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Growth and optical properties of Dy:$Y_3Al_5O_{12}$ crystal

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ABSTRACT

High optical quality Dy:$Y_3Al_5O_{12}$ (Dy:YAG) crystal has been grown by the Czochralski method. Absorption spectra, fluorescence spectra and fluorescence decay curve of Dy:YAG have been recorded at room temperature. The strongest emission of Dy:YAG crystal is near 583 nm, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. The Judd-Ofelt parameters Ω_2, Ω_4 and Ω_6 were calculated to be 1.49×10^{-20} cm^2, 0.94×10^{-20} cm^2 and 3.20×10^{-20} cm^2, respectively. The radiative transition rates, branching ratios and the emission cross sections were calculated. The fluorescence and radiative lifetimes are 0.40 ms and 1.02 ms, respectively, resulting in a quantum efficiency of 39.2%. The results indicate that the Dy:YAG crystal would be a promising yellow solid state laser material.

1. Introduction

Visible lasers around the yellow region of 560–590 nm have important applications in a variety of scientific and technological fields, such as astronomy, telecommunication, biotechnology and medical treatment [1–3]. Dy^{3+} ion is one of the best suitable candidates for yellow laser due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. In 2000, Kaminskii et al. demonstrated the visible laser operation of Dy^{3+} ions in $KY(WO_4)_2$ single crystals at nitrogen cryogenic temperature under Xe-flashlamp pumping for the first time [4]. Recent development of InGaN laser diode has stimulated interest in Dy^{3+} doped solid state materials for direct yellow laser emission [5]. In 2012, S. R. Bowman et al. demonstrated the first InGaN diode pumped solid state laser (Dy:YAG) [6] emitting in the yellow, but the laser was only operated in pulsed mode. Continuous-wave Dy,Tb:$LiLuF_4$ [7] laser and Dy:$ZnWO_4$ [8] laser were also reported under the pumping of InGaN diode lasers.

Yttrium aluminium garnet (YAG) crystal is an excellent laser gain medium due to its high thermal conductivity and excellent physical and chemical properties [9]. There are few reports on the spectroscopic characteristics of Dy:YAG crystals [10–12]. To the best of our knowledge, the crystal growth and the spectral parameters based on Judd-Ofelt theory has not been investigated yet. In this work, we demonstrated the growth of Dy:YAG crystal by Czochralski method. Spectroscopic characteristics relevant to potential yellow laser output were discussed in detail.

2. Experimental

2.1. Crystal growth

The Dy:YAG crystal was grown by the Czochralski method. The 99.999% pure Dy_2O_3, Y_2O_3 and Al_2O_3 powders were dried and weighed according to the formula $(Dy_{0.03}Y_{0.97})_3Al_5O_{12}$. After the compounds were ground and mixed, they were pressed into bulks and then sintered at 1300 °C for 20 h in the air. The crystal was grown at a pulling rate of 1 mm/h and a rotation rate of 10–20 rpm. High-purity nitrogen gas was introduced as a protective atmosphere. The as grown Dy:YAG crystal with the size of $\Phi 30 \times 55$ mm^3 is shown in Fig. 1. The crystal was yellowish and free from cracks, inclusions and precipitations.

2.2. XRD and ICP-AES measurement

The sample for X-ray powder diffraction (XRD) and inductively coupled plasmas atomic emission spectroscopy (ICP-AES) measurement was cut from the crystal adjacent the seed crystal positions and then grinded to powder in an agate mortar. Structure of the sample was

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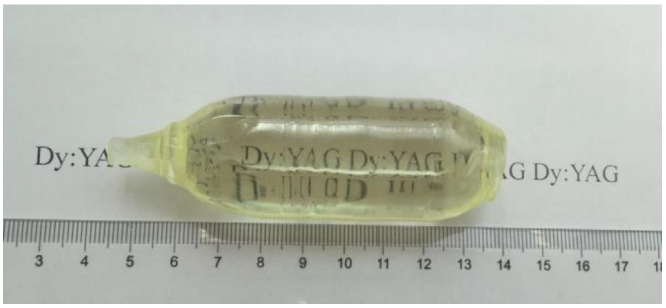

Fig. 1. The as-grown Dy:YAG crystal.

examined using an automated Ultima IV diffractometer (Rigaku, Japan). The power XRD pattern of as-grown Dy:YAG crystal is shown in Fig. 2. The diffraction peaks of the sample are in quite agreement with the standard JCPDS cards of YAG (PDF#33–0040) [13] and there are no additional impurity peaks in the pattern, which confirms their cubic system with space group Ia3d. The lattice parameter of Dy:YAG were calculated to be 12.0047Å, which is smaller than that of YAG (12.0116Å) [14].

The segregation coefficient K_m of Dy^{3+} ion in YAG crystal was calculated according to Eq.:

$$K_m = \frac{C_{top}}{C_0} \tag{1}$$

where C_{top} and C_0 are the concentrations of Dy^{3+} ions in the crystal and initial raw materials, respectively. The segregation coefficient of Dy^{3+} ion in YAG crystal was calculated to be 0.49.

2.3. Spectroscopic measurement

Samples for spectroscopic measurements were cut out of the boules and surfaces perpendicular to the <111> growth axis were polished. The absorption spectra were measured with a UV–VIS–NIR spectrophotometer (Model Cary-5000, Varian, USA) at room temperature. The fluorescence spectra, as well as the decay curve at 584 nm, were recorded using Edinburgh Instruments FLS980 spectrophotometer under 384 nm excitation.

