ELSEVIER

Spectrochimica Acta Part A 54 (1998) 2109–2116

SPECTROCHIMICA ACTA PART A

Effects of gamma irradiation and annealing treatments on the performance of Cr;Tm;Ho:YAG lasers

S.M. Kaczmarek [a,*], W. Żendzian [a], T. Łukasiewicz [b,c], K. Stępka [a], Z. Moroz [d], S. Warchoł [b,e]

[a] Institute of Optoelectronics, MUT, 2 Kaliski Str., 01-489 Warsaw, Poland
[b] Institute of Electronic Materials Technology, 133 Wólczyńska Str., 01-919 Warsaw, Poland
[c] Institute of Applied Physics, M.U.T., 2 Kaliski Str., Warsaw, 01-489, Poland
[d] Soltan Institute for Nuclear Studies, 05-400 Świerk, Poland
[e] Institute of Nuclear Chemistry and Technology, 16 Dorodna Str., 02-415 Warsaw, Poland

Received 12 September 1997; received in revised form 20 January 1998; accepted 11 February 1998

Abstract

Spectroscopic studies of Cr;Tm;Ho:YAG (CTH:YAG) crystal samples after succesive procedures of gamma irradiation and annealing, were carried out. The emission characteristics of the free-running laser, doped with these ions were measured. Mechanisms which cause changes of the laser properties are discussed. Previously observed favourable changes of the optical and laser emission properties induced by thermal annealing and gamma radiation, are also confirmed. In particular, a substantial lowering of the emission threshold of the laser (after annealing) as well as an increase of the pumping efficiency (after gamma exposure) was obtained. It is argued, that this last effect is due to the sensitization process of the active Ho^{3+} ions. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cr;Tm;Ho:YAG lasers; Thermal annealing; Gamma irradiation

1. Introduction

Quite often many solid-state lasers are designed to work in the strong external fields of ionizing radiation (e.g. cosmic rays, gammas, electrons, neutrons). For example, instruments in orbital space missions are subjected to integrated radiation doses, which can reach upwards of 10^3 Gy over a 5-year period and are conceivably higher for non-earth based missions [1]. Therefore, a study of the degradation induced in their active materials by such radiation is highly relevant. On the other hand, some improvement of the optical output induced by the ionizing radiation is sometimes observed [1–6]. Such irradiation and annealing of crystals, may also serve as an effective method of their characterization [6,7].

Studies of Cr;Tm;Ho:YAG (CTH:YAG) crystals subjected to ionizing radiation have been reported in many publications [2–6]. Both UV and gamma rays induce in CTH:YAG crystals colour centres, which trap the electron excitations caused by the xenon pumping lamp.

* Corresponding author.

PII S1386-1425(98)00126-7

Kopczyński et al. [8] have shown results of spectroscopic studies of CTH:YAG crystals along with the optical output of the laser rods in the free-running laser emission mode with natural air-cooling of the rod. The absorption coefficient in the range 250–6200 nm was measured and the colour centres induced by the γ-radiation and having their wavelength maxima corresponding to the transitions $^4A_2 \rightarrow {}^4T_1$ (430 nm) and $^4A_2 \rightarrow {}^4T_2$ (600 nm); Cr^{3+}, $^3H_6 \rightarrow {}^3F_2$, $^3F_4$ (680 nm) and $^3H_6 \rightarrow {}^3F_4$ (780 nm); Tm^{3+}, were observed. It was found, that the colour centres appearing under xenon lamp radiation are very unstable at room temperature and quickly disappear. The relaxation rate of such induced centres was 1% 1000 s^{-1}. Measurements of the optical output for a few rods were made with laser output mirrors having 20 and 49% transmissions. The thresholds of the laser emission at 2.11 μm were found to be E_{th} = 80, 115, 135 and 140 J dependent on the optical quality of a given rod.

