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Optical spectroscopy of Dy^{3+}-doped $CaGdAlO_4$ single crystal for potential use in solid-state yellow lasers

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ABSTRACT

The crystal growth, optical spectra and lifetime of Dy:$CaGdAlO_4$ crystal were investigated for the first time to our best knowledge. Single Dy:$CaGdAlO_4$ crystal with size of $\Phi4 \times 40$ mm^3 was grown by floating zone method. The peak absorption cross-sections were calculated to be $2.43 \times 10^{-21} cm^2$ and 1.28×10^{-21} cm^2 at 453 nm for σ and π polarizations. The Judd-Ofelt (JO) parameters of Ω_2, Ω_4 and Ω_6 were calculated to be $1.8 \times 10^{-20} cm^2$, $1.0 \times 10^{-20} cm^2$ and $0.5 \times 10^{-20} cm^2$, respectively. The emission cross-sections were calculated to be $0.51 \times 10^{-20} cm^2$ and $0.55 \times 10^{-20} cm^2$ for σ and π polarizations. The fluorescence decay time is 222 μs. The results indicate that the Dy:$CaGdAlO_4$ crystal is a potential candidate for yellow laser operation.

1. Introduction

Recent development of InGaN laser diode stimulates interest in rare earth doped solid state materials to be used as visible laser media [1,2]. Visible laser emission has potential applications in scientific and technological fields, such as astronomy, biomedicine, medical treatment and surgery [3,4]. Trivalent praseodymium (Pr^{3+}) is the most established rare earth ion for the generation of visible laser transition. Efficient laser emission has been demonstrated in the blue, green, orange, red and deep red spectral regions from Pr^{3+}-doped laser materials [5–9]. But there is still a blank region around the yellow emission which is not covered by Pr^{3+}-doped lasers. Trivalent dysprosium (Dy^{3+}) is a good candidate for realizing the yellow laser operation. In 2012, first InGaN diode pumped Dy:YAG solid-state laser emitting in the yellow was demonstrated with a slope efficiency of 12% [10]. In 2014, yellow laser with an output power of 55 mW and a slope efficiency of 13% was obtained by an InGaN diode pumped Dy^{3+}-Tb^{3+} codoped $LiLuF_4$ crystal [11]. Future increases in InGaN laser diode brightness should improve both the power and efficiency of the Dy^{3+}-doped laser materials.

$CaGdAlO_4$ crystal is a member of $ABCO_4$ crystals, where A = Ca, Sr or Ba, B is rare earth ion and C = Al or Ga. Rare earth doped $CaGdAlO_4$ crystals are considered to be outstanding laser media due to its easy growth, high thermal conductivity (6.9 $WM^{-1}K^{-1}$ and 6.3 $WM^{-1}K^{-1}$ along *a* and *c* axes) and excellent laser performances, and the spectra and laser performance of Yb^{3+}, Nd^{3+}, Er^{3+}, Tm^{3+}, or Ho^{3+}-doped $CaGdAlO_4$ crystals have been investigated [12–16]. Unfortunately, no investigations regarding Dy:$CaGdAlO_4$ crystal has been yet reported.

In this paper, crystal growth, optical spectra and lifetime of Dy:$CaGdAlO_4$ crystal were studied for the first time.

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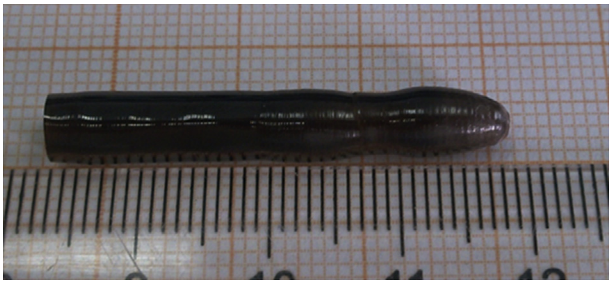

Fig. 1. The obtained Dy:$CaGdAlO_4$ crystal.

2. Experimental procedure

To grow this crystal, raw materials of $CaCO_3$, Gd_2O_3, Al_2O_3 and Dy_2O_3 with 5 N purity were weighted according to $CaGd_{0.97}Dy_{0.03}AlO_4$. The raw powders were mixed together, shaped into a rod and pressed under a hydrostatic pressure of 210 MPa for 2 min. The obtained rod was then put into an alumina crucible and sintered at 1250 °C for 20 h. A feed rod was thus obtained. Dy:$CaGdAlO_4$ single crystal was grown by the floating zone method in a floating zone furnace with two mirrors [17]. A ⟨100⟩-oriented $CaGdAlO_4$ single crystal with dimension of $\Phi 4 \times 20$ mm^3 was used as the seed. The growth atmosphere was air, the growth rate was 2–5 mm/h, and the rotation rate was 5–20 rpm for both the seed crystal and the feed rod. After crystal growth, the obtained Dy:$CaGdAlO_4$ crystal was cooled down to room temperature in 1–3 h.

