



# Radiation induced recharging of cerium ions in Nd, Ce:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystals

S.M. Kaczmarek <sup>a,\*</sup>, D.J. Sugak <sup>b</sup>, A.O. Matkovskii <sup>b,c</sup>, Z. Moroz <sup>d</sup>, M. Kwaśny <sup>a</sup>,  
A.N. Durygin <sup>e</sup>

<sup>a</sup> *Institute of Optoelectronics, Military University of Technology, 2 Kaliski Street, 01-489 Warsaw, Poland*

<sup>b</sup> *Institute of Materials, SRC "Carat", 202, Stryjska Street, Lviv 290031, Ukraine*

<sup>c</sup> *Institute of Physics HPS, 16A Rejtana Street, Rzeszow 35 310, Poland*

<sup>d</sup> *Soltan Institute of Nuclear Studies, 05-400 Świerk, Poland*

<sup>e</sup> *Institute of Physics, Polish Academy of Science, 32146 Al. Lotnikow, 02 668 Warsaw, Poland*

Received 30 June 1997; received in revised form 1 September 1997

---

## Abstract

Radiation induced recharging of Ce<sup>3+</sup> and Ce<sup>4+</sup> ions in Ce and Nd doped yttrium–aluminium garnet crystals was observed. This effect depends on the Ce<sup>3+</sup> ion concentration and the type of ionizing radiation. The crystals investigated were irradiated with gamma-rays, protons with fluences up to 10<sup>14</sup> protons/cm<sup>2</sup> and electrons with a fluence of 5 × 10<sup>16</sup> electrons/cm<sup>2</sup>. Changes in cerium concentration after gamma-irradiation were calculated from the formula of Smakula. © 1997 Elsevier Science B.V.

*PACS:* 61.72.Ji; 61.80.Ed; 42.70.Iij

*Keywords:* Additional absorption; Gamma-irradiation; Ionization; Proton and electron beams; Crystal growth; Annealing

---

## 1. Introduction

It is known that colour centres in neodymium doped yttrium–aluminium garnet (YAG:Nd) crystals produced by the ultraviolet part of a pumping lamp spectrum as well as by bombardment by various types of ionizing particles (gamma-rays, elec-

trons, protons, etc.) unfavourably influence the output characteristics of solid-state Nd:YAG lasers [1–3].

Many methods exist to make the optical characteristics of crystals less sensitive to irradiation. They are described e.g. in Ref. [1]. In particular, in one such method, in addition to the ordinary Nd<sup>3+</sup> dopant, the introduction of extra Ce<sup>3+</sup> ions is performed during the process of crystal growth. This method appears to be extremely advantageous, because the Ce<sup>3+</sup> ions, due to the energy

\*Corresponding author. Tel.: 48 22 6859019; fax: 48 22 6668950; e-mail: laslab@wat.waw.pl.

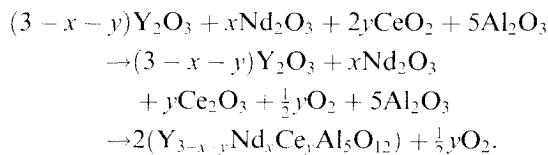
transfer  $Ce^{3+} \rightarrow Nd^{3+}$ , may also improve the luminescence of the  $Nd^{3+}$  ions [4,5].

It was shown in Ref. [6] that the influence of  $Ce^{3+}$  ions on the radiation sensitivity of YAG:Nd crystals is somewhat ambiguous. Namely, with the increase of the concentration by weight of the  $Ce^{3+}$  ions from 0.05% to 0.1% an additional absorption induced by radiation (labelled here as "AA") also increases. But, a further increase of this concentration (from 0.1% to 1% by weight) causes an essential drop of the AA factor.

In the present work we attempted to study in more detail the influence of gamma and proton radiation on the optical properties of the Ce, Nd:YAG crystals for various concentrations of Ce ions.

## 2. Experimental setup

The crystal samples were grown by the Czochralski method in iridium crucibles. The process was carried out in an  $N_2$  atmosphere with the addition of a 2% admixture of  $O_2$ . As a starting material the oxides  $Y_2O_3$ ,  $Al_2O_3$ ,  $Nd_2O_3$  and  $CeO_2$  of at least 4N purity were used. First they were dried to remove water, weighed and then mixed mechanically. After that the mixture was heated in an aluminium container to produce the reaction:



It should be noted that during heating a major part of the cerium ions should pass to the trivalent state. It is not excluded, however, that some of these ions remain in the  $Ce^{4+}$  state. For crystal growth a starting material was used, for which  $x=0.001$ ,  $y=0.005$ .

