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Growth and spectroscopic properties of Yb:$Lu_{1.5}Y_{1.5}Al_5O_{12}$ mixed crystal

Shishu Cheng [a,b], Xiaodong Xu [a,*], Dongzhen Li [a,b], Dahua Zhou [a,b], Feng Wu [a], Zhiwei Zhao [a], Jun Xu [c]

[a] Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China
[c] Key Laboratory of Transparent and Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China

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ABSTRACT

Yb^{3+}-doped $(Lu_{0.5}Y_{0.5})_3Al_5O_{12}$ (Yb:LuYAG) single crystal has been grown by the Czochralski method. The segregation coefficient of Yb^{3+} was studied by the inductively coupled plasma atomic emission spectrometry (ICP-AES) method. The crystal structure has been determined by X-ray diffraction analysis. The absorption and emission spectra and fluorescence lifetime of Yb:LuYAG crystal were measured at room temperature. The spectroscopic parameters of Yb:LuYAG crystal were compared with those of Yb:YAG and Yb:LuAG crystals with the same doping level. The results indicate that Yb:LuYAG crystals are potential candidates for high-power ultrashort pulse lasers.

1. Introduction

Recent development of InGaAs laser diodes has stimulated interest in Yb^{3+}-doped solid state materials as gain media for diode-pumped high-power lasers emitting in the spectral range near 1 μm [1–3], and Yb^{3+}-doped materials have been recently reported to be applied in laser cooling of the solids [4]. Broad gain bandwidth of these materials has stimulated their applications for generation of ultrashort pulses in mode-locked regime. YAG and LuAG are excellent host materials and possess many features for high average power laser applications [5–10]. However, a narrow emission band at the main emission peak limits shorter pulse laser output. For further shortening the mode-locked pulses, it is necessary to broaden the gain bandwidth of the material. One of the possible ways is to use the mixed crystals due to their disordered natures resulting in inhomogeneous broadening of fluorescence lines, with expectations of improving the laser performance in mode-locked regimes [11–14]. Optical grade single crystals of $(Lu_xY_{1-x})_3Al_5O_{12}$ (LuYAG) solid solution series can be easily grown by Czochralski method and the solidification points, lattice parameters, effective segregation coefficients, refractive indices and thermal properties of LuYAG crystals were reported [15]. Tm^{3+}-doped LuYAG mixed crystals are attractive media for laser-radar in the 2 μm region because its laser wavelength is superior to that of Tm:LuAG and Tm:YAG crystals [16]. Ytterbium ion in LuYAG mixed crystals is expected to exhibit a wider emission band due to disordered crystal-field in the crystals.

In this paper, Yb:$Lu_{1.5}Y_{1.5}Al_5O_{12}$ crystal was grown by Czochralski method for the first time to our knowledge. The spectroscopic properties of Yb:LuYAG were measured and compared with those of Yb:YAG and Yb:LuAG with the same Yb^{3+} concentration.

2. Experiments

Yb:$Lu_{1.5}Y_{1.5}Al_5O_{12}$ single crystal with 10 at.% doped concentration was grown by the Czochralski technique. The start materials used were Yb_2O_3, Lu_2O_3, Y_2O_3 and Al_2O_3 with at least 99.995% purity. The detailed crystal growth procedure was similar with that of Yb:YAG crystals described elsewhere [17] and it can also be referred in [15], which reported the growth of pure LuYAG crystal. Because the solidification point of $Lu_{1.5}Y_{1.5}Al_5O_{12}$ crystal is 1970 °C, which is lower than that of LuAG crystal (2010 °C), but higher than that of YAG crystal (1930 °C), we chose the <1 1 1>-oriented LuAG crystal as seed.

