



# Growth and spectral properties of Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal

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## ABSTRACT

A Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was successfully grown by the Czochralski method. The crystal structure and lattice parameters were determined by the powder X-ray diffraction method. The absorption and fluorescence spectra of the crystal were investigated at room temperature. The refractive index of NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was calculated according to the infrared-corrected Sellmeier equation. Based on the Judd-Ofelt theory, the intensity parameters  $\Omega_t$  ( $t = 2, 4, 6$ ) of Ho<sup>3+</sup> were derived. The spontaneous transition probabilities, the fluorescent branching ratios and the radiative lifetimes of the main multiplets of Ho<sup>3+</sup> ion were calculated as well. The stimulated emission cross section for the transition from <sup>5</sup>I<sub>7</sub> to <sup>5</sup>I<sub>8</sub> of Ho<sup>3+</sup> was calculated to be  $1.2320 \times 10^{-20} \text{ cm}^{-2}$  by the Füchtbauer-Ladenburg equation with the full width at half maximum of 117.8 nm.

**Keywords:** Spectral Properties, Czochralski Method, Single Crystal Growth, Molybdate, Laser Material.

## 1. INTRODUCTION

Laser emission around 2.0  $\mu\text{m}$  lies in the eye-safe wavelength range, and can be obtained via the transition <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> of Ho<sup>3+</sup> ion in laser materials. Lasers of this type have been widely used in various fields such as laser radar, atmospheric sensing, optical communication and medical surgery.<sup>(1-3)</sup> There are no suitable high power laser diodes commercially available for the pumping of Ho<sup>3+</sup> ions directly around 2000 nm. While for Yb<sup>3+</sup> or Tm<sup>3+</sup>, the broad absorption bands lie in the emission wavelength range of high power laser diodes (such as InGaAs or AlGaAs LDs). Therefore, Tm<sup>3+</sup> or Yb<sup>3+</sup> ions are co-doped with Ho<sup>3+</sup> ions as sensitizers in order to enhance the pump light absorption and transfer the energy to the upper laser level of Ho<sup>3+</sup> ions. Many research efforts

have been devoted to the Tm<sup>3+</sup> and Ho<sup>3+</sup> co-doped various laser hosts.<sup>(4-7)</sup> Typically, Yb<sup>3+</sup> ions have broad absorption bands near 940 and 980 nm. So Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped system can be effectively pumped by high power InGaAs laser diodes. The efficiency of energy transfer from the upper laser level <sup>2</sup>F<sub>5/2</sub> of Yb<sup>3+</sup> to the <sup>5</sup>I<sub>6</sub> level of Ho<sup>3+</sup> can be close to 100%<sup>(8)</sup>, and therefore the energy transfer from Yb<sup>3+</sup> to Ho<sup>3+</sup> is feasible and efficient. In addition, Yb<sup>3+</sup> ions can be co-doped with Tm<sup>3+</sup>, Er<sup>3+</sup>, or Ho<sup>3+</sup> ions in various hosts as sensitizers to realize upconversion luminescence under excitation of 980 nm, which has potential applications in three-dimensional display, optical data storage, UC lasers, temperature sensors, DNA detection and biological analyses.<sup>(9-11)</sup>

Double molybdates of the alkaline and rare earth metals with general formula of MR(MoO<sub>4</sub>)<sub>2</sub> ( $M = \text{alkali metal}$  and  $R = \text{rare earth}$ ) have been widely studied as laser hosts or phosphors in recent years, owing to their large rare

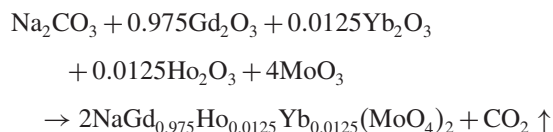
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earth ions admittance, high integral absorption and fluorescence cross sections and broadened lines of optical spectra of rare earth ions.<sup>(12–17)</sup> As a member of the MR(MoO<sub>4</sub>)<sub>2</sub> family, NaGd(MoO<sub>4</sub>)<sub>2</sub> belongs to the scheelite structure and crystallizes in the tetragonal system with space group *I*4<sub>1</sub>/*a* and point group 4/*m*. According to our knowledge, Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal has not been reported yet. In this paper, Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was grown by the Czochralski method and its spectral properties were investigated.

## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis and Crystal Growth

Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystals are congruently melting compounds and can be grown by Czochralski method. The raw materials of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> were synthesized by the solid-state reaction according to the following chemical reaction:



The initial reagents Ho<sub>2</sub>O<sub>3</sub> (99.99%), Yb<sub>2</sub>O<sub>3</sub> (99.99%), Gd<sub>2</sub>O<sub>3</sub> (99.99%), MoO<sub>3</sub> (99.95%) and Na<sub>2</sub>CO<sub>3</sub> (99.95%) were weighed according to the stoichiometric composition of NaGd<sub>0.975</sub>Ho<sub>0.0125</sub>Yb<sub>0.0125</sub>(MoO<sub>4</sub>)<sub>2</sub>. A 2 wt% excess amount of MoO<sub>3</sub> was added to compensate the volatilization during crystal growth process. The weighed chemicals were fully mixed in an agate mortar and extruded to tablets. After that the mixture was placed in an alumina crucible and pre-sintered at 950 °C in a programmable muffle furnace for 2 days to carry out the reaction.

