Spectroscopic and radiation-resistant properties of Er,Pr:GYSGG laser crystal operated at 2.79 μm*

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We demonstrate the spectroscopic and laser performance before and after 100 Mrad gamma-ray irradiation on an Er,Pr:GYSGG crystal grown by the Czochralski method. The additional absorption of Er,Pr:GYSGG crystal is close to zero in the 968 nm pumping and 2.7–3 μm laser wavelength regions. The lifetimes of the upper and lower levels show faint decreases after gamma-ray irradiation. The maximum output powers of 542 and 526 mW with the slope efficiencies of 17.7% and 17.0% are obtained, respectively, on the GYSGG/Er,Pr:GYSGG composite crystal before and after the gamma-ray irradiation. These results suggest that Er,Pr:GYSGG crystal as a laser gain medium possesses a distinguished anti-radiation ability for application in space and radiant environments.

Keywords: Er,Pr:GYSGG crystal, gamma-ray irradiation, anti-radiation ability, laser material

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1. Introduction

Trivalent-erbium-doped host materials can generate 2.7–3 μm mid-infrared lasers through the level transition from $^4I_{11/2}$ to $^4I_{13/2}$, which have been applied widely in the fields of biology and medical surgery owing to their strong water absorption characteristic. In addition, in outer space, there exists only little water vapor, and a laser travels in it only with weak absorption loss and energy attenuation; solid-state lasers at the 2.7–3 μm waveband could therefore be directly utilized in military and science exploration activities in space.[1] However, high-energy particles and cosmic rays in space would have a disadvantageous impact on the performance of laser devices. Radiation sources can pose serious damage by ionizing constituent atoms in the gain medium, which acts on the crystalline defect area to form color centers.[2] These colour centers are closely related to the impurities and O^{2-} vacancies in the crystal,[3] which are especially harmful to the optical properties of laser devices; therefore, laser crystal materials, as the most important and vulnerable parts of lasers, are required to have effective anti-radiation ability for operation in radiant environments.

At present, Er^{3+}-doped scandium garnet laser crystals have attracted much attention, such as Er:YSGG, Er:GSGG, and Er:GYSGG,[4–6] owing to their good physical characteristics and radiation-resistant capabilities. According to the literature,[7] the Sc^{3+} at the octahedral site in garnet crystals has higher covalent character and bond order in favor of preventing color center formation. In particular, Er^{3+}-doped GYSGG crystal exhibits excellent radiation-resistant performance.[6] It is known that single Er^{3+}-doped crystal is disadvantageous for the radiative transition from the $^4I_{11/2}$ level to the $^4I_{13/2}$ level, as the lifetime of the lower laser level $^4I_{13/2}$ is considerably longer than that of the upper laser level $^4I_{11/2}$. Further literature[8,9] reported that deactivator Pr^{3+}-doped Er:GYSGG crystal could decrease the lower level lifetime and effectively improve the laser efficiency. The level $^3F_4$ of Pr^{3+} is close to the level $^4I_{13/2}$ of Er^{3+}, which benefits the energy transfer from Er^{3+} to Pr^{3+}. However, it remains unclear what happens to the anti-radiation ability of Er,Pr:GYSGG crystal with the optimized concentration ratio of Er^{3+} and Pr^{3+}.

In this work, we investigate the anti-radiation ability of Er,Pr:GYSGG crystal grown by the Czochralski (Cz) method, and demonstrate the influence of 100 Mrad gamma-ray irradiation on the spectroscopic properties and laser performance.

2. Experimental setup

Using a JDG-60 furnace (CETC26th, China) with an automatic diameter controlled (ADC) growth system, an Er,Pr:GYSGG crystal was grown from a melt of congru-