To obtain samples with different concentrations of cerium, parallel crystal plates with a thickness of about 1 mm were cut from suitable places of the conical part of the crystal, perpendicularly to the  $\langle 111 \rangle$  growth direction. These samples were labelled correspondingly as S1, S2, S3 and S4, beginning from the top of the crystal. One of the samples

investigated, S5, was taken from another bulk crystal. The cut samples were polished to obtain optical quality, which was controlled by means of a Mach-Zehnder interferometer. Next, each sample was split into two parts: the first one was irradiated by gamma-rays while the second one was heated for 3 h in air at  $1400^\circ$ . Sample S4, after this annealing, was annealed in an  $N_2 + H_2$  mixture for 1.5 h and next gamma-irradiated with a dose of  $10^5$  Gy. Sample S5, after this annealing, was irradiated by 26 MeV protons with fluences of  $1 \times 10^{13}$ ,  $3 \times 10^{13}$  and  $1 \times 10^{14}$  protons/cm<sup>2</sup>.

The spectral dependence of the absorption coefficient for the crystals was calculated from their transmission spectra, taking into account the effect of multiple reflection by the surfaces. The transmission spectra were recorded by means of a Perkin-Elmer spectrophotometer LAMBDA-2, in the range from 190 to 1100 nm. Values of AA factors due to the irradiation or thermal processing were calculated from the formula

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

where  $d$  is the sample thickness and  $T_1$  and  $T_2$  are the transmissions of the sample obtained before and after gamma-irradiation or thermal treatment, respectively.

The samples were irradiated by means of a  $^{60}Co$  gamma source (average gamma energy 1.25 MeV) up to an absorbed dose of  $10^5$  Gy.

## 3. Results

In Fig. 1 the absorption spectra for the samples S1, . . . S5 are shown. It is seen that in wavelength range up to about 850 nm, additional low-energy bands with maxima at 458 and 338 nm can be clearly distinguished. They correspond to the transitions between 4f and 5d configurations in the  $Ce^{3+}$  ions. The remaining three bands, characteristic for the transitions 4f and 5d in  $Ce^{3+}$  in the structure of the garnet [7], lay on the absorption edge of the crystal and are in the range 220-250 nm.

As can be guessed from Fig. 1, when passing from the top of the crystal along the growth axis,

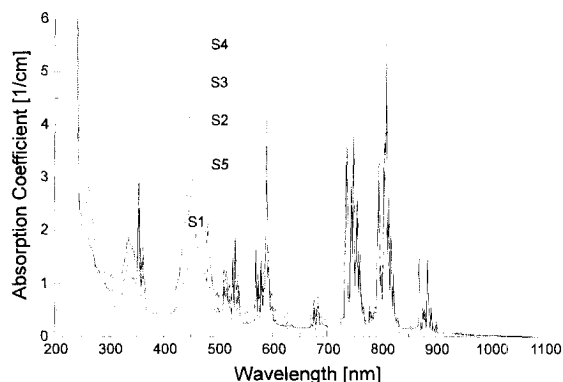


Fig. 1. Absorption coefficient of Ce, Nd:YAG (0.05 at%  $\text{Ce}^{3+}$ , 1 at%  $\text{Nd}^{3+}$ ) crystals (samples S1, ..., S5) in the range of 200–1100 nm.

the intensity of the absorption of  $\text{Ce}^{3+}$  bands increases, which indicates the growth of the cerium concentration.

It is known that there exists an unambiguous relation between the density of the absorption centres and the parameters of the absorption bands, which is expressed by the formula of Smakula, modified in Ref. [8] for cases where the shape of the absorption line is described by Gaussian or Lorentzian distributions. Using this formula we calculated the total concentration of  $\text{Ce}^{3+}$  ions in the samples as well as the relative change of  $\text{Ce}^{3+}$  concentration induced by the irradiation. For the calculations, the  $\text{Ce}^{3+}$  absorption band of 4f–5d transitions with the maximum at 458 nm was chosen, because according to [7] it has a Gaussian shape. In this case, the  $\text{Ce}^{3+}$  concentration can be calculated according to the formula

$$N_{\text{Ce}} = 0.87 \times 10^{17} \text{ cm}^{-3} KW [n/(n^2 + 2)^2] 1/f_o,$$