Kaczmarek et al. [3] and Matkovskii et al. [4] have reported a substantial instability of the laser emission for the CTH:YAG laser, whose active element before the gamma irradiation with 10^4 Gy had earlier been annealed at a high temperature (1400°C). The output energy value, which at the beginning was lower than that before the annealing, systematically increased with increase in the number of pumping pulses, up to the value observed before the irradiation.

A significant improvement of the optical output (a 4-fold increase in differential efficiency) was obtained for the 'as grown' crystal (without the preliminary annealing) and γ-irradiated with 5×10^4 Gy [5]. These authors also discussed the mechanism of the sensitization process due to the gamma exposure. It was found that, in the non-annealed crystal a large concentration of growth defects exist, which lowers the efficiency of the laser. After irradiation, these defects change their charge and form colour centres leading to energy transfer to the holmium ions.

Kaczmarek et al. [6] have reported the characteristics of the luminescence and the additional absorption of Cr;Tm;Ho:YAG crystal after gamma irradiation indicating an increase of the efficiency of the energy exchange between the ions Cr^{3+}, Tm^{3+} and Ho^{3+}. This is a consequence of the increase in concentration of Cr^{3+} ions after irradiation of the CTH:YAG crystal by gamma rays with 10^5 Gy (because of the change of the charge $Cr^{4+} \rightarrow Cr^{3+}$).

Kaczmarek et al. [2–6] only studied the CTH:YAG laser in an air-cooled rod.

The main goal of the present work is to study in more detail the mechanisms of the irradiation induced changes of the optical properties of CTH:YAG crystals. In particular, we are interested in the reasons for the instability of the laser emission, mentioned above, observed for the naturally air-cooled CTH:YAG laser, whose active element was annealed (1400°C in air) and next gamma irradiated with 10^5 Gy. These studies were also extended by us to water-cooled CTH:YAG rods.

2. Experimental conditions

The CTH:YAG crystals which are the subject of the present study, are often used in solid-state lasers emitting in the infrared (2.11 μm). According to [9], samples of CTH:YAG crystals obtained by the Czochralski method in the iridium crucible have the following form:

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

where $x = 0.0036$; $y = 0.057$; $z = 0.01$.

Crystal samples were produced in the Institute of the Electronic Materials Technology by the Czochralski method. Crystals were grown in a nitrogen atmosphere using an iridium crucible. A detailed description of the growth process of such crystals is given by Z. Frukacz and Z. Mierczyk [9].

An essentially technological problem met by these workers was that of producing a crystal with ion distributions sufficiently high and uniform both in longitudinal and transversal directions. In the course of our present studies, it became evident that this problem is also of great importance after irradiation of the crystals and their subsequent annealing in an oxidizing atmosphere. This is because in the CTH:YAG crystal, obtained using the technology described by Z. Frukacz and

Z. Mierczyk [9] and subsequently being annealed or irradiated, even for a relatively uniform concentration of chromium ions, there may be some ions, such as Cr^{2+}, Cr^{3+} and Cr^{4+}, which have concentrations which vary significantly along the crystal axis. Moreover Fe impurities occur and may be in two charge states: Fe^{2+} and Fe^{3+}, depending on the conditions of the crystal growth. As a result, YAG crystals containing iron impurities become photosensitive, i.e. they change their properties under light irradiation [7].

2.1. Spectroscopic studies

Spectroscopic studies were carried out on parallel plate samples of 0.77 mm thickness, cut from the CTH:YAG crystal perpendicularly to the growth axis in the $<111>$ plane and polished on both sides. Measurements of the transmission in the range of 190–1100 nm were made with a LAMBDA-2 (Perkin-Elmer) spectrophotometer for the samples before and after processing (gamma irradiation or thermal annealing). The additional absorption (AA) coefficient was then calculated from formula [3]:

$$\Delta K(\lambda) = \frac{1}{d} \cdot \ln \frac{T_1}{T_2} [1/\mathrm{cm}] \qquad (2)$$

where d = sample thickness; T_1, T_2 = transmissions of the samples before and after processing, respectively.