The synthesized polycrystalline materials were melted in a Φ50 × 50 mm<sup>3</sup> platinum crucible of a 2.5 kHz medium frequency induction furnace with a Eurotherm 818P temperature controller. A [0 0 1] orientated NaGd(MoO<sub>4</sub>)<sub>2</sub> single crystal bar was used as a seed. The crystal was grown in N<sub>2</sub> atmosphere at a pulling rate of 0.5–1.2 mm/h and a rotating rate of 10–25 rpm. After growth process, the crystal was cooled down to room temperature at a rate of 30–50 °C/h and then annealed in air at 850 °C for 40 h.

### 2.2. X-ray Diffraction

In order to check the structure and determine the lattice parameters of the as-grown crystal, powder X-ray Diffraction (XRD) analysis was performed. A sample of the Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was crushed and finely ground to powder for XRD measurement. The XRD data were recorded at ambient temperature on a XD-2 diffractometer (Beijing Purkinje General Instrument) using Cu Kα radiation (λ = 1.5406 Å) operated at an acceleration voltage of 36 kV and a filament current of 20 mA in the 2θ range 8–80° with a step size of 0.01°.

### 2.3. Absorption and Fluorescence Spectrum

A plate-shaped sample with the thickness of 1.5 mm was cut from the as-grown crystal and polished on both sides for spectral measurements. The absorption spectrum in the range of 400–2200 nm was measured using a Perkin-Elmer UV-VIS-NIR spectrophotometer (Lambda-900) at room temperature. The fluorescence spectrum at room temperature was measured using a HORIBA Jobin Yvon Triax 550 spectrometer excited by 980 nm laser diodes.

## 3. RESULTS AND DISCUSSION

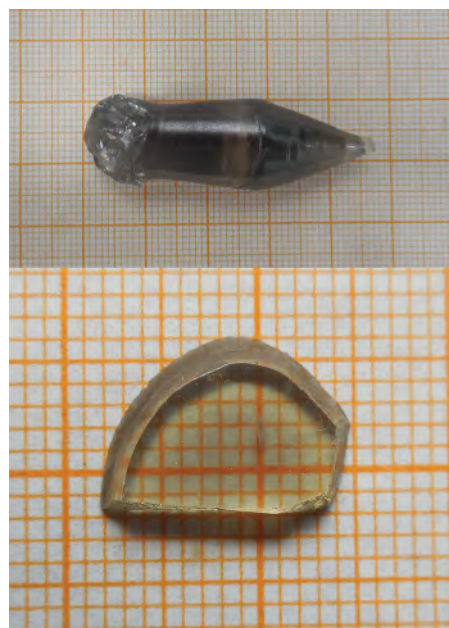
### 3.1. Crystal Growth and Segregation Coefficient

A Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal with dimensions of Φ15 × 40 mm<sup>3</sup> was obtained. The as-grown Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was brown in color because of color centers caused by oxygen vacancies in deficiency oxygen atmosphere.<sup>(18)</sup> After annealed in air at 850 °C for 40 h, the crystal faded to light brown and became almost transparent, as shown in Figure 1.

The concentrations of Yb<sup>3+</sup> and Ho<sup>3+</sup> in the crystal were determined to be 0.76 at% and 0.82 at% by the inductively coupled plasma atomic emission spectrometry (ICP-AES). Thus the segregation coefficients (*K*) of Yb<sup>3+</sup> and Ho<sup>3+</sup> in the Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal were calculated to be 0.608 and 0.656 according to the equation  $K = C'/C_0$ , where *C'* and *C*<sub>0</sub> are the concentrations of the doping ions in the crystal and in the raw materials respectively.

### 3.2. X-ray Diffraction Analysis

The X-ray power diffraction pattern of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal along with the pure NaGd(MoO<sub>4</sub>)<sub>2</sub>



**Fig. 1.** As-grown Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal and a polished plate-shaped sample.

crystal (JCPDS 25-0828) is shown in Figure 2. As can be seen in the patterns, the positions and relative intensities of the peaks in the pattern of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal match well with the standard JCPDS file, which demonstrates that the grown Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> has the same structure as the pure NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal. In other words, the dopants (Yb<sup>3+</sup> and Ho<sup>3+</sup> ions) do not affect the crystal structure of the NaGd(MoO<sub>4</sub>)<sub>2</sub> host crystal. The lattice parameters were estimated to be  $a = b = 5.2431 \text{ \AA}$  and  $c = 11.4803 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ) by cell refinement program of Jade software, which are slightly smaller than the parameters in JCPDS File No. 25-0828 ( $a = b = 5.244 \text{ \AA}$ ,  $c = 11.487 \text{ \AA}$ ). This can be interpreted as the replacement of Gd<sup>3+</sup> of larger ionic radius (1.06 Å for coordination number of 8) with the dopant Yb<sup>3+</sup> and Ho<sup>3+</sup> of smaller ionic radius (0.98 Å for Yb<sup>3+</sup> and 1.02 Å for Ho<sup>3+</sup>, for coordination number of 8)<sup>(19)</sup> in NaGd(MoO<sub>4</sub>)<sub>2</sub> host crystal.

