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UV AND GAMMA IRRADIATION EFFECT IN SPECTROSCOPIC AND LASING PROPERTIES OF Er^{3+} DOPED YTTRIUM-ALUMINIUM GARNET, YTTRIUM ORTHOALUMINATE AND LITHIUM NIOBATE CRYSTALS

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Optical features (absorption and luminescence spectra) for Er^{3+} doped yttrium-aluminium garnet (YAG), yttrium orthoaluminate (YAP) and LiNbO_3 crystals as well as their changes after UV and gamma irradiations are presented. Possibility of gamma-induced sensibilization process in Er^{3+} doped crystals is discussed. Positive result for non-pre-annealed gamma-irradiated rods of Er^{3+} :YAG crystal was stated.

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1. Introduction

Stimulated emission has been obtained previously from trivalent erbium ions in a number of different host materials and involving a number of different transitions. Host materials included CaWO_4 [1], CaF_2 [2], $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) [3], YAlO_3 (YAP) [4] and LiNbO_3 [5] crystals. Oscillation was observed most frequently in the wavelength region of 1.53–1.65 μm arising from transitions ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$, which form a quasi-three-level laser scheme with a correspondingly high threshold. Laser action was achieved either by decreasing the temperature to depopulate the higher lying levels of the ${}^4I_{15/2}$ manifold or by codoping the materials with trivalent ytterbium to improve the optical pumping efficiency via $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ energy transfer. Oscillation observed at 1.663 μm with relatively low threshold was

obtained in Er^{3+} :YAP crystal for transitions ${}^4S_{3/2} \rightarrow {}^4I_{9/2}$. This transition forms four-level laser operation at all temperatures.

In Er^{3+} :YAG crystal the transition ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ with emission wavelength of $2.94 \mu\text{m}$ at room temperature was observed. The first integrated optical laser in LiNbO_3 , doped by an indiffusion of Er^{3+} prior to channel-guide fabrication by Ti diffusion, for transition ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ at room temperature has been obtained.

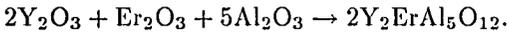
In the present paper we try to explain the next problem: positive or only negative is the influence of the external irradiation fields (UV of pump lamp, gamma) on the performance of Er^{3+} doped YAG, YAP and LiNbO_3 crystals?

2. Growth conditions for Er^{3+} doped YAG, YAP and LiNbO_3 crystals

Er^{3+} doped YAG, YAP and LiNbO_3 crystals were grown by the Czochralski method with the use of MSR-2 puller, made by Metals Research Limited, England. It was equipped in an analog digital convector (ADC) system of weighing growing crystals and Stanelco 30 kW r.f. generator. The melts zone was prepared in iridium or platinum crucibles, 50 mm in diameter and 50 mm in height. Apart from crucible the thermal system consisted of passive iridium afterheater 50 mm in diameter and 70 mm in height with upper lid and a set of alumina and magnesia heat shields around crucible and afterheater. The system was placed in the inductive coil in such a position to obtain appropriate axial and radial temperature gradients at the interface for good optical quality of obtained crystals.

2.1. Er^{3+} :YAG crystal

As the starting materials Y_2O_3 , Al_2O_3 and Er_2O_3 at least 4N purity were used. First they were dried to remove water, weighed and then mixed mechanically. After that the mixture was heated to realize the reaction



As the effect the Er:YAG (33.3 at.% of Er^{3+}) ($\langle 111 \rangle$ growth direction) crystal was obtained. Because of almost the same values of Er^{3+} and Y^{3+} ion radius (Er^{3+} ion substitutes Y^{3+} ion), the melt and the crystal composition are the same. The conditions of growth were such that the interface was convex towards the melt [6]. The growth rate was 2 mm/h. Good quality crystals were of pink colour.

2.2. Er^{3+} :YAP crystal

As the starting materials Y_2O_3 , Al_2O_3 and Er_2O_3 were used, similarly as for the Er:YAG crystal, but now the heated mixture realized the reaction



As the effect the Er:YAP (50 at.% of Er^{3+}) crystal was obtained. The growth was performed in the N_2 atmosphere with about 3% of O_2 and 2 mm/h growth rate and 30 rpm rotation rate, in b growth direction ($\langle 010 \rangle$) of orthorhombic $Pbnm$ symmetry. The conditions of growth were such that the interface was convex towards the melt. Good quality crystals were of orange colour.