As shown in Fig. 1, crack free Dy:$CaGdAlO_4$ crystal with 4 mm in diameter and 40 mm in length was thus obtained. No inclusions and low-angle grain boundaries was found. The color centers make Dy:$CaGdAlO_4$ crystal brown. After being annealed at 1250 °C for 20 h in H_2, the color changed to its original color-light yellow.

After determination of the optic axis by an YX-2 Orientator, the annealed Dy:$CaGdAlO_4$ crystal was cut along c-direction and polished to 1 mm in thickness for spectra measurements. The polarized absorption spectra of Dy:$CaGdAlO_4$ crystal in the range of 300–2000 nm were measured by a Cary 5EVarian spectrophotometere. The polarized emission spectra and the decay time of Dy:$CaGdAlO_4$ crystal were measured by Dong Woo Optron DM750 monochromator coupled to a R-928 Hamamatsu photomultiplier under 455 nm exciting. All the measurements were taken at room temperature.

3. Results and discussions

The polarized absorption spectra of Dy:$CaGdAlO_4$ crystal at room temperature are shown in Fig. 2. Because of the uniaxial structure, significant differences can be observed in the oscillator strength between two polarized directions. Absorption bands centered around 326, 352, 366, 387, 429, 453, 467, 757, 800, 904, 1076, 1253 and 1632 nm are corresponding to transitions from the $^6H_{15/2}$ ground state to the excited states of Dy^{3+}, and the transitions were assigned and marked in Fig. 2. The peak wavelength around 450 nm matches well with the emission wavelength of InGaN laser diodes. The maximum absorption cross-sections were calculated to be $2.43 \times 10^{-21} cm^2$ and 1.28×10^{-21} cm^2 at 453 nm for σ and π polarizations, and the full width at half maximum (FWHM) are 4.3 nm and 2.5 nm, respectively.

The JO theory, which is the most popular and useful method for estimating spectroscopic properties of rare earth ions in crystals and glasses, was also analyzed in our paper. The detailed calculation procedures were the same as other literature [18,19]. Nine absorption bands of Dy:$CaGdAlO_4$ crystal were used to determine the JO intensity parameters and the results of the average wavelength ($\bar{\lambda}$), FWHM, absorption cross-section (σ) and the oscillator strength (f_{ed}) are shown in Table 1. The root mean square deviation (RMS $\triangle f$) which was used as measurements of the fitting quality

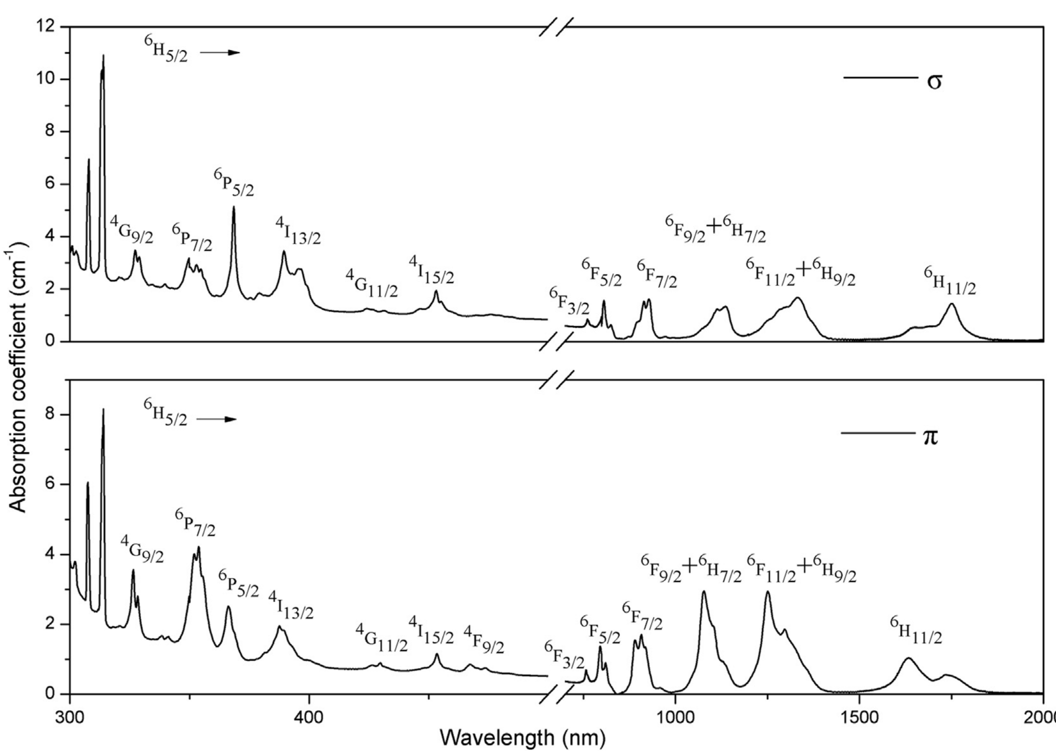

Fig. 2. Polarized absorption spectra of Dy:$CaGdAlO_4$ crystal.