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Crystal growth, polarized spectroscopy and Judd-Ofelt analysis of Pr:$YAlO_3$

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ABSTRACT

Pr^{3+}-doped $YAlO_3$ (YAP) single crystal was successfully grown by the Czochralski (Cz) method. Polarized absorption and polarized fluorescence spectra were measured at the room temperature. The spectroscopic parameters based on the polarized absorption spectra were calculated by Judd-Ofelt (J-O) theory for the first time. The fluorescence lifetime of $^3P_0$ energy level was fitted to be 19.16 μs with the quantum efficiency of 95.8%. Through the analyzing of the spectroscopic properties, Pr:YAP crystal was demonstrated to be a promising candidate for solid state laser operation.

1. Introduction

Visible lasers are highly useful for underwater detection, indoor optical communication, visible display and biomedical diagnosis [1–4]. In the past 20 years, the rise of blue GaN/InGaN LD has motivated a lot of research on visible lasers of rare earth doped materials [5], in which the direct pumping for visible laser highly improves the pumped efficiencies and decreases the complexity of the device.

The trivalent Pr^{3+} ion is very interesting because of the plentiful energy levels in visible laser region. So far, a large number of reports on the laser operation in Pr^{3+} ions doped materials have been published [6–14]. Among these materials, the fluoride crystals, which can decrease the non-radiative transition and absorption of the excited state due to the characteristic of low phonon energy, are the most prominent hosts. For example, the continuous-wave (cw) laser operation of Pr:$LiYF_4$ crystal at 639 nm has been realized with the output power of 112 mW pumped by the blue GaN/InGaN LD [14]. However, the thermo-mechanical properties of fluoride materials are not good. Therefore, it is desired for new materials with both low phonon energy and excellent thermo-mechanical properties.

YAP crystal belongs to a biaxial crystal which has prominent physical characteristics such as low phonon energy (570 cm^{-1}) [15], high hardness (Mohs hardness 8.5–9) and high thermal conductivity (~11 $W\,m^{-1}\,K^{-1}$ at 300 K) [15]. Moreover, rare ions doped YAP crystals have been investigated widely [16–20]. The spectra properties and laser operation of Pr:YAP crystal have also been studied [21–23]. Unfortunately, the JO theory analysis on polarization spectra of Pr:YAP has not been reported.

In this work, the polarization spectra properties and JO theory analysis of Pr:YAP crystal were discussed. Besides, the spectroscopic parameters of Pr^{3+} ions doped YAP and other host were compared.

2. Experiments

2.1. Crystal growth

Pr^{3+} doped YAP crystal was successfully grown by the Cz method. The Y_2O_3 (99.99%), Al_2O_3 (99.99%) and Pr_6O_{11} (99.99%) powders were used as starting materials and weighed according to the formula $Pr_xY_{1-x}AlO_3$ (x = 0.004). The powders were mixed in an agate jar, pressed into bulks and then sintered in air at 1300 °C for 20 h. The crystal was grown along the crystalline b-axis. The pulling rate was 1 mm/h and the rotation rate was 16–20 rpm. High-purity nitrogen gas was chosen as a protective atmosphere to prevent the Ir crucible from oxidation. The solid-melt interface was convex toward the melt which could prevent the dislocations and impurities into the crystal. In order to avoid cracking, the crystal was pulled off from the melt after its growth and then slowly cooled to room temperature. Finally, a Pr: YAP crystal ($\Phi 28 \times 80\ mm^3$) free from cracks and inclusions was obtained, which is shown in Fig. 1.

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Fig. 1. Photo of the as-grown Pr:YAP crystal.

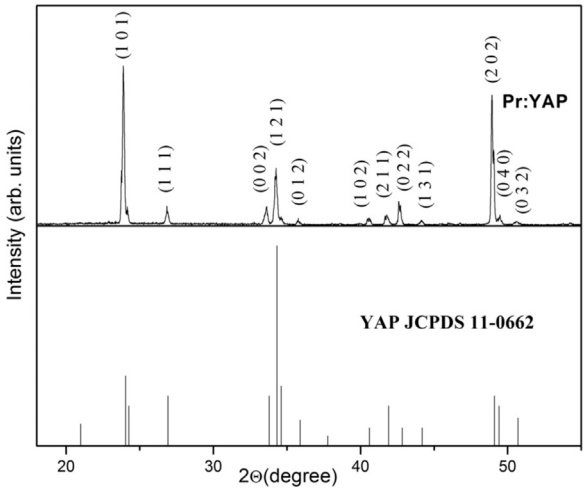

Fig. 2. Powder XRD pattern of the Pr:YAP crystal.