Table 1

Parameters of the absorption band of the  $\text{Ce}^{3+}$  ions with maximum at 458 nm and calculated values of the  $\text{Ce}^{3+}$  concentrations before and after gamma-irradiation for samples S1, ..., S5 of Ce, Nd:YAG crystal

| Sample no. | $K$ ( $\text{cm}^{-1}$ ) | $W$ (eV) | $N_{\text{Ce}}$ (at%) before | $N_{\text{Ce}}$ (at%) after irradi. | $\Delta N = [(N_{\text{after}} - N_{\text{before}})/N_{\text{before}}]100\%$ |
|------------|--------------------------|----------|------------------------------|-------------------------------------|--|
| S1         | 1.43                     | 0.212    | 0.0040                       | 0.0021                              | -48.1  |
| S2         | 3.93                     | 0.237    | 0.0122                       | 0.0122                              | 0  |
| S3         | 4.40                     | 0.234    | 0.0135                       | 0.0149                              | 10.1   |
| S4         | 5.04                     | 0.237    | 0.0157                       | 0.0167                              | 6.27   |
| S5         | 2.53                     | 0.219    | 0.0073                       | 0.0062                              | -15.3  |

where  $K$  is the value of the absorption coefficient at the band maximum, expressed in  $\text{cm}^{-1}$ ;  $W$  the FWHM of the absorption band, expressed in eV;  $n$  the crystal refractive index for the wavelength corresponding to the maximum of the absorption band; and  $f_o$  the oscillator strength for a given transition.

The parameters  $K$  and  $W$  were obtained experimentally and are given in Table 1. The refractive index  $n = 1.847$  was calculated from the relation

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

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

To calculate values of  $N_{\text{Ce}}$  it was assumed that the corresponding oscillator strength is  $f_o = 3 \times 10^{-3}$ . This is based on the results of Ref. [10], where the oscillator strengths were calculated for the transitions between different configurations of  $\text{Ce}^{3+}$  ions in various types of oxides.

As seen from the table, when passing from the top along the axis of the crystal growth, the concentration of the  $\text{Ce}^{3+}$  ions increases. However, the calculations give somewhat lower values of cerium concentrations than those prepared in the starting material. This fact can be explained by incomplete penetration of the Ce ions into the crystal (due to a small value of their distribution coefficient:  $\sim 0.07$ ), or by a not accurate enough estimation of the oscillator strengths for the transition.

In Fig. 2 the “AA” bands after the gamma-irradiation are shown for the samples S1, ..., S5. As seen from the figure these bands differ significantly. For samples S1, S3, S4 and S5, evident extrema (minima for S1 and S5 and maxima for S3 and S4)

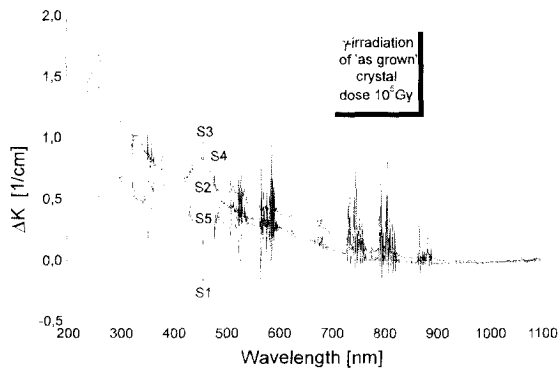


Fig. 2. Additional absorption bands of Ce, Nd:YAG as grown crystals irradiated by gamma-rays with a dose of  $10^5$  Gy.

are observed on the broad background of the structureless band extending from the edge of the fundamental absorption up to  $\lambda = 700$  nm. Their shape and position coincide with the absorption bands caused by transitions between different configurations in  $\text{Ce}^{3+}$  ions. In the AA spectrum for sample S2, only a broad structureless band is observed, without any singularities.

In Fig. 3 the "AA" spectra obtained during thermal treatment of the samples S1, ..., S4 at  $1400^\circ\text{C}$  in air are shown. The AA-bands for samples S1, S3 and S4 after thermal treatment have features opposite to those obtained after the gamma-irradiation: in sample S1, a maximum of AA is observed in the absorption region of  $\text{Ce}^{3+}$ , while in samples S3 and S4 - the corresponding minima are

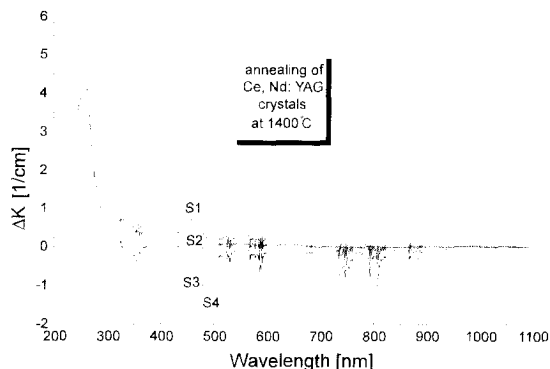


Fig. 3. Additional absorption bands in  $1400^\circ\text{C}$  thermally annealed in air Ce, Nd:YAG crystals.

present. In sample S2, practically no changes are observed in the  $\text{Ce}^{3+}$  absorption range.