2.2. Irradiation of samples by ionizing radiation

Gamma irradiations were carried out in a ^{60}Co chamber with an efficiency of 1.7 Gy s^{-1} in the Institute of Nuclear Chemistry and Technology in Warsaw. The gamma dose varied between 10^5 and 10^6 Gy. For the crystals subjected to different processing (annealing, gamma irradiation) the influence of UV irradiation from a xenon lamp on the colour centres was investigated. For this purpose a pulsed light source (xenon discharge lamp) was used. Each sample was irradiated by a sequence of ten pulses, each of energy 90 J, with a separation of 10 s between pulses.

2.3. Crystal annealing

Samples for spectroscopic studies were gamma irradiated before ('as grown') and after annealing at 400 and 1400°C in an oxidizing atmosphere. Rods for laser emission studies were subjected to annealing at 400, 800 and 1400°C. Two kinds of annealing processes were used: thermal relaxation and high temperature annealing in an oxidizing atmosphere.

Thermal relaxation was done by annealing previously irradiated samples in air for 3 h at 400 or 800°C to remove the colour centres produced by gamma irradiation. Annealing in an oxidizing atmosphere was carried out in air at 1400°C, also for 3 h, in order to change the defect structure of the crystal. The samples were heated in a resistive furnace with programmed temperature changes.

2.4. Laser emission studies

Laser emission studies were carried out for the CTH:YAG rod of length $l = 67.3$ mm and diameter $\Phi = 4$ mm. The optical output was measured under several conditions: first, after gamma exposure (10^5 Gy), second after annealing at 800°C in air for 3 h, third, after annealing at 1400°C for 3 h in air, and finally after gamma irradiation with 10^5 Gy followed by annealing at 400°C for 3 h in air.

To measure the optical output, a laser power supply (Analog Modulus) was used. The rod was placed in a Quantron K-1041 head with diffusive reflector and water cooling. Measurements were carried out by pumping the rod with a sequence of pulses of width 700 ms and frequency $f_1 = 1$ Hz. The scheme of the resonator used in these

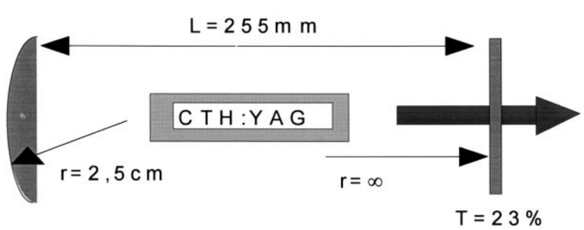

Fig. 1. The scheme of the CTH:YAG laser resonator used in our measurements. The rod was water cooled.

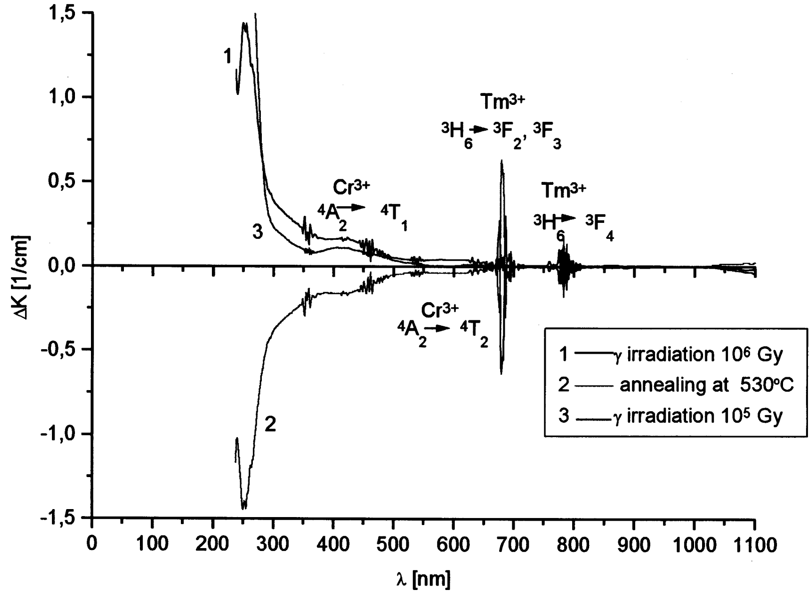

Fig. 2. AA versus wavelength for CTH:YAG sample. 1-γ-irradiation with a dose of 10^6 Gy, 2-thermal annealing at 400°C in air and 3-γ-irradiation with a dose of 10^5 Gy.

measurements and its parameters are shown in Fig. 1.