3. Results and discussion

3.1. Absorption spectrum and Judd–Ofelt theory analysis

The absorption spectra in the range from 300 to 1900 nm are shown in Fig. 3. We can see thirteen absorption bands in Dy:YAG crystal and the

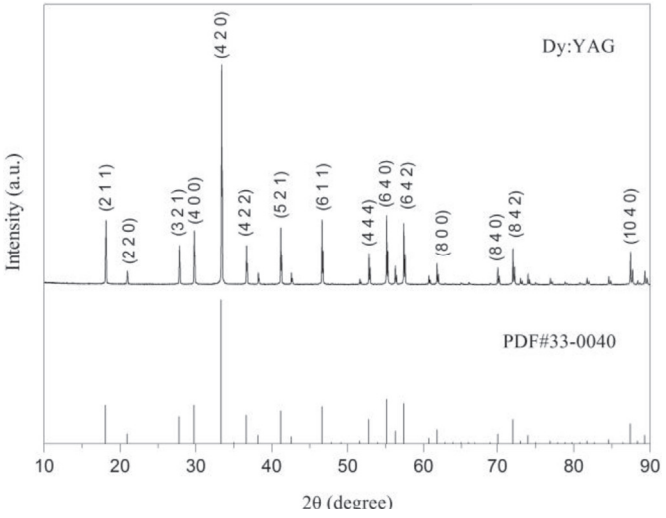

Fig. 2. XRD of the as grown Dy:YAG crystal.

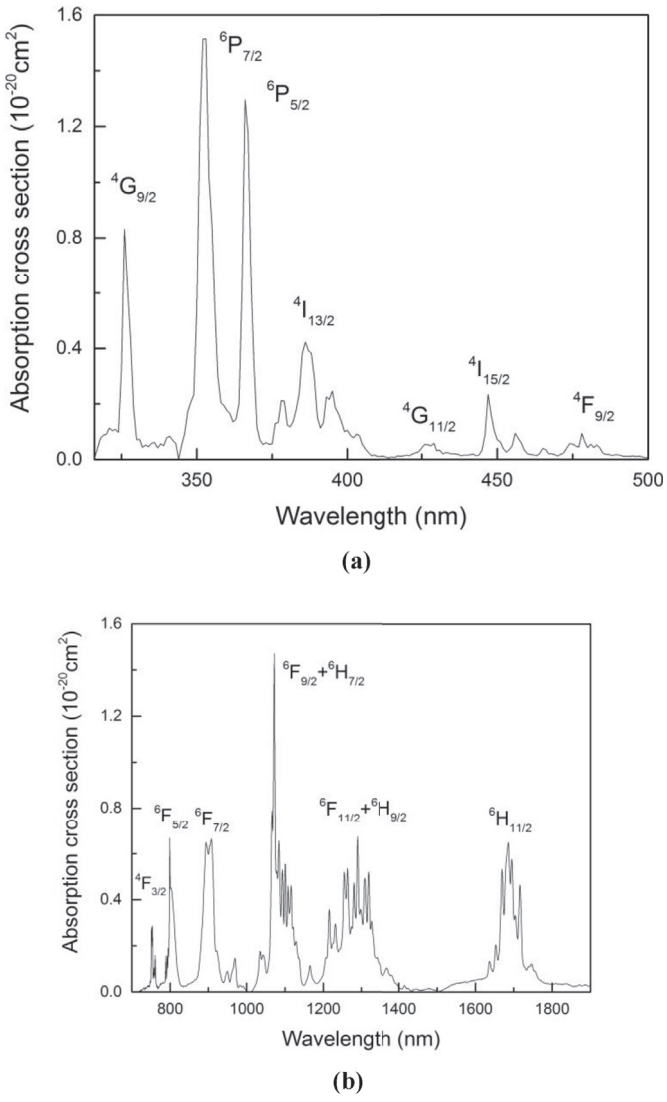

Fig. 3. Absorption spectra of Dy:YAG crystal at room temperature. (a) 300–500 nm; (b) 700–1900 nm.

absorption bands with peaks at 326 nm, 353 nm, 366 nm, 386 nm, 429 nm, 447 nm, 478 nm, 754 nm, 799 nm, 908 nm, 1072 nm, 1290 nm and 1686 nm are associated with Dy^{3+} transitions from the $^6H_{15/2}$ ground state to $^4G_{9/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^4F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$ + $^6H_{7/2}$, $^6F_{11/2}$ + $^6H_{9/2}$ and $^6H_{11/2}$ excited states, respectively. Among the absorption bands, the absorption peak at 447 nm corresponding to the $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition is suitable for blue laser diode pumping. The absorption cross section and the full widths at half-maximum (FWHM) at 447 nm were calculated to be 2.3×10^{-21} cm^2 and 1.9 nm. The absorption cross section is somewhat higher than the value of 1.6×10^{-21} cm^2 reported for Dy:YAG crystal [6] and 1.1×10^{-21} cm^2 reported for Dy:YAG ceramic [15].

The radiative transition of a lanthanide ion corresponding to the $4f^N$ configuration could be analyzed using the Judd-Ofelt (J-O) theory [16,17]. In this work, nine Dy^{3+} absorption bands were chosed to determine the J–O intensity parameters.

According to the J–O theory, the calculated line strength $S_{cal}(J, J')$ for electric-dipole transitions can be expressed as following:

$$S_{cal}(J, J') = \sum_{i=2,4,6} \Omega_t \left| \langle S, L, J || U^{(t)} || S', L', J' \rangle \right|^2 \tag{2}$$

where $\langle ||U^{(t)}|| \rangle$ is the squared reduced matrix elements, which was calculated by Carnall for Dy^{3+} [18], Ω_t (t = 2, 4, 6) are the J-O intensity