The AA-bands show that in samples S1, S3 and S4, under the influence of gamma-radiation and under thermal processing, changes of  $\text{Ce}^{3+}$  concentration take place. Results of calculations of the relative changes of  $\text{Ce}^{3+}$  concentrations after irradiation are shown in Table 1. In sample S2, no change of the  $\text{Ce}^{3+}$  density is observed.

One can obtain the same results comparing AA-bands after annealing the same sample (S4) in air and in an  $\text{N}_2 + \text{H}_2$  mixture, and comparing AA-bands for gamma-irradiation of the same sample (S4) as grown and after annealing in an  $\text{N}_2 + \text{H}_2$  mixture. Corresponding curves are presented in Fig. 4.

In Fig. 5 the AA spectra obtained after proton irradiation of sample S5 (irradiation after thermal annealing) are shown. As can be seen, another type of irradiation (immediate ionization) leads to AA-bands, where, in the case of the first dose ( $10^{13}$  protons/ $\text{cm}^2$ ), one can distinguish the  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  ionization process. In the second dose ( $3 \times 10^{13}$  protons/ $\text{cm}^2$ ), the concentration of  $\text{Ce}^{3+}$  ions increases. Under the third dose ( $10^{14}$  protons/ $\text{cm}^2$ ) the above mentioned process reverses. In this figure one can also see 1 MeV electron-irradiation influence on the Ce:YAG crystal (0.05 at%  $\text{Ce}^{3+}$ ) in the over-threshold type interaction. One can

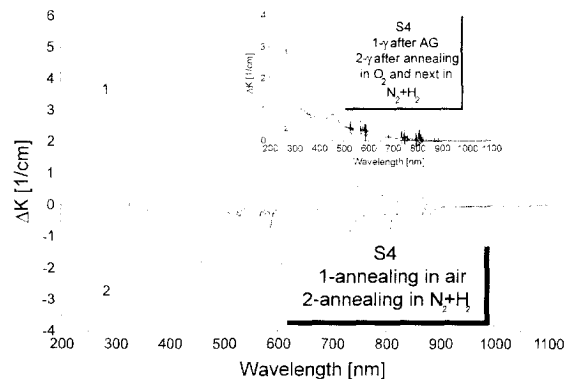


Fig. 4. AA-bands of Ce, Nd:YAG crystal (S4) for annealing in air compare to annealing in an  $\text{N}_2 + \text{H}_2$  mixture. Small figure presents AA-bands after gamma-irradiation of as grown Ce, Nd:YAG crystal (S4) compare to the same crystal annealed in an  $\text{N}_2 + \text{H}_2$  atmosphere.

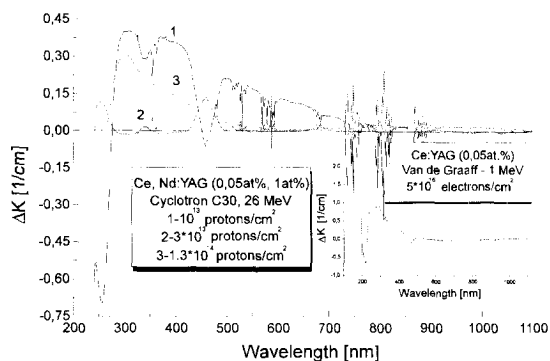


Fig. 5. AA-bands for Ce, Nd:YAG crystal after annealing in air and 26 MeV proton irradiation with fluences from  $1 \times 10^{13}$  to  $1.3 \times 10^{14}$  protons/cm<sup>2</sup>. Small figure presents AA-bands in Ce:YAG (0.05 at%) crystal after electron irradiation to a fluence of  $5 \times 10^{16}$  electrons/cm<sup>2</sup>.

see that values of AA are much greater than after gamma and proton irradiation and that for 458 nm AA decreases (the ionization process  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  takes place).