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ent composition containing 22 at% Er^{3+} and 0.3 at% Pr^{3+} by the Cz method. The oxide powders of Er_2O_3 (5 N), Pr_2O_3 (5 N), Gd_2O_3 (5 N), Y_2O_3 (5 N), Sc_2O_3 (4.5 N), and Ga_2O_3 (4.5 N) were used as starting materials, which were weighed accurately according to the structural formula $(Er_{0.66}Pr_{0.009}Gd_{1.17}Y_{1.161})Sc_2Ga_3O_{12}$. An extra 2 wt% Ga_2O_3 was overweighed to compensate its evaporation loss during the growth process. After being mixed thoroughly and pressed into disks, the mixture was loaded into an Al_2O_3 crucible and sintered at 1250 °C for 48 h to synthesize the polycrystalline material. Then, Er,Pr:GYSGG crystal was grown in an iridium crucible and Ar atmosphere, and a ⟨111⟩-oriented GYSGG seed was used with a rotation speed of 7 rpm and a pulling rate of 1 mm/h. Finally, a crack-free crystal with the dimensions of approximately Ø25 mm×100 mm was obtained, as shown in Fig. 1. The as-grown crystal was annealed in air atmosphere at 1500 °C for 72 h. Sample disks with 2 mm thickness were perpendicularly cut to the growth direction ⟨111⟩ for spectral measurements and polished on both sides. For laser experiment, an Er,Pr:GYSGG crystal sample with parallel and polished end faces was bonded thermally with an undoped GYSGG crystal as end cap to get a GYSGG/Er,Pr:GYSGG composite crystal. The size of the GYSGG/Er,Pr:GYSGG composite crystal is 2 mm×2 mm×7 mm (the undoped part is 2 mm×2 mm×2 mm and the doped part is 2 mm×2 mm×5 mm). The crystal samples were divided into two groups. One of the two groups was radiated by a ^{60}Co gamma-ray source with a dose rate of 82 Gy/min and radiation time of 200 h at room temperature, corresponding to the dose of approximately 100 Mrad. The irradiated and non-irradiated samples were measured under the same experimental conditions. Values of induced difference spectrum or additional absorption (AA) due to the irradiation were calculated by[9]

$$\Delta K = \frac{\ln\left(\frac{T_1}{T_2}\right)}{d}, \tag{1}$$

where d is the sample thickness, T_1 and T_2 are the crystal transmissions before and after 100 Mrad gamma-ray irradiation, respectively.

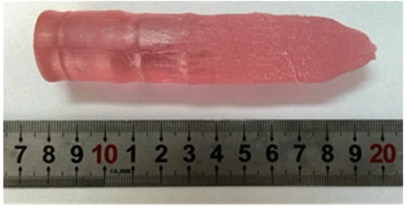


Fig. 1. (color online) Photograph of the as-grown Er,Pr:GYSGG laser crystal.

A Perkin–Elmer Lambda-950 Spectrophotometer was utilized to record the absorption spectra in the range of 320–3000 nm. The fluorescence spectra were measured by a fluorescence spectrometer (Edinburgh FLSP 920) with an excitation source of a 968 nm laser diode (LD), and the fluorescence decay curves were obtained using an excitation of OPO (Opolette 355 I) laser. The experiment configuration based on a simple plane-parallel cavity is illustrated in Fig. 2. A fibre-coupled InGaAs LD emitting approximately 968 nm in continuous wave (CW) mode was used as a pumping source. An uncoated GYSGG/Er,Pr:GYSGG composite crystal sample was wrapped in indium foil and mounted in a copper holder with a cooling water passage, which was maintained at a temperature of 15 °C. A plane-parallel cavity with a length of 14 mm was used as a resonator. The input mirror was a K9 glass plate with an antireflection coating of high transmission (> 95%) at 968 nm and reflectivity of 100% at 2.79 μm. The output mirror (CaF_2 substrate) with transmission of 2% at 2.79 μm was employed to obtain the optimal laser output. The laser output power was measured by a power meter (OPHIR 30A-BB-18). In order to obtain an accurate comparison, the spectra measurements and laser experiments of the irradiated and non-irradiated samples were performed under the same conditions.

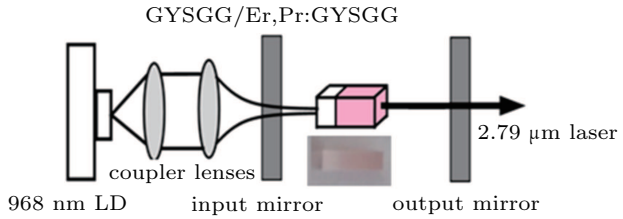


Fig. 2. (color online) Schematic diagram of LD end-pumped GYSGG/Er,Pr:GYSGG composite crystal.

