Journal of Luminescence 205 (2019) 109–114

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Growth, defects, radiation resistant and optical properties of 30 at% Er:GSAG laser crystal

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ARTICLE INFO

Keywords:
Crystal growth
Chemical etching
2.6–3.0 μm laser
Radiation resistant property
Spectra

ABSTRACT

30 at% Er^{3+}:GSAG single crystal was successfully grown by the Czochralski method. The dislocation of (111) face is studied using the chemical etching with the phosphoric acid etchant. The luminescence properties at 2.6–3.0 μm are systematically studied by measuring the fluorescence spectra and lifetimes to the transition of $^4I_{11/2} \rightarrow {}^4I_{13/2}$. The long fluorescence lifetime, high fluorescence intensity, and large gain σ_{em} spectra indicate that the 30 at% Er:GSAG crystal has the great potential for the multi-wavelength laser output at 2.6–3.0 μm. Meanwhile, the absorption and fluorescence properties of 30 at% Er:GSAG crystal under the gamma-ray radiation with three different intensities (35, 70, and 105 Mrad) have been investigated, indicate that this crystal can be considered as a promising MIR laser gain medium for being used under radiant environment. In addition, the luminescence property of 30 at% Er:GSAG crystal in visible and 1.5–1.7 μm was also studied, which shows the possibility to generate the laser around 1.6 μm.

1. Introduction

Over the past few decades, Er^{3+} doped laser materials for solid-state lasers in visible and infrared ranges have received considerable attentions due to its abundant energy level structure. Lasers at 550 and 670 nm corresponding to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions attract much more attention due to the search for all-solid compact laser devices operating in the violet-blue-green region, infrared quantum counter detectors, temperature sensors, and three-dimensional display [1–4]. The Er^{3+} doped lasers around 1.6 and 3.0 μm have been widely used in laser chemistry, nonlinear laser spectroscopy and other applications, such as coherent laser radar, laser distance measurement and laser medicine [5–7]. Generally, the crystals with low Er ions doping concentration are beneficial for visible and 1.6 μm laser output. Er^{3+} doped crystals emitting the laser at 2.7–3.0 μm need highly doped concentration of Er ions to overcome the self-terminating effect.

Er^{3+}-doped laser crystals with the garnet structure such as Er doped gadolinium scandium gallium garnet (GSGG), yttrium scandium gallium garnet (YSGG), and YAG have been subjected to numerous researches due to their good physical characteristics and laser performance [8–11]. It is well known that the solid-state laser will encounter an effect of gamma-ray radiation and high-energy particles in outer space and some harsh radiation environment. Therefore, it is attractive and necessary to develop novel crystals that improve their radiation resistant property for the laser device application under the radiation environment. Currently, Sun et al. report that the luminescent properties of Er doped GSGG and gadolinium yttrium scandium gallium yttrium (GYSGG) crystals are not damaged by ^{60}Co gamma radiation up to 100 Mrad [12,13]. Meanwhile, the laser performance of Er:GYSGG crystal at 2.79 μm is unaffected even if illuminated by 100 Mrad radiation doses [13]. However, both of the GSGG and GYSGG crystal contain easily volatile element Ga, which is not benefit for keeping compositions consistency and growing large-size single crystals. GSAG is a kind of crystal that colligates the advantages of GSGG and YAG crystals [14,15]. Currently, Nd doped GSAG crystal is considered to be a promising laser materials for space application [16]. The stable laser diode (LD) pumped mode-locked and tunable single frequency injection-seeded Q-switched Nd:GSAG laser around 942 nm has been demonstrated for the further development of quasi-three-level Nd^{3+} laser [17,18]. Er doped GSAG can be deemed to a potential laser material for generating visible and infrared laser. It is currently accepted that the change of Er^{3+} concentration has a great effect to the structure and luminescence of Er^{3+} doped crystal [19,20]. Er^{3+} doped crystals emit

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https://doi.org/10.1016/j.jlumin.2018.08.065
Received 10 March 2018; Received in revised form 22 July 2018; Accepted 20 August 2018
Available online 23 August 2018

the laser at 2.7–3.0 μm, which need highly doped concentrations of Er ions to overcome the self-terminating effect. Thus, the high Er ions concentration doped GSAG crystal can be consider as a promising 2.7–3.0 μm laser material.

In this work, 30 at% Er:GSAG crystal was grown by the Czochralski (Cz) method, and the defects, radiation resistant and optical properties of this crystal were investigated. The crystal defect was analyzed by the chemical etching technique. Particular attention was paid to investigate its fluorescence spectra at 2.7–3.0 μm. The absorption and fluorescence spectra of Er:GSAG crystal were investigated under gamma radiation with different doses. Meanwhile, the mechanism of luminescence and radiation resistance of Er:GSAG are also analyzed and discussed. In addition, the luminescence performance in the visible and near infrared (NIR) regions of this crystal was compared with that of 1 at% Er:GSAG crystal to study the influences of cross relaxation (CR), cross upconversion (CU) and excited state absorption (ESA) process in the visible and infrared laser generation.