Samples for spectroscopic measurements were cut from the boule and surfaces perpendicular to the <1 1 1>-growth axis were polished. The thickness of the sample is 1.2 mm. The absorption spectra were measured in the wavelength range from 300 to 1200 nm using a Lambda 900 spectrophotometer (Perkin-Elmer Company). The luminescence spectrum of the sample was recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon, Edision, USA) equipped with a Hamamatsu R928 photomultiplier tube. A 940 nm continuous wave diode laser was used as the excitation source. The decay time was measured using a computer controlled

* Corresponding author. Tel.: +86 21 69918484; fax: +86 21 69918607.
E-mail address: xdxu79@yahoo.com.cn (X. Xu).

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transient digitizer. All measurements were performed at room temperature.

The actual concentrations of Yb^{3+}, Y^{3+} and Lu^{3+} ions in the crystals were measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The sample was cut from the upper part of the as-grown Yb:LuYAG crystal, and then was ground to powder in an agate mortar for measurement. The crystal structure of as-grown Yb:LuYAG single crystal was analyzed by X-ray diffraction (XRD) using Cu Kα radiation (Ultima IV diffractometer, Rigaku, Japan) at a scan width of 0.02° within $2\theta = 10–90°$. Fine ground powder of the as-grown Yb:LuYAG single crystal was used as the sample.

3. Results and discussion

The Yb:LuYAG single crystal of good optical quality up to 40 mm in length and 30 mm in diameter is shown in Fig. 1, and the crystal boule was cyan in color and free from cracks, inclusions and scattering centers. The cyan color could be removed by annealing the samples in air atmosphere at 1200 °C for 24 h. The crystals became navy blue after annealed in hydrogen atmosphere at 1000 °C for 24 h.The segregation coefficient for Yb^{3+} in Yb:LuYAG crystal can be calculated according to the following formula [17]:

$$K_m = C_t/C_0 \quad (1)$$

where C_t is the Yb^{3+} concentration at the growth starting position in the crystal; C_0 is the initial Yb^{3+} concentration in the melt. The segregation coefficient of Yb^{3+} in Yb:LuYAG crystal was calculated to be 1.10. The segregation coefficient for Y ions is 0.85, which is not far from that in $Lu_{1.5}Y_{1.5}Al_5O_{12}$ crystal (0.89) [15]. It is widely known that for bulk crystals grown by Czochralski technique, the transversal dopant distribution is almost uniform, but if the segregation coefficient is not equal to 1, the longitudinal distribution will vary a lot in different parts of the boule. The actual concentration of Yb^{3+} in different parts can be calculated by the equation:

$$C_s = C_0 K_m (1-g)^{K_m - 1} \quad (2)$$

where g is the crystallized fraction of the melt, K_m is the segregation coefficient and C_0 is the initial Yb^{3+} concentration in the melt.

The structure of Yb:LuYAG has been determined by X-ray diffraction analysis, which is shown in Fig. 2. The result reveals the Yb:LuYAG crystal crystallizes in cubic with space group Ia3d and has the cell parameters: $a = 1.1949$ nm, $V = 1.7061$ nm^3. The cell parameter is much smaller than that of $Lu_{1.5}Y_{1.5}Al_5O_{12}$ crystal ($a = 1.1958$ nm) [15]. The radius of Yb^{3+} ion (0.0985 nm) is not far from the radius of Lu^{3+} ion (0.0977 nm), but smaller than that of Y^{3+} (0.1019 nm). The Yb^{3+} ions of smaller radius are in the place of Y^{3+} ions of larger radius resulting in smaller cell parameter [18].

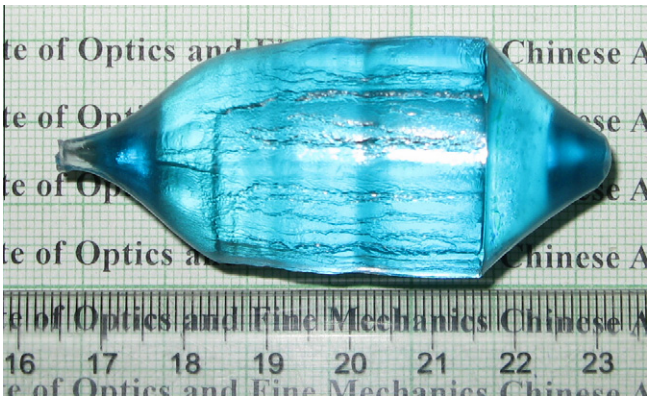

Fig. 1. The photograph of as-grown Yb:LuYAG crystal boule.