3. Results and discussion

3.1. Absorption spectra

The transmission spectra of Er,Pr:GYSGG crystal before and after 100 Mrad gamma-ray irradiation are shown in Fig. 3. There is little change in the transmissivity in the 900–3000 nm region, but it shows a certain degree of decline below the 900 nm region. Then the transmission spectra of Er,Pr:GYSGG crystal are transformed into absorption spectra, as shown in Fig. 4. The absorption coefficient above the 900 nm wavelength range almost remains constant before and after gamma-ray irradiation. The inset of Fig. 4 shows that Er,Pr:GYSGG crystal has a high absorption coefficient of 5 cm^{-1} at 968 nm, which can match well with the mature InGaAs (970 nm) LD used as a pumping source. Moreover, the near-zero absorption coefficient in the range of 2700–3000 nm is conducive to the radiative transition of Er^{3+} from $^4I_{11/2}$ to $^4I_{13/2}$ as well as the output of the mid-infrared laser.

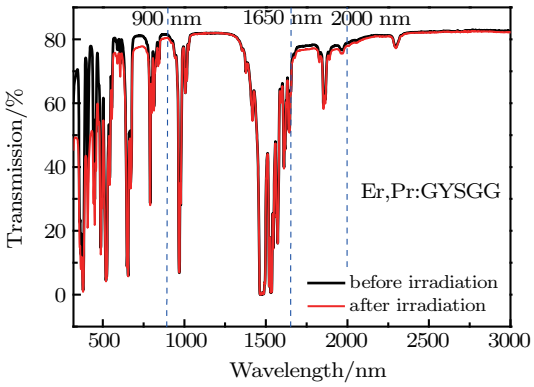


Fig. 3. (color online) Transmission spectra of Er,Pr:GYSGG crystal before and after 100 Mrad gamma-ray irradiation.

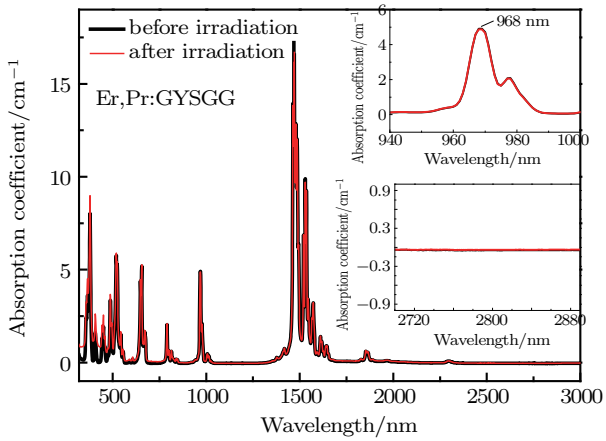


Fig. 4. (color online) Absorption spectra of Er,Pr:GYSGG crystal before and after 100 Mrad gamma-ray irradiation. Insets: enlarged absorption coefficient curve around 970 and 2790 nm.

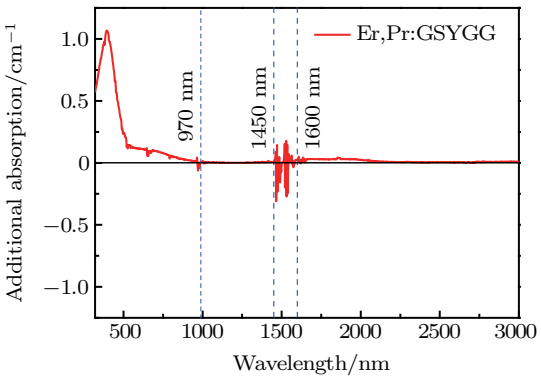


Fig. 5. (color online) Additional absorption spectrum of Er,Pr:GYSGG crystal after 100 Mrad gamma-ray irradiation.

The AA spectrum of Er,Pr:GYSGG crystal after 100 Mrad gamma-ray irradiation is exhibited in Fig. 5. The absorption losses at the 968 nm pumping wavelength and in the laser output region of 2.7–3 μm are as small as the level of 10^{-2} cm^{-1}. These figures indicate that Er,Pr:GYSGG crystal possesses a good performance in resisting gamma-ray irradiation. However, the color centre absorption generated by the irradiation can be easily observed through the positive AA peak of the 320–900 nm range. Crystals grown under anoxic conditions would produce many oxygen vacancies, which capture one or two electrons to form F^+ or F centers after gamma-ray irradiation.[10] In addition, slightly unexpected Fe^{3+} impurity might be introduced into the as-grown crystal,[11] and therefore Fe^{3+} ions would also capture free electrons to form Fe^{2+} by $Fe^{3+} + e \rightarrow Fe^{2+}$. According to available reports,[10–15] the AA band in the 320–900 nm region result from mutual factors of various color centres. Some irregularly negative and positive AA peaks in the range of 1450–1600 nm may be caused by experimental error. Fagundes-Peters *et al.*[16] reported that the AA peak at the 1700 nm wavelength was related to Fe^{2+} ions. Therefore, the small drop in transmission in the 1700–2000 nm region could be linked to the rise of Fe^{2+}.

