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Growth, structure and radiation resistant properties of Er,Pr:GSAG laser crystals

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ABSTRACT

Er, Pr co-doped GSAG laser crystal with high optical quality was successfully grown by the Czochralski method for the first time. X-ray rocking curve exhibit the high crystalline quality of this crystal. The intensities of optical transmission and luminescence of Er,Pr:GSAG crystal were not deteriorate after the gamma-ray irradiation even with a dose of 1.16×10^6 Gy, confirming the excellence radiation resistant property of Er, Pr:GSAG crystals. The efficiencies of energy transfer from $^4I_{11/2}$ to $^1G_4$ and $^4I_{13/2}$ to $^3F_4$ between Er^{3+} and Pr^{3+} ions in GSAG crystal are determined as 16.7% and 94.9%, which indicate that the Pr^{3+} can act as an deactivator ions for Er^{3+} ions in Er,Pr:GSAG crystal. Additionally, the luminescence spectra of Er,Pr:GSAG crystal are compared with that of Er:GSAG crystal in the visible and near-IR regions, which provided that Pr^{3+} ions can efficiently depopulate the $^4I_{13/2}$ level and reduce the fluorescence lifetime. All the results demonstrate that Er,Pr:GSAG crystal can realize multi-wavelength laser output at 2.6–2.9 μm under harsh radiation environment.

1. Introduction

Efficient lasers at wavelength range from 2.6 to 3.0 μm have attracted widespread attentions for numerous applications in remote sensing, military countermeasures, atmosphere pollution monitoring, and medical treatments due to strong water absorption in this waveband [1–4]. Additionally, 2.6–3.0 μm laser is also a preferable pumping source for 3.0–13 μm optical parameter oscillation (OPO) lasers [5]. However, the transition of $^4I_{11/2} \rightarrow {}^4I_{13/2}$ is commonly believed to be self-terminating because the lifetime of the upper laser level ($^4I_{11/2}$) is less than that of the lower laser level ($^4I_{13/2}$). Highly doped concentrations of Er^{3+} ions is an effective way to overcome this self-terminating "bottleneck" effect by inducing upconversion (UC) and cross-relaxation (CR) processes [6,7]. Besides, Pr^{3+} can be used as deactivator ions, which is advantageous to population inversion by reducing the lifetime of the lower laser level [8,9]. Knowles and Jenssen [10] reported in detail the Er:BaY_2F_8 crystal codoped with Pr ions. In 2009, Tu et al. [11] determined the efficiencies of energy transfer of Er, Pr:GGG crystal, which are 64.2% and 96.5% for $^4I_{11/2}$ and $^4I_{13/2}$ energy levels between Er^{3+} and Pr^{3+}, respectively. In addition, a 284 mW laser output at 2.79 μm has been achieved in Er,Pr:GYSGG crystal, and the lifetime of the lower laser level ($^4I_{13/2}$) decreases from 3.9 to 0.6 ms. Compared with the 315 mW threshold of Er:GYSGG laser, the one of Er,Pr:GYSGG laser was reduced to be 112 mW due to the doped 0.3 at.% Pr^{3+} ions [12].

For outer space and some harsh radiation environment applications, the solid-state laser may be exposed to high-energy particles and cosmic rays [13]. It is attractive and necessary to search novel crystals that have great radiation resistant property for the application of laser device under the radiation environment. At present, the common host materials of 2.7–3.0 μm erbium lasers are $Y_3Al_5O_{12}$ (YAG), $LiYF_4$, $Y_3Sc_2Ga_3O_{12}$ (YSGG), and $Gd_3Sc_2Ga_3O_{12}$ (GSGG) et al. [14–18]. Unfortunately, the radiation resistance ability of YAG [19], $LiYF_4$ [20] and YSGG [21] is weak and not suitable for application in an environment of ionizing radiation. Although the radiation resistance ability of GSGG crystal is strong, but it contains easily volatile Ga element and leads to the crystal growth with large size and compositions consistency are difficult. GSAG is a kind of crystal that colligates the advantages of GSGG and YAG crystals [22]. The GSAG crystal does not contain the volatile Ga element and also exhibits better radiation resistance ability than YAG crystal [23,24], which means that GSAG crystal can be deemed as a potential material with large size growth for applying in irradiation environment such as outer space. Up to now, the growth, spectral analysis and laser action of Er:GSAG crystal only with low Er^{3+} doped concentration have been carried out [25]. For exploring a novel 2.6–3.0 μm laser materials with excellent radiation resistant property

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and high laser efficiency, it is meaningful to grow Er, Pr:GSAG crystals and investigate their physical and optical properties.

In this study, Er,Pr:GSAG crystal was grown by Czochralski method, and the growth, structure, crystalline quality and radiation resistant properties of this crystal were investigated. The absorption and fluorescence spectra of Er,Pr:GSAG crystal were investigated before and after gamma radiation. Meanwhile, the luminescence properties in visible and near-IR regions are also measured to explore the function of deactivator ion of Pr^{3+}. Optical parameters related to the laser performance of Er,Pr:GSAG crystal is compared and analyzed to Er:GSAG crystal.

