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Effect of ionizing radiation on optical and lasing properties of $Y_3Al_5O_{12}$ single crystals doped with Nd, Er, Ho, Tm, Cr ions

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Abstract

The influence of gamma irradiation on optical and lasing properties of YAG:Er, YAG:CTH, YAG:Nd and YAG:Cr^{4+} single crystals were studied. For no thermal annealed rods from YAG:Er and YAG:CTH crystals the increase of laser output energy was established. The mechanisms of radiation sensibilization are discussed.

1. Introduction

It is well-established that color centers (CC) 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 including reviews and monographs [1–3] are devoted to this problem. The most thoroughly investigated aspect was the influence of various types of ionizing radiation (gamma quanta, electrons, neutrons) on generation features of YAG crystals activated with Nd ions [2].

Absorbing not only pump light but laser light as well, the CC originated in the crystals significantly increase energy losses in lasers [4]. However, the possibility of a positive effect of ionizing radiation on the generation features of a YAG crystal should not be rejected. Recently the improvement of generation characteristics of YAG:Nd lasers was reported as an effect of small dose of gamma and electron irradiation [5].

During optical investigations of YAG:Nd crystals particular attention was paid to Cr ions, because they not only sensibilize the laser medium but — at certain concentrations — they may also reduce the sensitivity of YAG crystals to ionizing radiation effects [6].

In recent years, many other crystals, besides YAG:Nd, came into market and took an important position. They include $Y_3Al_5O_{12}$:Er (YAG:Er) and $Y_3Al_5O_{12}$:Ho, Tm, Cr (YAG:CTH) crystals applied in medicine and generating in bands of 2.94 μm and 2.01 μm, respectively [7]. Strong attention is attracted by $Y_3Al_5O_{12}$:Mg^{2+}, Cr^{4+} (YAG:Cr^{4+}) crys-

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tals, which afford tunable generation within a bandwidth of 1.35–1.60 μm [8].

The effect of ionizing radiation on properties of the above-mentioned crystals has been hardly investigated till now. We met only one paper devoted to the influence of gamma radiation on optical properties of YAG:Er crystals [9]. In Ref. [10] the authors examined the effect of the spectral composition of pump light on lasing and spectral-luminescence properties of $Y_3Sc_2Ga_3O_{12}$ and $Gd_3Sc_2Al_3O_{12}$ crystals doped with Ho, Tm or Cr ions. They stated a negative effect of transient CC produced by the light with a wavelength λ less than 370 nm.

The present work regards both the effects of gamma radiation on optical characteristics of YAG:Er, YAG:CTH, YAG:Cr^{4+} crystals and examinations of generation characteristics of active elements made from YAG:Er or YAG:CTH crystals irradiated with gamma quanta as well. For comparison, optical characteristics of YAG and YAG:Nd crystals are presented.

2. Experimental

The examined crystals were pulled by the Czochralski technique from iridium crucibles in N_2 atmosphere (for YAG, YAG:Nd, YAG:Er, YAG:CTH) and an atmosphere composed of 97% N_2 and 3% O_2 (for YAG:Cr^{4+}). The contents of Nd in the crystals was of the order of 1 at%. The content of erbium in the YAG:Er crystals was equal to 33 at% which corresponds to the formula $Y_2ErAl_5O_{12}$. The composition of the YAG:CTH crystals was

$$(Y_{1-x-y}Ho_xTm_y)_3(Al_{1-z}Cr_z)_5O_{12}$$

where $x = 0.0036$, $y = 0.057$, $z = 0.01$, while the composition of the YAG:Cr^{4+} crystals was

$$(Y_{1-x}Mg_x)_3(Al_{1-y}Cr_y)_5O_{12}$$

with $x = 0.01$ and $y = 0.0017$. The detailed description of the applied growth process of the crystals is presented in Refs. [11–13].

The irradiating gamma rays were emitted by a ^{60}Co emitter with an expositional dose power of 170 R/s and the samples absorbed doses of the order of 10^2–10^5 Gy.