2.3. $Er^{3+} : LiNbO_3$ crystal

The following starting materials were used: Nb_2O_5 , Puratronic from Johnson Matthey, Li_2CO_3 , 4N purity, from Institute of Electronic Materials Technology, Poland, MgO , 3N purity, Reachim, Russia, Er_2O_3 and Tm_2O_3 , 4N purity, Johnson Matthey. After mixing of adequate amounts of reagents they were calcined at $1100^\circ C$ for 6 h. The dopants were extra added to the charge. The conditions of growth were: growth rate: 1–2 mm/h, rotation rate: 5–20 rpm, axial temperature gradient over melt: 10–30 deg/cm, atmosphere: air. The temperature gradient was regulated by shifting the crucible in relation to afterheater and the system crucible–afterheater in relation to the induction coil.

Single crystals of *Y* and *Z* orientation up to 80 mm in diameter and up to 90 mm in length, weighing up to 1800 g were obtained. The as-grown crystals are regular, free of macroscopic defects and of pale-pink colouration in the case of erbium. The colouration is more intensive for crystals with higher concentration of erbium. Single crystal containing 0.3 at.% of Er was studied in the present paper.

3. Discussion

3.1. Er^{3+} doped YAG crystals

For Er^{3+} doped YAG crystals the short-wave absorption edge appears at 200 nm, long-wave at 6000 nm, respectively. Er^{3+} ions occupy *Y* sites, *Y* is substituted in position *c* but often it appears in position *a*, where it has different ion radius, thus many defects can appear in as-grown crystals (aluminium vacancies and oxygen vacancies also). It is necessary to carry out an annealing process.

For non pre-annealed crystal, after gamma irradiation, many defects arise (colour centres CCs), giving additional absorption bands (AA) in UV and visible parts of the spectrum. These AA are connected with noncontrolled impurities (Fe^{3+} and Fe^{2+}) and vacancies (O_2 or Al). They can colour the crystal and induce the sensibilization process in Er:YAG lasers [7, 8]. Restoration of original crystal spectrum irradiated by gamma quanta occurs after annealing the crystal at temperature of 673 K. Figure 1 presents effects of influence of UV and γ irradiation on optical features of Er:YAG crystal. For γ irradiated crystals AA bands appear at 240, 310 and 400 nm.

Figure 2 presents luminescence spectrum for Er:YAG crystal in the range of 0.7–3.2 μm . The stronger emission is seen at 980 nm, 1030 nm, 1.5 μm , 1.56 μm , 1.60 μm , 1.64 μm , 1.67 μm , 2.61 μm , 2.70 μm , 2.84 μm and 2.94 μm , respectively.

Figure 3 shows optical output changes vs. pump energy for (33.3 at.%) Er:YAG rod, for two laser head types: single-ellipse gold-plated cavity (1) and diffusive cavity (2). The difference in threshold values is seen for these two cases.

In gamma-irradiated Er:YAG crystal, a sensibilization process is possible [7, 8]. After gamma irradiation AA bands arise, which include ${}^2H_{9/2}$, ${}^2H_{11/2}$ and ${}^4F_{9/2}$ states, improving population inversion (by nonradiative transitions to ${}^4I_{11/2}$ state) between ${}^4I_{11/2}$ and ${}^4I_{13/2}$ states. Energy of the laser increases 2 times.

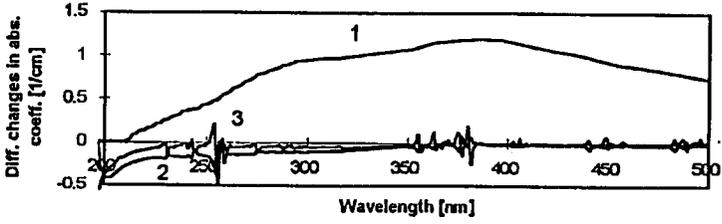


Fig. 1. Influence of UV and γ irradiation on optical features of Er:YAG crystal $\Delta K(\lambda) [1/cm] = (1/d) \ln T_1(\lambda)/T_2(\lambda)$, d — sample thickness, T_1, T_2 — optical transmissions before and after irradiation.

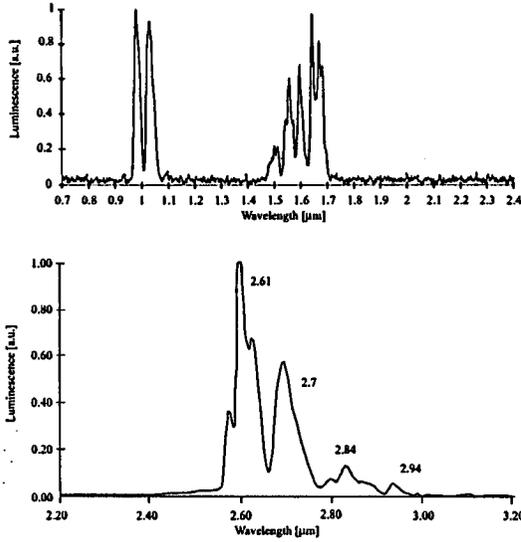


Fig. 2. Luminescence spectrum of Er:YAG crystal in different spectral regions (wavelength of excitation 488 nm).

