of electrons and protons with over-threshold fluency ( $10^{14}$  particles/cm<sup>2</sup> for protons) a change in  $Ce^{3+} \leftrightarrow Ce^{4+}$  equilibrium balance due to Frenkel defects can take place.

In the case of protons, for small fluencies (about  $10^{13}$  protons/cm<sup>2</sup>) an increase in luminescence of Ce:YAG crystal (S4) was observed due to domination of the recharging process of  $Ce^{4+}$  ions formed in the crystal after growth. For greater ones ( $> 10^{14}$  particles/cm<sup>2</sup>) a decrease takes place due to a high level of radiation defects.

In the low-doped crystal  $Ce^{4+}$  ions probably occupy the places of  $Y^{3+}$ , while in highly doped crystals they seem to appear also in the interstitial positions. In the first case we are dealing with recombination of  $Ce^{4+}$  ions by electrons emitted due to, e.g., Compton effect. In the second case we are dealing with the ionisation of  $Ce^{3+}$  ions located in the interstitial positions. An exception is the Ce, Mg:YAG crystal which, due to the presence of magnesium, exhibits the presence of  $Ce^{4+}$  ions. This crystal after gamma irradiation behaves as Ce:YAG with a low cerium concentration. The results of calculations of the relative changes of  $Ce^{3+}$  after radiation, shown in Table, give evidence that a change of Ce concentration in Ce:YAG and Ce, Mg:YAG crystals depends on its initial concentration.

The obtained results can be explained as follows. For given growth conditions (growth method, purity of the starting material, growth atmosphere, technological parameters), a certain definite subsystem of the point defects appears in the crystal (doping ions, oxide vacancies, interstitial defects), which at the end of the growth process is electrically balanced and remains in a metastable state. The interaction of the external factors, such as radiation and thermal treatment, may lead to the transition of the defect subsystem from one metastable state to another. During this transition point defects can change their charge state. Mutually reversible changes of the charge state  $Ce^{3+} \leftrightarrow Ce^{4+}$  were observed earlier in  $Lu_2O_3:Ce$  crystals during their heating in various atmospheres [6].

The presence of  $Ce^{4+}$  in Ce:YAG as grown crystals may be explained in this way, that if, during the synthesis,  $CeO_2$  is used as the starting material, not all of the Ce ions pass to the trivalent state.

The luminescence which was investigated in this paper was green luminescence connected with emission from  $5d_1$  state. Also  $5d_2$  state can be a source of residual luminescence in the UV range [13].

In addition to the usual green luminescence, by hot luminescence measurements at the 266 nm excitation wavelength, we found in our Ce:YAG crystal two UV luminescence bands picked at 384 and 411 nm [14]. They have a decay time of 230 microsecond at room temperature and are probably connected with uncontrolled Tb ions.

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