2.2. Spectra measurements

To verify the structure of Pr:YAP crystal, X-ray powder diffraction (XRD) was analyzed. The sample was ground to be powders and then measured by an automated Ultima IV diffractometer (Rigaku, Japan). The XRD pattern of Pr:YAP crystal is shown in Fig. 2. The diffraction peaks of sample are in good agreement with JCPDS 11–0662 and no noteworthy change was found in the lattice structure after Pr^{3+} ions doped into YAP crystal. The cell parameters of Pr:YAP crystal were calculated to be a = 0.5318 nm, b = 0.7385 nm and c = 0.5175 nm, which were very similar to the unalloyed YAP parameters (a = 0.5330 nm, b = 0.7375 nm and c = 0.5180 nm) [24]. The results indicate that Pr:YAP belongs to a biaxial crystal with the orthorhombic D_{2h}^{16} space group. The sample was cut into 7 mm × 6 mm × 5 mm from the grown crystal and the six faces were mechanically polished. Each face of the sample was perpendicular to one of the three principal crystallographic directions a, b, c, respectively. The concentration of Pr^{3+} ions at the head position of Pr:YAP crystal was obtained to be 0.25 at.% by inductively coupled plasma and atomic emission spectrometry (ICPAES, Ultima2, Jobin-Yvon). What's more, the segregation coefficient of Pr^{3+} ions in Pr:YAP crystal was calculated to be 0.524. The polarized absorption spectra from 400 to 2500 nm with the resolution of 1 nm were performed by a Spectrometer (Lambda900, Perkin-Elmer UV–VIS–NIR) and the polarized emission spectra were measured by a Fluorescence Spectrophotometer (FSP920, Edinburgh). Fluorescence lifetime was recorded by a spectrometer (FLS-980, Edinburgh). All the measurements in this paper were taken at room temperature.

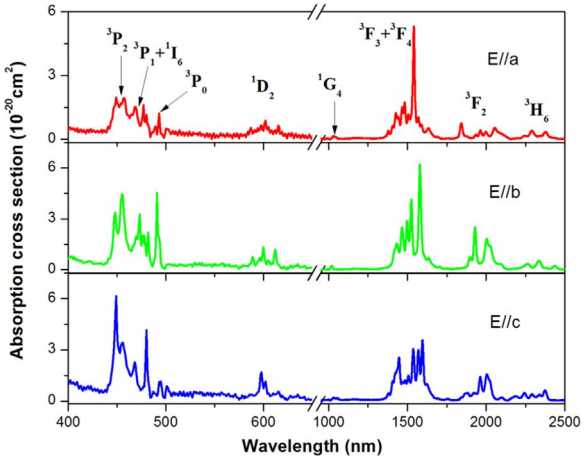

Fig. 3. Polarized absorption spectra of Pr:YAP crystal.

3. Results and discussion

3.1. Absorption spectra

The room-temperature polarized absorption spectra of Pr:YAP crystal measured in the range from 400 to 2500 nm are shown in Fig. 3. It can be found that the absorption spectra are polarization dependent where the relative absorption intensities of three polarized directions are different with each other [21]. All the absorption transitions from the ground level $^3H_4$ are marked in Fig. 3. The absorption spectra consists of mainly eight absorption bands which are corresponding to the transitions $^3H_4 \rightarrow {}^3P_2$, $^3P_1 + {}^1I_6$, $^3P_0$, $^1D_2$, $^1G_4$, $^3F_3 + {}^3F_4$, $^3F_2$ and $^3H_6$ respectively. The different peaks of each absorption band are because of the stark splitting of energy levels by the host crystal field. Besides, the $^1G_4$ multiplet is poorly resolved from the backdrop noise due to the thermal population of the sub-levels of the ground state $^3H_4$ [11]. Furthermore, some absorption bands are difficultly resolved from the neighboring absorption bands on account of the interaction with neighboring energy levels through strong energy overlap and crystal field, which their energy level separations are relatively lower than the neighboring energy level. The peak wavelengths for a, b and c polarization are at 449 nm, 448 nm and 449 nm, respectively. The corresponding absorption coefficients of Pr^{3+} ions are 0.71 cm^{-1}, 1.43 cm^{-1} and 2.65 cm^{-1}, FWHM are 6.8 nm, 5.2 nm and 5.6 nm, and the absorption cross sections are 1.69×10^{-20} cm^2, 3.41×10^{-20} cm^2 and 5.64×10^{-20} cm^2, respectively. The absorption cross sections of Pr:YAP crystal are higher than that of Pr, Mg:$CaAl_{12}O_{19}$ (1.1×10^{-20} cm^2) [25] and Pr, Mg:$SrAl_{12}O_{19}$ (1.3×10^{-20} cm^2) [26], which makes Pr: YAP crystal to be easier for laser operation pumped by the GaN/InGaN LD.

3.2. J-O analysis

The J-O theory [27,28] is an useful method for analyzing spectroscopic properties of rare earth ions in glasses and crystals. Generally, most of the absorption bands are mainly from electric-dipole. So in this calculation, the magnetic-dipole transitions were not taken into account [29,30]. The absorption line strength $S_{exp}(J, J')$ from the ground state $^3H_4$ can be calculated by:

$$S_{exp}(J, J') = \frac{3hc(2J+1)}{8\pi^3 e^2 N} \frac{9n}{(n^2+2)^2} \frac{\ln 10}{\bar{\lambda} L} \int OD(\lambda) d\lambda \quad (1)$$

where $\bar{\lambda}$ indicates the mean wavelength, $OD(\lambda)$ represents the measured optical density and n is the refractive index of YAP crystal which can be obtained by the following equation [31]:

$$n^2(\lambda) = 1 + \frac{A\lambda^2}{\lambda^2 - B} \quad (2)$$