The crystal samples prepared to examine the gamma irradiation effects on their optical properties were plane-parallel plates of 1–3 mm in width, cut-out perpendicularly to the growth axis in the plane (111). Absorption spectra of the crystals were measured in spectral range 0.2–0.9 μm by means of the spectrophotometer SPECORD M40. Additional absorption (AA) induced by irradiation was assumed to be

$$\Delta k = d^{-1}\ln(T_1/T_2), \qquad (1)$$

where d is the thickness of the sample and T_1, T_2 are the transmissions of the sample before and after the process of irradiation.

To examine gamma radiation effects on lasing characteristics of YAG:Er crystals, an active rod of 5 mm in diameter and 85 mm in length was used. The rod was not subjected to preliminary annealing and it had no antireflection coatings on its end faces. The detailed characteristics of the rod, designated as E21, are published in [11].

In the case of YAG:CTH crystals the investigations of their generation characteristics were conducted on two non-annealed active rods, designated as G21 and G32. The first of them has got a diameter of 4 mm and a length of 63 mm, while the second one was 4 mm and 67 mm, respectively. The G32 rod was also annealed in an oxidizing atmosphere at 1500°C. The end faces of the rods were not antireflectionally coated. The designations of the rods correspond to those in Ref. [12], where their generation characteristics are presented.

To measure the generation characteristics of YAG:Er and YAG:CTH rods a plane-parallel resonator of 19 cm length was used. The transmission of output mirrors was equal to 20% for YAG:CTH rods and 30% for YAG:Er ones. The examinations were carried out in the ellipsoidal reflective head made of gold-covered brass. The pump was a xenon lamp of 4 mm diameter and 0.5–2.5 kV power with a 160 μF capacitor battery. The pulse duration of the lamp was about 580 μs. The laser light was detected with high-sensitive HgCdTe photoconductor and the time characteristics of the lamp were observed using a Si photodiode. The energy of the laser pulses was measured by a Gen-Tec radiometer with ED-500 gauge head.

3. Results and discussion

3.1. Optical properties

The short-wave edge of the absorption spectrum of YAG:Er crystals approaches 52000 cm^{-1}. Some absorption bands caused by intracenter transitions in Er^{3+} ions are placed within their transparency band (Fig. 1a). The absorption spectrum of YAG:Er crystals is described in Ref. [11]. After gamma irradiation a wide, complex AA band appears within the range of 48000–12000 cm^{-1}. The peaks of absorption are placed in the surroundings of 42000 cm^{-1}, 32000 cm^{-1}, 25000 cm^{-1} and 16000 cm^{-1} (240, 310, 400, 625 nm). With the increase of gamma irradiation dose from 10^2 to 10^4 Gy the AA bands grow larger and larger and become saturated for doses of 10^4–10^6 Gy. The AA spectra of YAG:Er crystals are shown in Fig. 1a. Fig. 1b shows comparatively the corresponding, gamma-induced AA spectra of YAG:Nd crystals. It may be noticed that the gamma-induced absorption spectrum of YAG:Nd crystals has got a similar form as that of YAG:Er crystals and nearly the same peaks can be distinguished in both spectra. The same shape and position of the AA peaks is observed in the spectrum of nominally pure YAG crystals.