3. Results

3.1. Spectroscopic investigations

The 'as grown' sample was exposed to 10^6 Gy of gamma-rays and next annealed at 400°C in air, then irradiated a second time with 10^5 Gy and annealed at 1400°C in air. Finally, the sample was once more irradiated with 10^5 Gy and, then subjected to a sequence of ten UV pulses from the xenon lamp (pulse energy: 90 J, period: 10 s). In the last irradiation, we studied how each pulse influences the absorptive properties of the crystal.

As a result of the gamma-ray exposure of the sample, the AA bands appear. They are mainly observed on the short-wave edge and are shown in Fig. 2. Annealing of the crystal at 400°C in air fully bleaches the radiative colour centres as illustrated by curve 2 in Fig. 2. This curve appears to be almost a mirror-reflection of curve 1, the latter describing the response of the 'as grown' crystal to the gamma irradiation with 10^6 Gy. The intensity of the AA bands depends on the gamma dose, as is illustrated by curves 1 and 3. At 430 nm the AA intensity is 0.2 (cm^{-1}) for 10^6 Gy and 0.15 (cm^{-1}) for 10^5 Gy. Annealing at high temperature (1400°C) leads to the changes in the AA-spectrum shown by curve 2 in Fig. 3.

Akhmadulin, Migatchev and Mironov [7] suggest that an increase of AA at 256 nm is caused by an increase in concentration of Fe^{3+} ions. At 313 nm, a lowering of the absorption takes place, most probably due to the drop of the concentration of Fe^{2+}. An increase at about 430 and 600 nm is due to an increase of Cr^{3+} [6]. Further gamma irradiation with 10^5 Gy (curve 3) caused a decrease in the absorption at 256 nm, some increase at 313 nm and a drop for the bands with maxima at 430 and 600 nm. Absolute values of the additional absorption in these bands are comparable with those obtained after annealing at 1400°C, though they have an opposite sign. This can be related to a drop in concentration of Cr^{3+} ions after gamma irradiation of the crystal annealed in an oxidizing atmosphere.

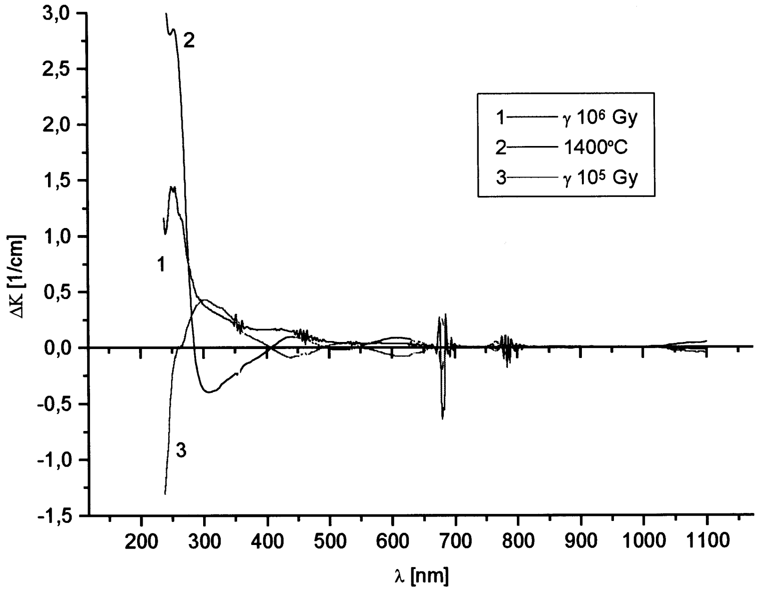

Fig. 3. AA bands in CTH:YAG sample after: 1-γ-irradiation with a dose of 10^6 Gy, 2-annealing at 1400°C in air and 3-γ-irradiation with a dose of 10^5 Gy.