#### 4. Discussion

The above results can be explained as follows. For given growth conditions (e.g. growth method, purity of the starting material, growth atmosphere, technological parameters) some definite sub-system of point defects appears in the crystal (e.g. doping ions, vacancies or interstitial defects). At the end of the growth process it is electrically balanced and is left in a metastable state. Some external factors, like irradiation or thermal processing, may lead to the transition of this sub-system from one metastable state to another. During this transition point defects may change their charge state.

Reasoning along this line one can guess that in samples S1 and S5, where the  $\text{Ce}^{3+}$  concentration is small, the state of the sub-system is such, that after the excitation of the crystal by gamma-radiation part of the Ce ions pass from the trivalent state to another one, most probably to  $\text{Ce}^{4+}$ . In sample S2 the ratio  $\text{Ce}^{3+}/\text{Ce}^{4+}$  does not change. In samples S3 and S4 radiative recharging of the Ce ions goes in the opposite direction i.e.  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ .

In sample S5, under proton irradiation, change of charge state  $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$  is more evident and dependent on the radiation dose.

Mutually reversible changes of the charge state,  $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$ , were observed earlier in  $\text{Lu}_2\text{O}_3:\text{Ce}$  crystals during heating in various atmospheres [11]. In this work it was also shown that the appearance of  $\text{Ce}^{4+}$  ions in the YAG crystal increases absorption for  $\lambda < 350$  nm, where the charge transport band between oxygen ions and  $\text{Ce}^{4+}$  is situated. A similar behaviour is observed in our samples.

#### 5. Conclusions

The presence of  $\text{Ce}^{4+}$  ions in the as grown Ce, Nd:YAG (also in Ce:YAG's) single crystals can be explained by the fact that if, during the synthesis, cerium dioxide ( $\text{CeO}_2$ ) is used as the starting material, not all of the Ce ions pass to the trivalent state.

The appearance of the broad background band observed in the AA-spectrum can be explained by the production of other colour centres (F-type centres, hole centres in the vicinity of the kation sublattice, recharging of the uncontrolled dopants etc.).

In conclusion, it was experimentally observed that under gamma and proton irradiation as well as in thermal processing, a change of the concentration of  $\text{Ce}^{3+}$  ions takes place in Ce, Nd:YAG crystals, as a result of recharging processes of the type  $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ .

#### Acknowledgements

The authors deeply acknowledge M.Sc. Z. Frutkacz (ITME-Warsaw) for the supply of the Ce, Nd:YAG crystal samples used in the present studies and J. Wojtkowska for performing the proton irradiations.

#### References

- [1] A.O. Matkovskii, D.J. Sugak, S.B. Ubizskii, O.I. Shpotiuk, E.A. Chernyi, N.M. Vakiv, W.A. Mokryckii, Infl-

- ence of Ionizing Radiation on Electronic Materials, Svit, Lviv 1994, p. 212 (in Russian).
- [2] M.R. Biedilov, H.B. Bejsembajeva, P.K. Habibulajev, R.P. Saidov, *Ukr. Fiz. Žurn.* 31 (1) (1986) 59 (in Russian).
- [3] G.N. Pirogova, W.E. Krickaja, N.A. Anisimov, L.G. Demiaszkina, *Neorg. Mater.* 11 (10) (1975) 1812 (in Russian).
- [4] J. Kvapil, Jos. Kvapil, B. Perner, J. Kubelka, B. Manek, V. Kubecek, *Czech. J. Phys. B* 34 (1984) 581.
- [5] J. Mares, *Czech. J. Phys. B* 35 (1985) 883.
- [6] N.S. Kovaleva, A.O. Ivanov, E.P. Dubrovina, *Kvantovaja Elektronika* 8 (11) (1981) 2433 (in Russian).
- [7] T. Tomiki, H. Akamine, M. Gushiken, Y. Kinjoh, M. Miyazato, T. Miyazato, N. Toyokawa, M. Hiraoka, N. Hirata, Y. Ganaha, T. Futemma, *J. Phys. Soc. Japan* 60 (7) (1991) 2437.
- [8] D.L. Dexter, *Phys. Rev.* 101 (1956) 48.
- [9] A.A. Kaminskii, *Lasing Crystals*, Nauka, Moscow, 1975, p. 215.
- [10] G.A. Slack, S.L. Dole, V. Tsoukala, G.S. Nolas, *J. Opt. Soc. Am. B* 11 (6) (1994) 961.
- [11] W.M. Yen, S. Basun, U. Happek, M. Raukas, *Acta Physica Polonica A* 90 (2) (1996) 257.