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Crystal growth and spectral characterizations of Ho^{3+}-doped $Li_3Ba_2La_3(MoO_4)_8$ crystal

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Abstract: A large Ho^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ crystal with high optical quality and well-developed appearance was grown by the flux method. The main spectral properties of the crystal, including the absorption spectra, fluorescence spectra and fluorescence decay curves were recorded at room temperature. The Judd-Ofelt (J-O) theory was applied to calculate the oscillator strength parameters Ω_t (t=2, 4, 6), spontaneous emission probabilities, fluorescence branching ratios, and radiative lifetimes of Ho^{3+} ions undergoing transitions from ground state $^5I_8$ to the excited states. The stimulated emission cross-section for the $^5I_7\rightarrow^5I_8$ transition was estimated to be 1.32×10^{-20} cm^2 at 2045 nm by Fuchtbauer-Ladenburg (F-L) equation and the quantum efficiency of the $^5I_7$ level was calculated to be 89%.

Keywords: crystal growth; optical properties; Judd-Ofelt theory; rare earths

Solid-state lasers operating in the eye-safe spectral region around 2 μm have a large variety of applications in fields of medicine, remote sensing, gas detection, etc. Among the rare earth ions, Ho^{3+} and Tm^{3+} are the most frequently studied active ions to realize laser operation in this spectral region. The $^5I_7\rightarrow^5I_8$ transition of Ho^{3+} ions gives rise to a strong emission band around 2.05 μm, which is characterized by high gain cross-sections and long-operating laser wavelength. However, Ho^{3+} ions have no absorption to match the emission of commercially available laser diodes, so it has to be co-doped with a second ion, e.g. Tm^{3+}, Yb^{3+}, Nd^{3+}, which serves as sensitizer to improve the pump efficiency[1–4]. By contrast, the $^3F_4\rightarrow^3H_6$ transition of Tm^{3+} ions has been paid more attention for the development of 2.0 μm lasers in recent years, since Tm^{3+} ions possess a strong absorption band around 800 nm and can be efficiently pumped by the high power and well-developed AlGaAs lasers. Moreover, under the 800 nm radiation, the $^3F_4$ upper laser level could be effectively populated through a cross-relaxation process ($^3H_4+^3H_6\rightarrow^3F_4+^3F_4$), which means that a pump quantum efficiency near two can be expected.

During the last decade, a new series of triple molybdate compounds, with the general formula $Li_3Ba_2RE_3(MoO_4)_8$ (RE=La-Lu), have aroused extensive concern as promising solid state laser materials[5–10]. The main advantages of these crystals include moderate growth condition, broad absorption and emission bands, as well as high quantum efficiency. Previously, we reported some physical and spectral properties of Nd^{3+}, Er^{3+} and Dy^{3+}-doped $Li_3Ba_2Re_3(MoO_4)_8$ crystals, which confirmed them to be good candidates for solid-state lasers[5–7]. Meanwhile, Cascales et al. demonstrated the efficient laser operations around 1.0 and 2.0 μm in Yb^{3+}:$Li_3Ba_2Gd_3(MoO_4)_8$[8] and Tm^{3+}:$Li_3Ba_2Lu_3(MoO_4)_8$[9] crystals, respectively. It is worth mentioning that with a Ti:laser as the pump source, a maximum output power of 515 mW around 2.0 μm, with a slope efficiency up to 71%, was obtained in Tm^{3+}:$Li_3Ba_2Lu_3(MoO_4)_8$ crystals, which is the best laser performance obtained in Tm-doped disordered crystal so far. However, as far as we know, the detailed spectroscopic properties of Ho^{3+} ions in these compounds have never been reported. So, in this paper a systematic investigation on the spectral properties of Ho^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ crystal was presented, and the main spectroscopic parameters relevant to laser applications were calculated to access its potential laser performance around 2.0 μm.

1 Experimental

In our previous research, it was found that $Li_3Ba_2La_3(MoO_4)_8$ crystal melt incongruently and cannot be grown by the convenient Czochralski method[5]. As a result, the crystal was grown by the top seeded solution growth method (TSSG) using Li_2MoO_4 as flux. The ini-

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tial Ho^{3+} concentration in the raw materials was 4 at.% and the molar ratio of $Li_3Ba_2La_3(MoO_4)_8$ to Li_2MoO_4 is 1/5. A single crystal bar with [010] orientation was used as seed. Other details about crystal growth are similar to those of Er^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ and Dy^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ crystals[5,7]. The as-grown Ho^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ crystal with dimensions of 50 mm×20 mm×10 mm was obtained, as shown in Fig. 1(a). We can see that the grown crystal possesses regular appearance and well- developed faces, and no cracks or inclusions is found within the crystal. However, the grown crystal is slightly opaque as the volatilized MoO_3 corrods the surface of the crystal during the growth process.