The influence of UV radiation on the sample previously annealed and gamma irradiated, is shown in Fig. 4. Additional absorption bands, in particular at 430 and 600 nm, are seen. In general, these bands correspond to those obtained by gamma irradiation of the 'as grown' crystal, suggesting that UV radiation changes the valence of the Cr^{4+} to Cr^{3+}. It seems reasonable that the following interaction scheme takes place: UV + $Fe^{2+} \rightarrow ((e^-) + Fe^{3+})$; $(e^- + Cr^{4+} \rightarrow Cr^{3+})$. That is, UV is ionizing the Fe^{2+} ions and the resulting electrons are captured by the Cr^{4+}.

3.2. Results of the laser emission studies

In this case (with water-cooling) the output energy of the laser was measured as a function of the pumping energy for the same rod after the processes mentioned above (Section 2.4). Threshold energies for laser emission and slope efficiencies for the CTH:YAG rod were also measured. In Fig. 5. the influence of gamma irradiation and annealing in an oxidizing atmosphere are shown. Four optical outputs were obtained for the CTH:YAG laser rod. After anealing at 800°C a decrease of the threshold energy of about 20 J is observed, in comparison with an 'as grown' crystal irradiated with 10^5 Gy. Subsequent annealing at 1400°C in air and then (after optical polishing of the rod faces only) irradiation of the same sample with 10^5 Gy caused a rise of the threshold energy to 134 J and an increase of the differential efficiency to 0.169%. Annealing at 400°C caused relaxation of the radiative colour centres and a lowering the differential efficiency of the laser.

4. Discussion

UV and gamma radiation causes the appearance of colour centres in CTH:YAG crystals in the wavelength range 250–710 nm, with maxima at 256, 313, 385, 430 and 600 nm. The intensity of the additional absorption bands increases with the gamma-ray dose (Fig. 2). Accordingly to the results of Kopczyński et al. [8], the bands at 430 and 600 nm are related to the defects caused by the introduction of Cr^{3+} ions into the YAG lattice. The remaining defects are characteristic of those of YAG lattice, e.g. Fe^{3+} ions ($\sim$ 256 nm),

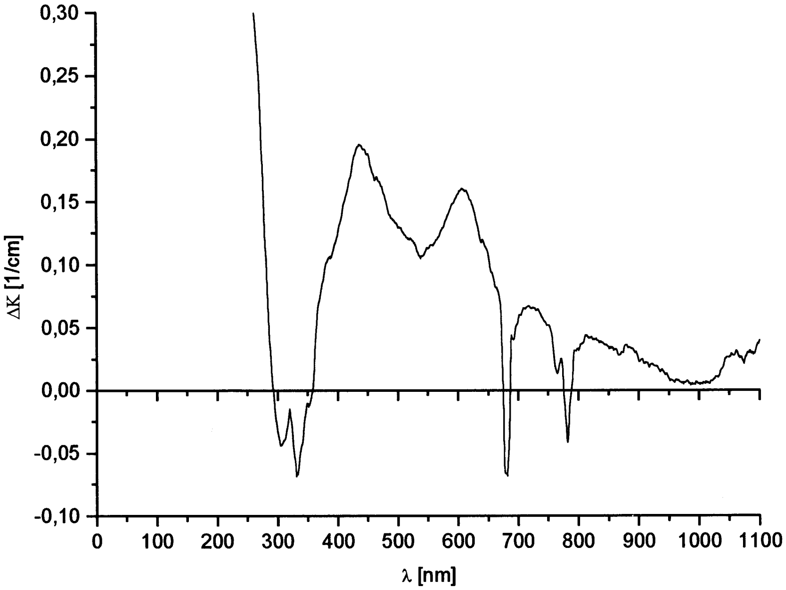

Fig. 4. Additional absorption bands of the CTH:YAG crystal irradiated by UV, after earlier annealing at 1400°C and gamma irradiation with 10^6 Gy.