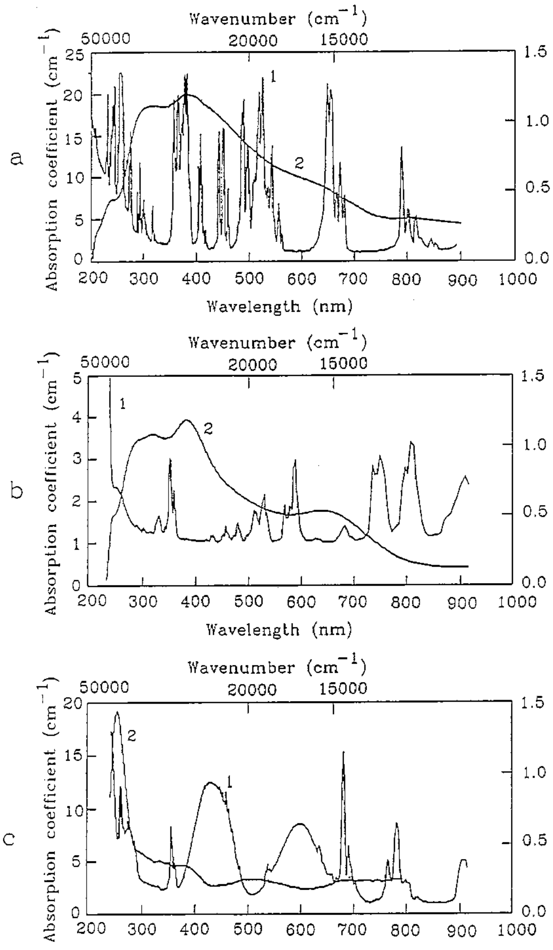

Fig. 1. Absorption spectra (1) and additional absorption spectra (2) of YAG:Er (a), YAG:Nd (b) and YAG:CTH (c) single crystals after gamma irradiation with 1.25 MeV energy and a dose of 10^5 Gy.

It should be stated that the AA spectrum of YAG:Er crystals which was measured during our examinations slightly differs from that described in Ref. [9] and taken for the YAG:Er crystal grown in an inert atmosphere and irradiated by an UV pump lamp. After UV irradiation the maximum AA was observed at ~ 32000 cm^{-1} and the total intensity of AA was reduced more than five times. For crystals grown in vacuum and irradiated with UV light the intensity of AA at ~ 26000 cm^{-1} increases considerably.

The analysis of the published reports on radiation-induced coloration of YAG and YAG:Nd crystals [3,14] shows that the form and intensity of the AA spectrum depend for a great part on the growth conditions of the crystals (method and atmosphere of growth, purity of starting material, addition of an activator etc.). At the same time in some papers [15,16] the existence was reported of specified AA bands placed in 40000–42000 cm^{-1}, ~ 32000 cm^{-1} and ~ 22000–26000 cm^{-1} regions. The bands within the 40000–42000 cm^{-1} range are usually explained as caused by absorption of non-controlled Fe^{3+} impurities. The band placed near 32000 cm^{-1} is attributed mostly to absorption of Fe^{2+} ions or CC connected with oxygen vacancies. The absorption bands within the 22000–26000 cm^{-1} range are interpreted as the effect of O^- hole centers localized near defects of the cation sublattice.

Consequently, it can be assumed that the AA bands observed in gamma-irradiated YAG:Er crystals are connected with CC produced by gamma-induced recharging of growth defects that may be non-controlled impurities of Fe ions, oxygen vacancies or defects of cation sublattice (e.g. rare-earth ions instead of Al^{3+} ions). The fact remains that the precise definition of nature of the CC demands more detailed investigations.

To measure the thermal stability of optical property changes caused by irradiation an isochronous annealing of irradiated samples was performed at temperatures of 293–673 K (15 min duration at each temperature with steps of 20–30 K). It was found that the AA value in all the bands considered decreases according to the same dependence of the rise of temperature. However, the complete return to the previous, what means before irradiation, optical features of the crystals was not reached after annealing.

In YAG:CTH crystals some absorption bands caused by intracenter transitions in Cr^{3+}, Tm^{3+} and Ho^{3+} ions are placed in their spectrum within the range of 42000–11000 cm^{-1} (Fig. 1c). The absorption spectra of the YAG:CTH crystals are published in [12].

Under irradiation by gamma quanta a wide AA band appears in the crystal spectrum in the range of 40000–14000 cm^{-1} (Fig. 1c). The intensive absorption peak at 39000 cm^{-1} (225 nm) and some smaller peaks in the region 31000–20000 cm^{-1} (320–500 nm) can be distinguished in this AA band. When the dose of gamma irradiation increases, the intensity of AA saturates. Comparison between the presented investigations of YAG:CTH with those published in Ref. [17], where radiation-induced coloration of YAG:Cr crystals (Cr concentration was 0.05 wt%) was examined, shows that in both cases the AA bands close to 26000 cm^{-1} and 20000 cm^{-1} were measured.

As was stated for YAG:Nd and YAG:Er crystals, CC can be produced from defects of cation sublattice, oxygen vacancies or defects connected with ions of non-controlled impurities. Isochronous annealing of the irradiated samples of YAG:CTH crystals revealed that — unlike irradiated YAG:Er crystals — YAG:CTH crystals returned to their previous optical properties at a temperature of 500 K.