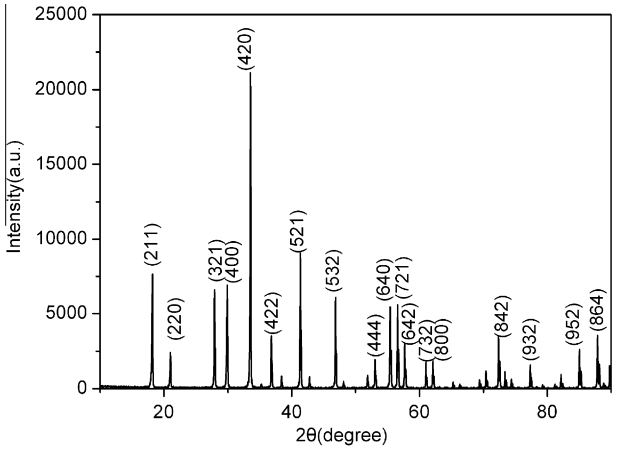

Fig. 2. Powder XRD pattern of Yb:LuYAG crystal.

Fig. 3 shows the absorption spectra of as-grown and after annealed Yb:LuYAG crystal in the visible wavelength region at room temperature. There are two absorption bands locating at wavelengths 372 and 610 nm, respectively, in as-grown and H_2-annealed Yb:LuYAG crystals. The absorption peak at 372 nm corresponds to the f → d electron transition of Yb^{2+} ions in the crystal, while the absorption peak at 610 nm is due to the Re-F color centers in the crystal [19]. The crystal was grown in an inert atmosphere, which brought a lot of oxygen vacancies and formed Re-F color centers. Yb^{2+} and Re-F color centers are detrimental to the intrinsic spectroscopic performances of Yb:LuYAG. After H_2-annealing, the color center absorption peaks increased in intensity, and the main band position moved a little to the longer wavelength. On the other hand, the absorption bands disappeared after air-annealing, as Yb^{2+} ions have been oxidized to be Yb^{3+} and oxygen vacancies have been filled, consequently eliminating the color centers.

The absorption spectrum of Yb:LuYAG crystal in the range of 850–1050 nm is presented in Fig. 4. The absorption bands of Yb^{3+} ion were centered at 916, 939, 969 and 1029 nm, corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}. The multi-peak absorption is attributed to the crystal-field splitting in the host material. The maximum absorption band at 939 nm has a FWHM (full width at half maximum) of 25 nm, which is suitable for InGaAs diode-laser pumping. The absorption coefficients at 939 and 969 nm are 10.04 and 6.40 cm^{-1}, respectively. The absorption cross-sections are 0.66×10^{-20} cm^2 and 0.42×10^{-20} cm^2 at 939 and 969 nm in turn. A wide FWHM means the laser crystal is less sensitive to diode

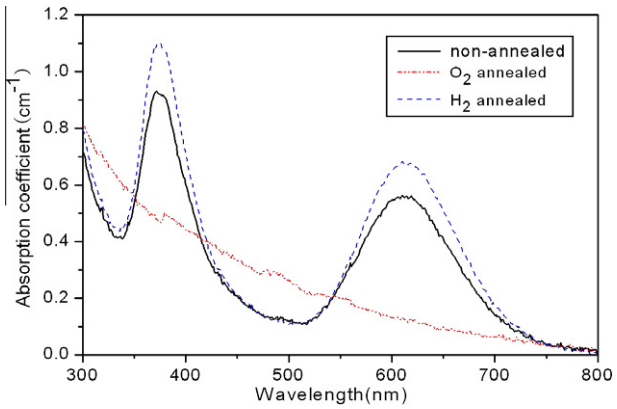

Fig. 3. Absorption spectra of as-grown and after annealed Yb:LuYAG crystal in the visible wavelength region.