Fe^{2+} ions (313 nm) or oxygen vacancies V_O and holes O^- (385 nm) and for the crystal annealed in an oxidizing atmosphere (while for a crystal annealed in a reducing atmosphere F^- centres result [7]).

Additional absorption bands at 430 and 600 nm indicate an increase after gamma irradiation of the Cr^{3+} concentration, which could be a result of the process: $\gamma + Cr^{4+} \rightarrow Cr^{3+}$.

According to Kaczmarek et al. [3] the annealing process has a very strong influence on the behaviour of the gamma irradiated laser using CTH:YAG crystal. If the laser is air-cooled in a natural way, the output energy of the gamma-irradiated rod, subsequent to earlier annealing in air, drops significantly at first, but after subsequent pulses it rises to the value before irradiation. An explanation of this effect can be found in Figs. 3 and 4. After an annealing in air at 1400°C for 3 h of the 'as grown' crystal after gamma ray irradiation with 10^6 Gy, the transitions $Fe^{2+} \rightarrow Fe^{3+}$ and $Ce^{3+} \rightarrow Ce^{4+}$ are observed. The AA-value after annealing of the gamma irradiated crystal with 10^6 Gy suggests that in the crystal before annealing Cr^{2+} ions were present (the AA-values after irradiation of the 'as grown' crystal and for the annealed crystal are equal) in a quantity at least equal to that of Cr^{4+}. Subsequent gamma irradiation of the annealed crystal with 10^5 Gy leads to a drop in Cr^{3+} concentration. Probably, under the influence of gamma rays, the transition $Cr^{3+} \rightarrow Cr^{2+}$ takes place. An increase of Cr^{3+} ions takes place only after UV irradiation, as shown in Fig. 4, where the results are given for a CTH:YAG sample UV irradiated by a xenon lamp after previous annealing and gamma irradiation. This explains why the next pumping pulse, which increases the Cr^{3+} concentration, also increases the output energy of the laser.

Annealing of the CTH:YAG rod in case of the air-cooled (in a natural way) laser system, favours the process of fast relaxation of the colour centres and the change in the concentration of Cr ions. As is evident in Fig. 5, in the water-cooled rod, the relaxation processes are very slow and do not influence the behaviour of the laser, so that its output is stable. As this Fig. 5 shows, the laser with the 'as grown' crystal rod (curve 1—characteristic obtained 6 months after irradiation) has a