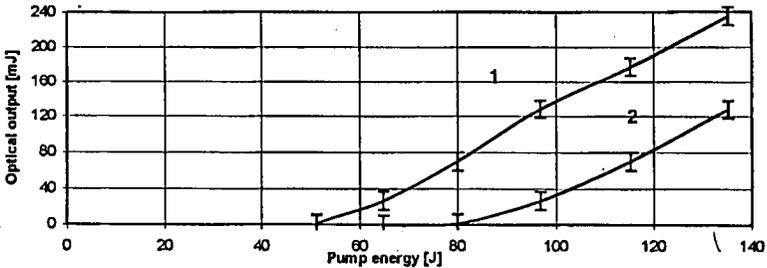


Fig. 3. Optical output for (33.3 at.%) Er:YAG rod (the best one) [6] with the diameter of 4 mm and length of 84 mm, $T_0 = 30\%$ for 2.94 μm , $T_r = 0\%$ — gold, $L_{res} = 230$ mm in a classic cavity (2) and 210 mm in diffusive one (1).

3.2. Er^{3+} doped YAP crystals

After obtaining some positive results connected with the gamma-induced sensibilization process [7, 8] for Er:YAG (33 at.%) crystals, we have to obtain the same for Er:YAP (50 at.%) crystals, where a strong colouration effect takes place. Our investigations showed three interesting features of Er:YAP crystals which are seen after thermal and external radiative field influence.

First: after thermal annealing ($\approx 1280^\circ\text{C}$ and 30% N_2 , 70% H_2 atmosphere) of Er:YAP crystals AA bands appear near 300 nm in double annealed sample in comparison to single annealed one. Second: UV AA bands (10 pulses with energy of 115 J and time interval of 15 s) have wave numbers greater for double annealed crystal (8 cm^{-1}) and the greatest among known host materials (YAG, YAP, $LiNbO_3$) doped with different rare-earth ions. Fortunately, these changes take place in the wavelength region before pump absorption bands (near short-wave of absorption edge and in the region of 250–330 nm). Third feature seems serious in consequence. The strong AA bands after gamma irradiation appear in the range of pump absorption bands and are the greatest among other known host materials doped with Er^{3+} ions ($\approx 26\text{ cm}^{-1}$ for 370 nm) (Fig. 4). Thus, their influence on

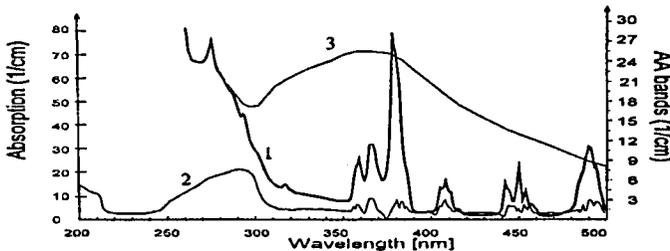


Fig. 4. Relative positions of AA bands for UV (2), gamma (3) and non irradiated (1) Er:YAP crystal. The dose of gamma irradiation was 10^5 Gy. UV irradiation: 10 pulses of 115 J energy with time interval of 15 s.

laser performance of Er:YAP crystals is very important. With the aim of determining of this influence, the two rods with the length of 68 mm and diameter of 4 mm (with axis parallel to $\langle 010 \rangle$ crystallographic direction) were manufactured and then they were gamma irradiated with the dose of 7×10^5 Gy (colour of the rods changed from orange to dark violet). It was stated that after UV irradiation of such gamma pre-irradiated crystals the persistent brightness took place after a few pulses of 115 J (return to orange colour).

Figure 5 shows luminescence spectrum for Er:YAP crystal. It is seen that the strong luminescence appears for 1.0, 1.59 and 1.62 μm , respectively. We have not observed the stimulated emission at 1.7 μm (only a weak one at 2.94 μm), but it is evident that gamma-induced sensibilization process (in classic pumping method) for this wavelength is impossible.

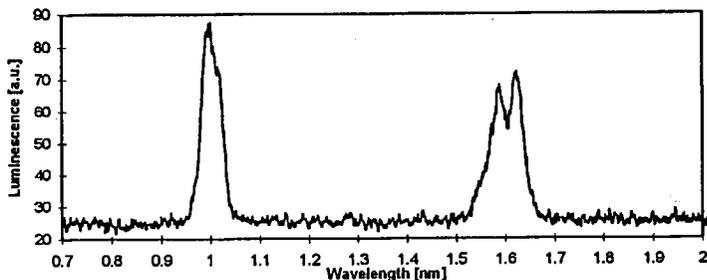


Fig. 5. Luminescence spectrum for Er:YAP crystal in the range of 0.7 to 2 μm . Excitation wavelength: 488 nm. The stronger maxima of the luminescence are: 1.0 μm (87 a.u.), 1.59 μm (68 a.u.) and 1.62 μm (72 a.u.).