3.2. Fluorescence spectra

Figure 6 shows the fluorescence spectra of Er,Pr:GYSGG crystal excited by 968 nm LD before and after 100 Mrad gamma-ray irradiation. There are three strongest peaks, namely 2636, 2701, and 2793 nm, which correspond to the transition of different Stark sublevels between $^4I_{11/2}$ and $^4I_{13/2}$. The fluorescence decay curves of Er,Pr:GYSGG crystal are also recorded under the excitation of the 968 nm OPO pulsed laser, which show an approximate single exponential decay behavior, as shown in Fig. 7. The lifetimes of the upper level $^4I_{11/2}$ and the lower level $^4I_{13/2}$ are both reduced by only approximately 20 μs after gamma-ray irradiation, as listed in Table 1. As seen from the above results, the influence of gamma-ray irradiation on the fluorescence properties and the level lifetimes could be almost disregarded. In addition, the lifetimes of the upper level $^4I_{11/2}$ and the lower level $^4I_{13/2}$ are 1.2 and 3.9 ms in Er:GYSGG,[6] respectively, which demonstrates that Pr^{3+} can reduce them by the resonant energy transfer from $^4I_{11/2} \rightarrow {}^1G_4$ (ET_1) and $^4I_{13/2} \rightarrow {}^3F_4$ (ET_2). The efficiency of the energy transfer from the Pr^{3+} to Er^{3+} ions can be calculated based on the following equation:[17]

$$\eta_\tau = 1 - \frac{\tau_1}{\tau_2}, \tag{2}$$

where τ_1 is the level lifetime of Er,Pr:GYSGG and τ_2 is the level lifetime of Er:GYSGG. According to Eq. (2) and the aforementioned level lifetimes of Er:GYSGG and Er,Pr:GYSGG, the energy transfer efficiencies, ET_1 and ET_2, are 63.3% and 85.5%, respectively. Therefore, the larger energy transfer rate of ET_2 is advantageous to achieve high-power 2.79 μm laser output.

Table 1. Energy level lifetimes and laser performance of Er,Pr:GYSGG crystal before and after 100 Mrad gamma-ray irradiation.

	Level lifetimes/μs		Output	Optical-optical	Slope
	$^4I_{11/2}$	$^4I_{13/2}$	power	efficiency	efficiency
Before irradiation	441	564	542	15.6%	17.7%
After irradiation	421	545	526	15.1%	17.0%

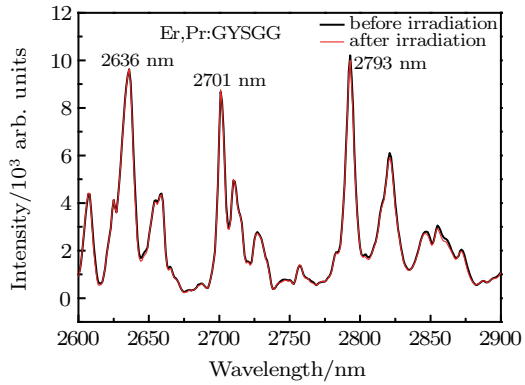


Fig. 6. (color online) Fluorescence spectra of Er,Pr:GYSGG crystal excited by 968 nm LD before and after 100 Mrad gamma-ray irradiation.