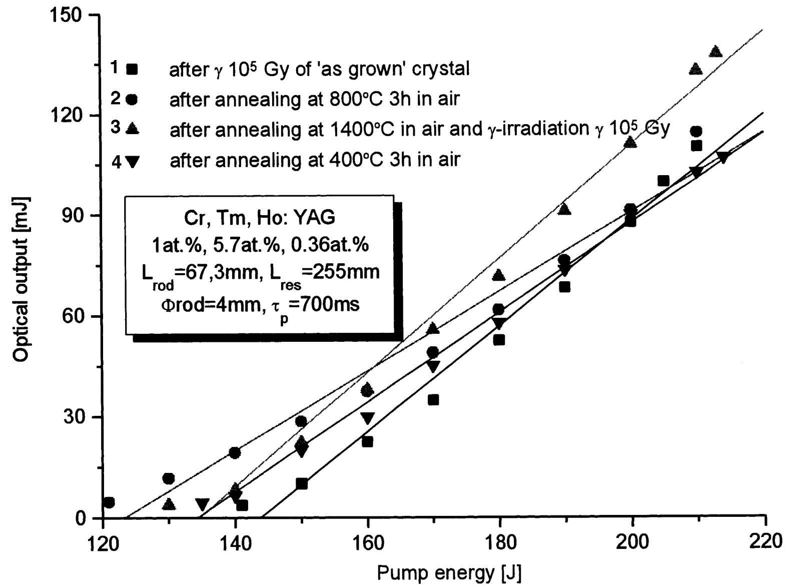

Fig. 5. Optical output of CTH:YAG laser after: γ-irradiation with a dose of 10^5 Gy, after annealing at 800°C in air, after annealing at 1400°C in air and after γ-irradiation with a dose of 10^5 Gy for the same CTH:YAG rod with a length of 67.3 mm and $\Phi = 4$ mm.

higher slope efficiency than that of the laser with the rod which had been annealed at 800°C (curve 2). In the latter case, the threshold is lower, as can be explained by a decrease in the number of point defects after annealing at 800°C.

The same rod annealed at 1400°C and gamma irradiated with 10^5 Gy (curve 3) has the highest slope efficiency (0.17%) but the threshold for generation is somewhat higher than that after annealing at 800°C. This is a result of the fact that at 1400°C some dopants contained in the crystal are reduced, so that the optical characteristics (transparency) changes both on the rod faces and its side surface. After annealing, the rod faces were polished again but the side surface was left unpolished. This causes a shift of the threshold of generation. Because the rod is repolished between experiments, we believe that on the basis of a single experiment it can not be disregarded that the observed changes may be also a consequence of different lasing conditions that may arise after repolishing.

Annealing of the rod at 400°C (curve 4) only lowered its slope efficiency, as expected, because at this temperature the colour centres are destroyed.

Gamma irradiation leads to a substantial improvement in the optical output of the CTH:YAG laser. The growth defects existing in the crystal, after the recharging processes due to irradiation, improve the slope efficiency of the laser (radiation-induced sensitization). Annealing of the rod in an oxidizing atmosphere, in order to remove a part of the point defects remaining after the growth and gamma irradiation is also advantageous.

To avoid the necessity for re-processing the side surfaces of the rod, it is best to carry out the annealing of the crystal after its growth but before cutting out the rods. Rods 'as grown' and subjected to gamma exposure have a high threshold energy value (curve 1, Fig. 5). A lowering of the threshold is achieved after annealing of the rod at 800 and 1400°C (curves 2 and 3, Fig. 5).

Further improvement of the quality of the rod is achieved after gamma irradiation with 10^5 Gy.

5. Conclusions

Previously reported observations, that irradiation of the CTH:YAG crystals by UV or gamma rays leads to additional bands in the absorption spectrum are confirmed. The intensities of these bands depend on the radiation dose and their shape depends mainly on, whether the crystals were annealed or not before the irradiation as well as on the atmosphere in which the annealing was carried out.

The largest changes are observed near the short-wave edge of the absorption band, at 256, 313, 385 nm and for the wavelengths corresponding to the transitions $^4A_2 \rightarrow ^4T_1$ (430 nm) and $^4A_2 \rightarrow ^4T_2$ (600 nm) in Cr^{3+} and $^3H_6 \rightarrow ^3F_2$, $^3F_4$ (680 nm) and $^3H_6 \rightarrow ^3F_4$ (780 nm) in Tm^{3+}. In the case of the first two peaks defects of Fe^{3+} and Fe^{2+} are involved. The next peak is due to oxygen vacancies and O^- holes, and the two bands are due to the recharging mechanism of Cr^{3+} ions.

Annealing at 400°C in air causes removal of the radiative colour centres. Annealing at 800°C again leads to the removal of the radiative colour centres and additionally, to other effects produced during the crystal growth (variation of the laser emission threshold).