2. Experimental setup

30 at% Er:GSAG crystals was grown successfully using the Cz method, using a JGD-60 furnace (CETC 26th, China) with an automatic diameter controlled growth system through monitoring the weight rate during growth. The Er^{3+} doped GSAG crystal was designed according to the formula of $Er_{3\times}Gd_{(2.88-3\times)}Sc_{1.89}Al_{3.23}O_{12}$ (x = 0.3). The raw materials Er_2O_3 (5N), Gd_2O_3(4N), Sc_2O_3(4N) and Al_2O_3(5N) were weighed according to the appropriate stoichiometric ratio and mixed accurately. The mixture was pressed into disks and loaded into an iridium crucible. The crystal was grown in nitrogen atmosphere with rotation speed of 4.0–8.0 rpm and pulling rate of 0.5–2 mm/h. The samples were cut from the as-grown crystal perpendicular to the growth direction polished on both sides to 2 mm in thickness.

The slice of Er:GSAG crystal along < 111 > direction was etched with phosphoric acid for approximately 80 min at 200 °C. Then the etched surface was washed with deionizer water and dried by gently pressing between two filter papers. The dislocation etching pit patterns were immediately examined using an optical microscope with a digital camera. Besides, three Er:GSAG samples were illuminated by a ^{60}Co gamma-ray source with the dose rate of 26 Gy/min, radiation times of 220, 440, and 660 h at room temperature, corresponding to the doses of about 35, 70, and 105 Mrad, respectively. The concentration of Er element in the as-grown crystal was measured by the X-ray fluorescence analysis (XRF-1800). A spectrophotometer (PE Lambada 950 UV/VIS/NTR) was performed to record absorption spectra with a spectral interval of 0.2 nm. A fluorescence spectrometer (Edinburgh FLSP 920) was applied to measure the fluorescence spectra and the fluorescence decay curves. The excitation sources of the fluorescence spectra were a 450 W Xenon lamp (visible spectra) and a 972 nm InGaAs LDs (infrared spectra). And a microsecond lamp and an optical parametric oscillation (OPO) laser (Opolette 355 I) were used as the excitation light for the fluorescence lifetime measurement. To obtain accurate comparison, the absorption and luminescence measurements under gamma radiation were performed using the same samples and under the same conditions. All the measurements were carried out at the room temperature.

3. Results and discussion

3.1. Crystal defects

Fig. 1 shows the photograph of the as-grown Er:GSAG crystals. The crystal is transparent and crack-free with the dimension of Ø 30 mm × 90 mm. Under the illumination of a 100 mW 532 nm laser, no scattering point was observed. In the as-grown crystal, the microstructural imperfections or crystal defects plays the very important role to research the physical and chemical properties. The crystal defects may destroy the mechanical, electrical, and optical properties of the crystal including the optical homogeneity and laser output efficiency, which affect the applications of the crystal [21]. Chemical etching is an important characterization technique employed to investigate the defect structure of a single crystal. The key to the etching technique is the use of a dislocation etchant that preferentially dissolves the dislocation sites. Fig. 2 presents the dislocation etching pit pattern of the Er:GSAG on the (111) crystallographic face. The sizes and shapes of the dislocation etching pits on the (111) crystallographic face is observed as triangular funnel, which is analogous to that of the Er:YAG crystal. And the corresponding edges of each dislocation etching pit are parallel to each other. In general, the shapes of the etching pits are determined by the lattice structure and symmetry. The atomic arrangement diagram observed along < 111 > direction of the Er:GSAG crystal is obtained with the Crystalmaker 2.3, as shown in Fig. 3. By comparison, it can be noted that the dislocation etching pit patterns of the Er:GSAG crystal are consistent with the corresponding lattice structure and symmetry.

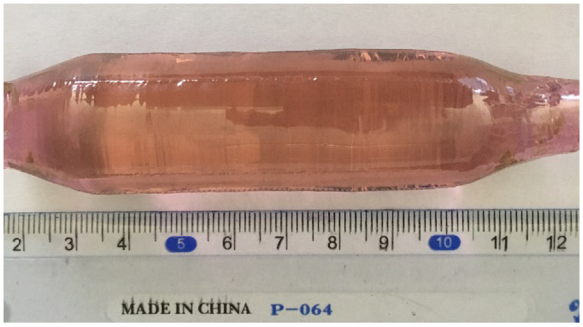

Fig. 1. Photographs of the as-grown Er:GSAG crystal by Cz method.

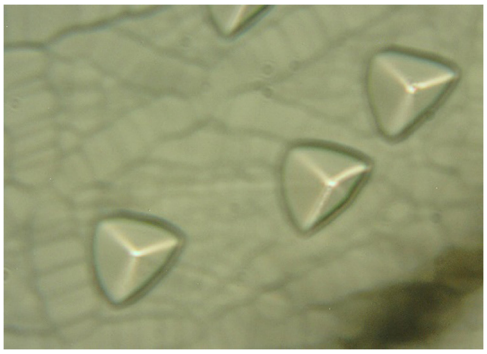

Fig. 2. Dislocation etching pit pattern of the Er:GSAG crystal on (111) crystalline face.

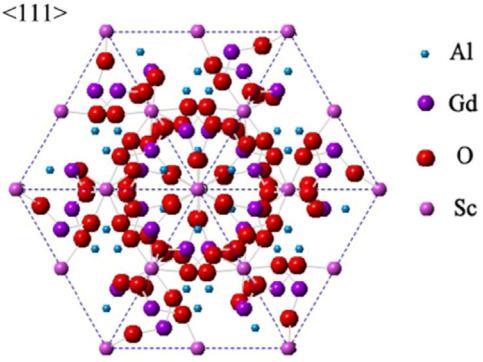

Fig. 3. Atomic arrangement diagram viewed at < 111 > crystalline directions for the Er:GSAG crystal.