2. Experimental details

2.1. Crystal growth

High quality Er,Pr:GSAG crystal was grown along the < 111 > direction using Czochralski (CZ) method. The initial raw materials were Gd_2O_3 (5 N), Sc_2O_3 (5 N), Al_2O_3 (5 N), Er_2O_3 (5 N), and Pr_6O_{11} (5 N) oxide powders. The GSAG crystal was designed according to the formula of $Gd_{2.88}$ $Sc_{1.89}Al_{3.23}O_{12}$ in Ref. [26]. The oxides were mixed adequately for 24 h and pressed into disks. All the disks were loaded into an iridium crucible. The crystal was grown in nitrogen atmosphere with a rotation speed of 4.0–8.0 rpm and a pulling rate of 0.5–2 mm/h. The photograph of the as-grown Er,Pr:GSAG crystals are shown in Fig. 1. The as-grown crystal is transparent and crack-free with the dimension of Φ 30 mm × 70 mm, and no scattering points can be observed by a 100 mW 532 nm laser. The samples with the thickness of 2 mm were cut along < 111 > direction from the as-grown crystal and polished on both sides for the spectroscopic experiments.

2.2. Characterization

A high resolution X'pert Pro multipurpose powder diffractometer (MPD) with a hybrid $K\alpha_1$ monochromatic was used to collect the X-ray rocking curve (XRC) to identify the crystalline quality of the crystals. The crystal structure was examined by X-ray powder diffraction (XRD) using Cu kα radiation (X'pert PRO). The diffraction data were collected from 10° to 90° in 2θ range. The X-ray fluorescence analysis (XRF-1800) was used to measure the concentrations of Er and Pr elements in the as-grown crystals. The Er,Pr:GSAG samples for irradiation measurement were illuminated by $a^{60}Co$ gamma-ray source with the dose rate of 26.89 Gy/min, radiation times of 240, 480, and 720 h at room temperature, corresponding to the doses of about 3.9×10^5, 7.7×10^5, and 1.16×10^6 Gy, respectively. The absorption spectra were recorded by a spectrophotometer (PE Lambada 950 UV/VIS/NTR) with a spectral interval of 0.2 nm. The fluorescence spectra and the fluorescence decay curves were measured by a fluorescence spectrometer (Edinburgh FLSP 920). The excitation sources of the fluorescence spectra were a 450 W Xenon lamp (visible spectra; Xe 900) and a 968 nm InGaAs laser diodes (infrared spectra; nLIGHT OPTOTOOLS DL System). And a microsecond lamp (Edinburgh μF 920H) and an OPO laser (Opolette 355 I) were used as the excitation sources for the fluorescence lifetime measurement. All

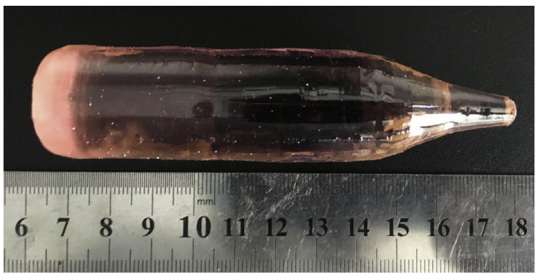

Fig. 1. Photograph of the as-grown Er, Pr:GSAG crystal.

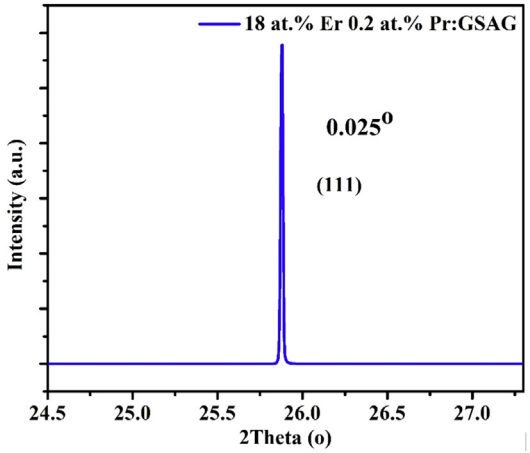

Fig. 2. X-ray rocking curve for Er, Pr:GSAG crystals of (111) face.

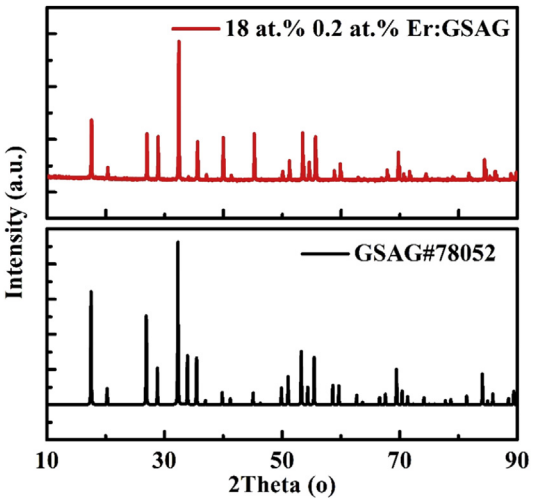

Fig. 3. XRD patterns of Er, Pr:GSAG single crystal.

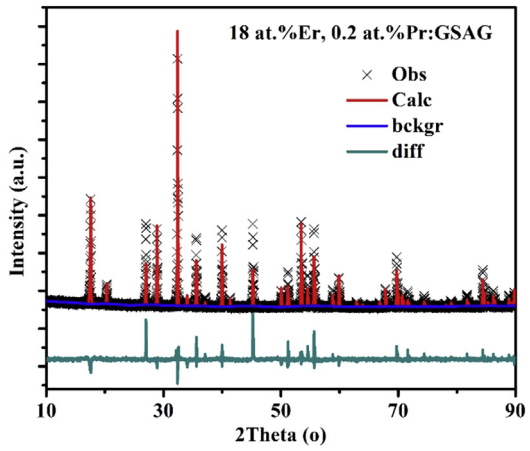

Fig. 4. Rietveld refinement results of Er, Pr:GSAG crystal obtained from the XRD data.