The absorption spectrum of $YAG:Cr^{4+}$, Mg^{2+} is presented in Fig. 2 and consists of wide electronic oscillating absorption bands with the maxima at 22000, 16500 and 10000 cm^{-1}. According to [18] these bands correspond to the intracenter transition in Cr^{4+} ions situated in octahedric (22000 cm^{-1}) and tetrahedric structural positions (16500 and 10000 cm^{-1}) $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow {}^3T_1$ correspondingly.

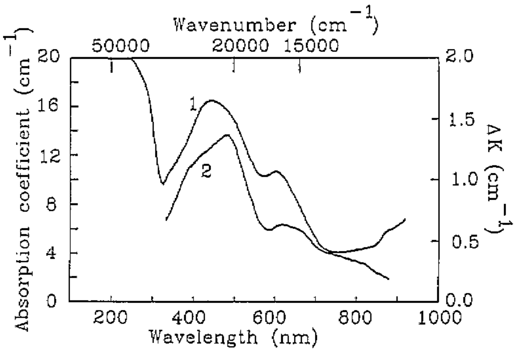

Fig. 2. Absorption spectra (1) and additional absorption spectra (2) of the $YAG:Cr^{4+}$ single crystal after gamma irradiation with 1.25 MeV energy and a dose of 10^5 Gy.

After gamma-quanta irradiation the AA spectrum completely coinciding by its shape and spectral position with the Cr^{4+} ions absorption appeared in the $YAG:Cr^{4+}$ crystals. As is known [18] in $YAG:Cr^{4+}$ crystals a part of Cr ions are found in the trivalent state and probably as a result of radiation treatment it changes into a fourvalent state increasing the absorption in the range of Cr^{4+} intracenter transitions.

3.2. Lasing properties of YAG:Er and YAG:CTH

After gamma irradiation the lasing properties of YAG:CTH and YAG:Er crystals are significantly changed. Thus, for the samples of YAG:CTH that were not preliminary annealed the laser output energy immediately after irradiation increases in some cases. However, these changes are of metastable character — the value of the output energy decreases to some extend with the course of time. The sequential multiple influence of the light pumping pulses also decreases the output energy to the unirradiated level crystal.

The changes caused by gamma irradiation for the preliminary annealed G32 YAG:CTH sample have a contrary nature. In this case the output energy decreases more than 2 times (Fig. 3). The sequential influence of the light pumping pulses partially restores the energetic characteristics of the laser (Fig. 3, Fig. 4).

The increase of the laser output energy is also observed for YAG:Er after influence of gamma-rays.

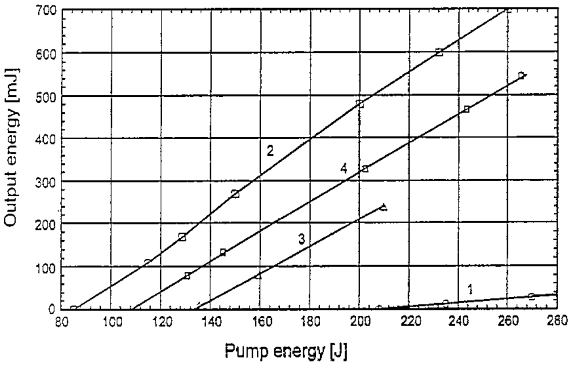

Fig. 3. Output energy dependence on pumping energy for YAG:CTH laser rod: 1 – before annealing; 2 – after annealing in air at 1773 K; 3 – after gamma irradiation with a dose of 10^5 Gy; 4 – after annealing in air for 8 h at 673 K of the irradiated rod.