3.3. Er^{3+} doped LiNbO_3 crystals

The short-wave absorption edge for Er^{3+} doped LiNbO_3 crystals is placed at 330 nm and long-wave at 5100 nm, respectively. Absorption values are proportional to the dopant contents. Er^{3+} ions first occupy Li^+ sites. At higher concentration (> 0.3 at.%) Er^{3+} ions start to occupy also another sites in LiNbO_3 lattice which we suggest to be Nb^{5+} sites [9].

After gamma irradiation of Er:LiNbO₃ crystals, a wide AA band with two maxima at 384 and 490 nm appear in the absorption spectrum. The first one is relevant to F-centres, and the second one to Fe^{2+} and Nb^{4+} ions [10]. AA bands for gamma irradiated crystals are higher (0.24 and 0.2 cm^{-1}) than for UV one (0.04 and 0.03, respectively).

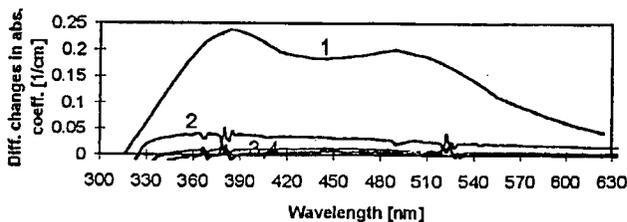


Fig. 6. Differential changes in Er:LiNbO₃ (0.3 at.%) crystal after gamma (dose of 10^5 Gy) and UV (10 pulses with energy of 90 J) exposure: 1 — just after gamma exposure, 2 — just after UV exposure, 3 — 5 h later, 4 — 20 h later.

As is seen from Fig. 6, the influence of UV irradiation is very weak. The nonstable colour centres arising after UV irradiation are short-living in the room temperature, and after 20 hours the crystal returns to its initial absorption values. Colour centres after gamma irradiation are stable at room temperature, although AA bands are smaller compared to Er:YAG or Er:YAP crystals. Restoration of original crystal spectrum irradiated by gamma quanta occurs after annealing the crystal in the air at temperature higher than 450 K [11]. Formation of CCs in

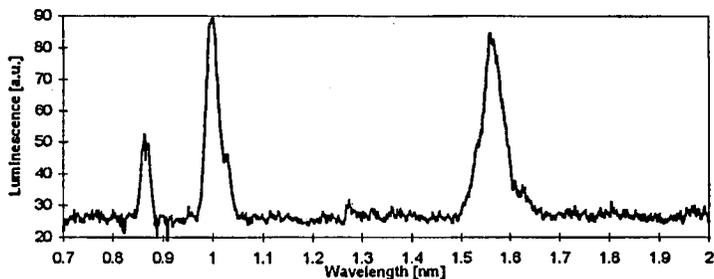


Fig. 7. Luminescence of Er:LiNbO₃ (0.3 at.%). One can see three luminescence peaks: 863 nm (52 a.u.), 1.0 μm (89 a.u.) and 1.56 μm (85 a.u.), respectively. Excitation wavelength: 488 nm.

LiNbO₃ crystal during irradiation is connected with ionization recharge process of the crystal growth defects (their concentration may reach up to 10^{19} cm^{-3}) [10].

Figure 7 shows the luminescence spectrum for Er:LiNbO₃ (0.3 at.%) crystal. The stronger luminescence appears at 1000 nm and 1560 nm, respectively. We have not obtained the emission at 1.56 μm .

4. Conclusion

UV irradiation strongly influences the Er³⁺:YAP crystal, giving AA bands (about $5\text{--}8 \text{ cm}^{-1}$) in the range of 250–310 nm. Er³⁺:YAG and Er³⁺:LiNbO₃ crystals are less susceptible to UV irradiation. All these crystals demand the thermal annealing process, which in the case of Er³⁺:YAP crystal manifests in AA bands appearing near 300 nm wavelength. The thermal annealing process can improve laser performance of the crystals, translating the threshold of stimulated emission and increasing the slope efficiency. But in the case of non pre-annealed Er³⁺:YAG crystals, the gamma-induced sensibilization process is possible, which increases also the slope efficiency. The probable scheme of that phenomenon is an increase in inversion population by exciting the ²H_{9/2}, ²H_{11/2} and ⁴F_{9/2} states. In the case of Er³⁺:YAP and Er³⁺:LiNbO₃ crystals this process for classical type pumping is impossible (in YAP crystal UV irradiation damages gamma-induced AA bands, in LiNbO₃ crystal AA bands appear behind pump absorption bands).

For all the investigated materials the strong luminescence at about 1 μm and 1.6 μm was stated.

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