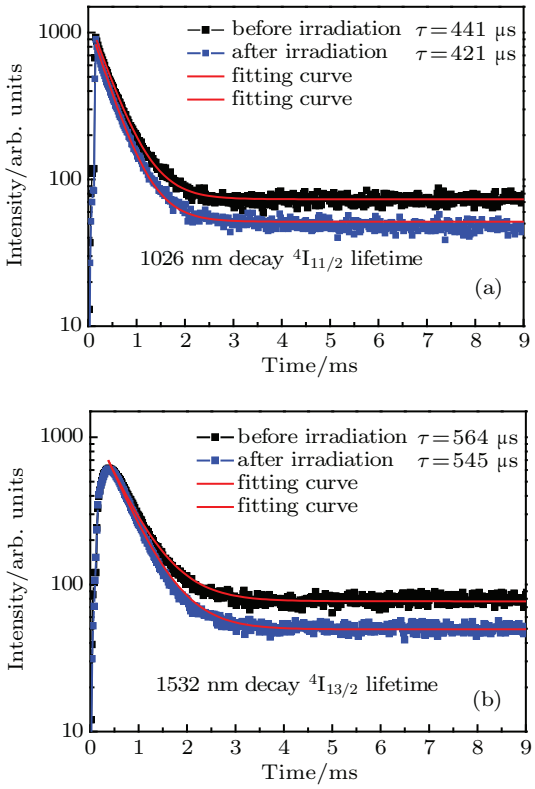


Fig. 7. (color online) Fluorescence decay curves of Er,Pr:GYSGG crystal before and after gamma-ray irradiation. (a) 1026 nm for $^4I_{11/2}$; (b) 1532 nm for $^4I_{13/2}$.

3.3. Laser performance

The laser spectrum was measured by an FLSP 920 fluorescence spectrometer, and the laser central wavelength is located at 2.796 μm. The laser output powers as a function of the pump power for GYSGG/Er,Pr:GYSGG composite crystal before and after 100 Mrad gamma-ray irradiation are illustrated in Fig. 8. In CW mode, the composite crystal before gamma-ray irradiation produces a maximum output power of 542 mW, corresponding to an optical–optical efficiency of 15.6%, and a slope efficiency of 17.7%. A maximum output power of 526 mW, an optical–optical efficiency of 15.1%, and a slope efficiency of 17.0% are obtained for the composite crystal after gamma-ray irradiation, as listed in Table 1. We note that the maximum output power is influenced slightly and the laser efficiency is decreased by only approximately 4% after such a high gamma-ray irradiation (100 Mrad). Meanwhile in comparison, the laser output of the commonly used Nd:YAG laser was found to be in a seriously deteriorated condition and the output energy dropped by an order of magnitude after 1 Mrad gamma-ray exposure.[18] The radiation resistance micromechanism of Er,Pr:GYSGG could be attributed to the Er^{3+}, Pr^{3+}, and Y^{3+} partly replacing Gd^{3+} and occupying the same dodecahedron sites instead of Sc^{3+}, with the effect that the Sc^{3+} can still maintain its higher covalent character and bond order at the octahedral sites;[6,7] therefore, Er,Pr:GYSGG crystal has an excellent ability to resist color center formation. It is believed that the high-energy particles have only a slight impact on the laser performance of Er,Pr:GYSGG crystal. These results suggest that Er,Pr:GYSGG crystal has excellent radiation-resistance abilities, and is a potentially new 2.79 μm anti-radiation laser material that can be applied in space and radiant environments.

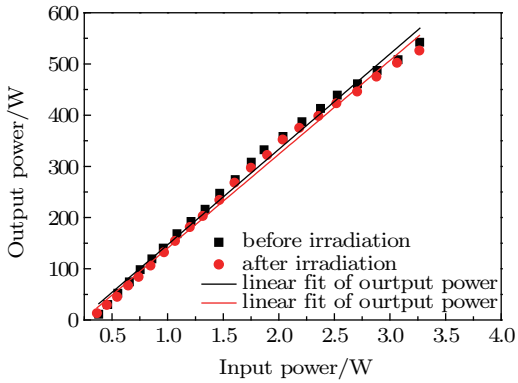


Fig. 8. (color online) Laser output powers versus pump power for the GYSGG/Er,Pr:GYSGG composite crystal before and after 100 Mrad gamma-ray irradiation.

4. Conclusions

We demonstrate the influence of 100 Mrad gamma-ray irradiation on the spectroscopic properties and laser performance of Er,Pr:GYSGG crystal. The absorption spectra with slight color center absorption generated by the irradiation are nearly unchanged in the 968 nm pumping and 2.7–3 μm laser wavelength regions. The variation in lifetimes of the upper and lower levels can be ignored. In the CW mode, the maximum laser output powers of the GYSGG/Er,Pr:GYSGG composite crystal before and after gamma-ray irradiation are 542 and 526 mW, respectively, corresponding to slope efficiencies of 17.7% and 17.0%. The laser performances are only influenced slightly after such a high dosage gamma-ray irradiation. These results suggest that Er,Pr:GYSGG crystal possesses an excellent anti-radiation ability and can be employed as a new promising laser material for application in space and radiant environments.

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