As the $Li_3Ba_2La_3(MoO_4)_8$ crystal belongs to the monoclinic system, whose indicatrix principal axes are not totally consistent with the crystallographic axes, we must first determine the indicatrix principal axes for spectral measurement. In the monoclinic system, one of the indicatrix principal axes is parallel to the crystallographic *b* axis and the other two principal axes are in the same plane as crystallographic *a* and *c* axes but rotated. Detailed orientation process can be found in Ref. [7]. Since the precise values of the refractive index for the three principal axes were not measured, the three indicatrix principal axes are herein temporarily named as *a'*, *b'* and *c'*, respectively. As shown in Fig. 1(b), the principal axis collinear with the crystallographic *b* axis is named as *b'*; *a'* is clockwise rotated with respect to crystallographic *a* axis by 25º, while *c'* is clockwise rotated with respect to crystallographic *c* axis by ~26º, as the sample is viewed from the minus direction of *b* crystallographic axis.

The accurate concentration of Ho^{3+} ions in the sample, which is an important parameter in the spectral analysis, was measured to be 2.43 at.% by the inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Thus, the corresponding concentration and the segregation coefficient of Ho^{3+} ions in the grown crystal were 1.12×10^{20} cm^2 and 0.61, respectively. The polarized absorption spectra were recorded using a spectrophotometer (Lambda-900, Perkin-Elmer) with a wavelength range from 300 to 2200 nm. The polarized fluorescence spectra and the fluorescence decay curves were measured using an Edinburgh Instruments FLS920 spectrophotometer. All the measurements were carried out at room temperature.

2 Results and discussion

2.1 Absorption spectra and Judd-Ofelt analysis

Fig. 2 shows the polarized absorption spectra of Ho^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ crystals a measured at room temperature. For all polarizations, seven evident absorption bands around 360, 418, 455, 537, 643, 1160 and 1955 nm can be observed, which can be assigned to the intrinsic transitions of Ho^{3+} ions from the ground state $^5I_8$ to the excited multiplets of $^5G_5$+$^3H_6$, $^3G_5$, $^5G_6$+$^5F_1$, $^5S_2$+$^5F_4$, $^5F_5$, $^5I_6$ and $^5I_7$, respectively. One can see that the shapes of the absorption spectra for the three polarizations show little difference, but the absorption intensities depend strongly on the polarizations and absorption bands for *E*//*b'* are in most cases much more intense than those for the other two polarizations.

Since it was put forward by Judd and Ofelt in 1962[11,12], the Judd-Ofelt (J-O) theory has been widely used in the analysis of spectroscopic properties of rare earth ions in crystals and glasses. According to the J-O theory, the experimental oscillator strength $f_{\exp}$ of a transition from the ground multiplet $^5I_8$ to an upper *J'* multiplet can be obtained from the corresponding absorption band by the following equation:

$$f_{\exp,q}=\frac{mc^2}{\pi e^2\bar{\lambda}_{\mathrm{abs}}^2}\int\sigma_a^q(\lambda)\mathrm{d}\lambda \tag{1}$$

where *m* and *e* are the mass and charge of an election, respectively, and *c* is the velocity of light, *q* is the polarization of the absorption spectra, *c* is the velocity of light, λ_{abs} is the mean wavelength of the absorption bands and $\int\sigma_a^q(\lambda)\mathrm{d}\lambda$ is the integrated absorption cross sections. The total oscillator line strength includes both the electric-dipole (ED) and the magnetic-dipole (MD)

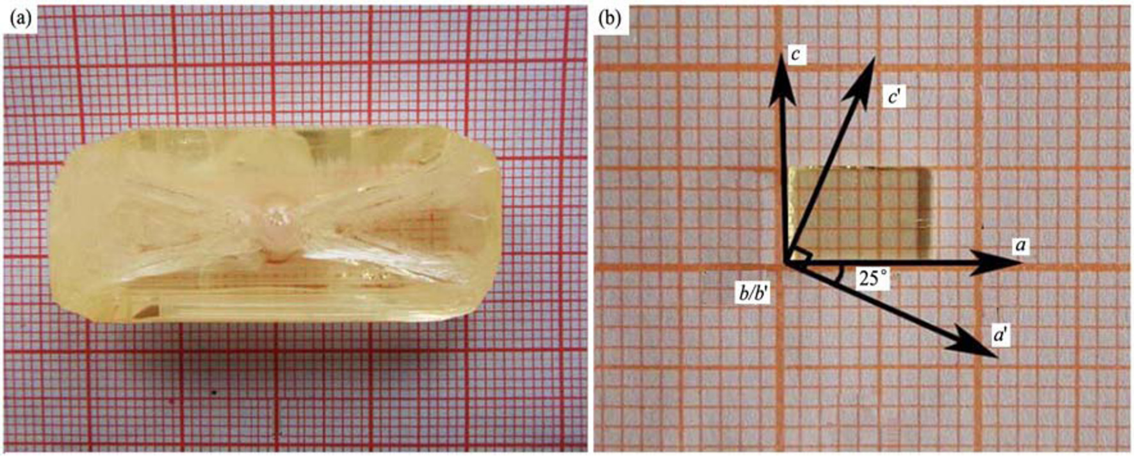

Fig. 1 Grown crystal of Ho^{3+}:$Li_3Ba_2La_3(MoO_4)_8$ (a) and relative position between the optical indicatrix and the crystallographic axes (b)