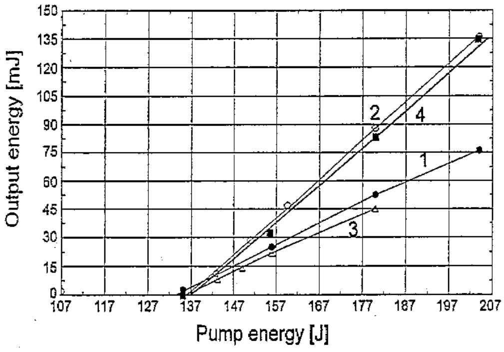

Fig. 5. Output energy dependence on the pumping energy for the YAG:Er laser rod: 1 – before gamma irradiation; 2 – after gamma irradiation with a dose of 10^5 Gy; 3 – after annealing in air by 3 h at a temperature 673 K of the irradiated rod; 4 – after repeated gamma irradiation with a dose of $5 \cdot 10^4$ Gy.

At a pumping level of 205 J the output energy increases from 75 mJ for an nonirradiated crystal to 135 mJ for the sample irradiated with a dose equal to 10^5 Gy (Fig. 5). The annealing of the crystals after irradiation at a temperature of 673 K during 3 h restores the initial characteristics of the laser. The subsequent gamma irradiation again increases the laser power efficiency.

The obtained results point to the direct influence of the color centers on the processes of formation of the inverse population of the laser levels of YAG:Er and YAG:CTH crystals.

In the unannealed YAG:CTH samples there is a great concentration of different types of genetic (growth) defects which significantly decrease the laser efficiency.

As was shown earlier [3], after gamma irradiation in the crystals with garnet structure a rearrangement and recharging of the defects takes place which causes the change of the pumping energy transfer efficiency to the emitting centers and the increase of laser output energy. For the G32 sample, having a reduced concentration of the growth defects due to high temperature annealing, the color centers emerging during gamma irradiation increase the active losses of the laser.

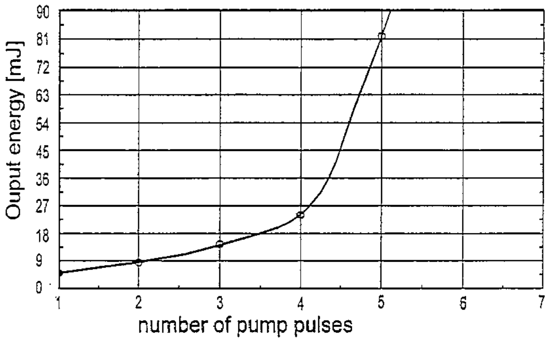

Fig. 4. Output energy dependence on the number of pump pulses (1 min time interval) for the irradiated YAG:CTH rod.

In case of YAG:Er crystals the emerging color centers to our opinion may fulfil the function of sensibilizators providing the increase of the pumping efficiency. Comparison of the AA spectra with the absorption spectrum of Er^{3+} ion (Fig. 1a) shows that the AA bands are superimposed with the most intensive bands corresponding to the transitions from the main state $^4I_{15/2}$ to the multiplets of $^2H_{9/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ through which the laser pumping takes place and the sensibilization may occur.

It should be noted that in the lasers generating in the 2–3 μm range the passive losses due to the absorption of the color centers are absent because of the great spectral distance from the value of the laser radiation wavelength to the band of additional absorption.

For YAG:Nd crystals the color center absorption bands are also well superimposed with the most intensive bands of pumping ($^4I_{9/2} \rightarrow {}^2G_{9/2}$, $^4G_{7/2}$, $^2G_{7/2}$ and $^4G_{5/2}$). However after gamma irradiation the laser output energy is decreased [19]. This fact may be accounted for the circumstance that in YAG:Nd crystals side by side with the possible process of sensibilization by energy transfer from CC to Nd^{3+} ions the passive losses on laser generation wavelength significantly increase.

4. Conclusion

After gamma irradiation of YAG:Er, YAG:Nd and YAG:CTH a wide complex of AA bands appeared. These bands are connected with CC caused by gamma-induced recharging of growth defects that may be non-controlled impurities of Fe ions, oxygen vacancies or defects of cation sublattice. In YAG:Cr crystals gamma irradiation induced increasing of concentration of Cr-ions in fourvalent state ($Cr^{3+} \rightarrow Cr^{4+}$) and absorption in bands corresponding to the transitions in Cr^{4+} ions.

In YAG:Er crystals CC may fulfil the function of sensibilizators providing the increase of the pumping efficiency and output energy of laser generation at $\lambda = 2.94$ μm.

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