After an annealing of the crystal at 1400°C an increase in Cr^{3+} and Fe^{3+} concentrations is observed, indicating that in the initial crystal in addition to Cr^{3+}, Cr^{2+} (the amount of which in the CTH:YAG crystal is at least the same as that of Cr^{4+} before annealing) and Fe^{2+} also occur. After gamma irradiation of the crystal a decrease of Cr^{3+} and Fe^{3+} concentrations is observed; this is of same order as the previous increase. Additional irradiation of annealed and gamma irradiated crystals with UV-radiation from a xenon arc lamp leads to an increase in Cr^{3+} and Fe^{3+} concentrations. That is, UV-radiation leads to the reaction: $Fe^{2+} + UV \rightarrow (e^- + Fe^{3+})$; $(e^- + Cr^{4+}) \rightarrow Cr^{3+}$, resulting in an increase in Fe^{3+} and Cr^{3+}. This explains the performance of the CTH:YAG laser with air cooled head which was observed by Kaczmarek et al. [3].

Gamma irradiation of a crystal annealed in air at 1400°C causes an improvement in the laser emission properties of a CTH:YAG crystal with water cooled head. This is due to an increase of the Cr^{3+} ion concentration, which participate in the sensitization process of the active Ho^{3+} ions (by the transition $Cr^{4+} \rightarrow Cr^{3+}$).

References

[1] T.S. Rose, M.S. Hopkins, R.A. Fields, Characterization and control of gamma and proton radiation effects on the performance of Nd:YAG and Nd:YLF lasers, IEEE J. Quantum Electron. 31 (1995) 9.

[2] S. Kaczmarek, Z. Mierczyk, K. Kopczyński, A.O. Matkovskii, D. Yu. Sugak, Z. Frukacz, Interaction of ionizing radiation with rare-earth doped YAG crystals, Proc. Intermol. Interact. Matter (1995) 134–141.

[3] S. Kaczmarek, A.O. Matkovskii, Z. Mierczyk, K. Kopczy(ski, D. Yu. Sugak, A.N. Durygin, Z. Frukacz, Possiblity of gamma-induced sensybilization process in rare-earth doped YAG crystals, Acta Phys. Pol. A 2 (90) (1996) 285–294.

[4] A.O. Matkowski, D.J. Sugak, M. Vakiv, A. Durygin, S. Kaczmarek, K. Kopczyński, Z. Frukacz, T. Łukasiewicz, Radiation effects in laser crystals, Proceedings of SPIE, vol. 3178, 1997, 273–278; J. Żmija, A. Majchrowski, J. Rutkowski, J. Zieliński, Growth and Characterization, Conference on Solid State Crystals, Materials Science and Applications, October 7–11, Zakopane, 1996.

[5] A.O. Matkowski, D. Yu. Sugak, A.N. Durygin, S. Kaczmarek, K. Kopczyński, Z. Mierczyk, Z. Frukacz, T. Łukasiewicz, A.P. Shakhov, Effect of ionizing radiation on optical and lasing properties of $Y_3Al_5O_{12}$ single crystals doped with Nd, Er, Ho, Tm, Cr ions, Opt. Mater. 6 (1996) 353–358.

[6] S. Kaczmarek, K. Kopczyński, T. Łukasiewicz, Z. Frukacz, R. Piramidowicz, A.O. Matkovskii, D.Y. Sugak, A.N. Durygin,,Influence of gamma-radiation on active materials, Proceedings of SPIE, vol. 3186, 1997, pp. 129–134, STL Świnoujście, November 1996.

[7] I.S. Akhmadulin, S.A. Migachev, S.P. Mironov, Thermo- and photoinduced defects in $Y_3Al_5O_{12}$ crystals, Nucl. Instrum. Methods Phys. Res. B65 (1992) 270–274.

[8] K. Kopczyński, S. Kaczmarek, Z. Mierczyk, Spectroscopic and laser emission studies of Cr, Tm, Ho:YAG crystals, Biuletyn WAT (in Polish) 9 (1993) 3–9.

[9] Z. Frukacz, Z. Mierczyk, Materiały Elektroniczne 22 (69) (1994) (in Polish).