### 3.3. Refractive Index

The refractive indices can be calculated according to the infrared-corrected Sellmeier equation:

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

where  $A, B, C$  and  $D$  are Sellmeier parameters and  $\lambda$  is the wavelength. The Sellmeier parameters of pure NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal are  $A = 2.155$ ,  $B = 1.715$ ,  $C = 0.1998$ ,  $D = 0.012$  for ordinary ray and  $A = 2.658$ ,  $B = 1.256$ ,  $C = 0.2231$ ,  $D = 0.016$  for extraordinary ray.<sup>(20)</sup> The dispersion curve for refractive indices of NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal can be calculated according to the above equation. On account of the low doping concentrations of Yb<sup>3+</sup> and Ho<sup>3+</sup> ions in the NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal, the refractive index of the grown Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal can be considered the same as that of the pure NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal.

### 3.4. Absorption Spectrum and Judd-Ofelt Analysis

The absorption spectrum of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal at room temperature is shown in Figure 3. A gradually increase in the intrinsic optical absorption of the

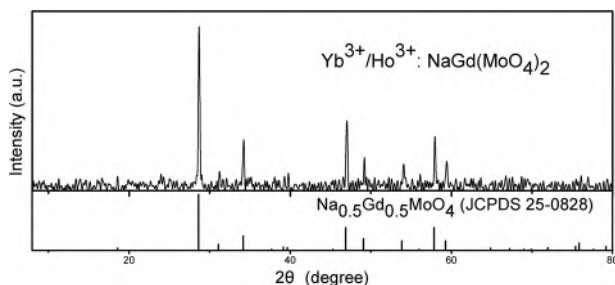


Fig. 2. The XRD patterns of the Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> and pure NaGd(MoO<sub>4</sub>)<sub>2</sub> crystals.

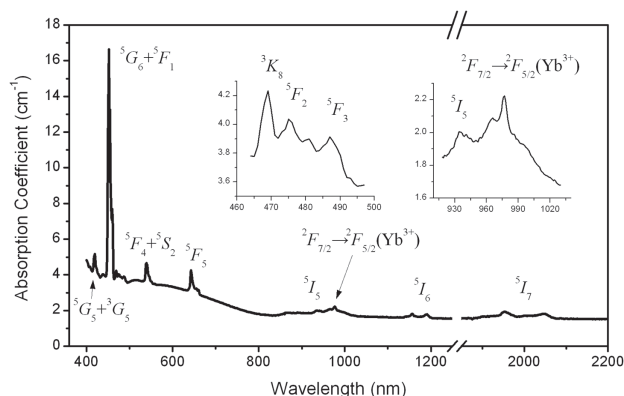


Fig. 3. Absorption spectrum of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal at room temperature.

host crystal is observed from visible light to ultraviolet region. Some absorption bands related to  $f-f$  transitions of Yb<sup>3+</sup> and Ho<sup>3+</sup> are observed in the spectrum, among which the strongest absorption band lies at 469 nm. The broad absorption band from 920 to 1000 nm consists of two main peaks at 934 and 977 nm. The absorption band at 977 nm is attributed to the transition of Yb<sup>3+</sup> from the ground state  $^2F_{7/2}$  to  $^2F_{5/2}$ . The other absorption bands at 419, 452, 469, 475, 487, 539, 643, 934, 1157 (1191), 1953 (2045) nm, are ascribed to the transitions of Ho<sup>3+</sup> from ground state  $^5I_8$  to  $^5G_5 + ^3G_5$ ,  $^5G_6 + ^5F_1$ ,  $^3K_8$ ,  $^5F_2$ ,  $^5F_3$ ,  $^5F_4 + ^5S_2$ ,  $^5F_5$ ,  $^5I_5$ ,  $^5I_6$ ,  $^5I_7$ . Because of low doping concentration of Yb<sup>3+</sup> in the grown crystal, the intensity of absorption band at 977 nm is not very strong. Nevertheless, the full width at half maximum of the band reaches 49 nm, which is in favor of being pumped by high power InGaAs laser diodes. The absorption cross section at 977 nm is calculated to be  $\sigma_{abs} = 0.461 \times 10^{-19} \text{ cm}^{-2}$  by the formula:

$$\sigma_{abs} = \alpha(\lambda) / \alpha(\lambda) N_c \quad (2)$$

where  $N_c$  is the number density of the rare earth ion.

Judd-Ofelt theory has been widely used for the quantitative characterization of electronic transitions between the states of  $4f^N$  electronic configuration of rare earth dopant ions in different hosts.<sup>(21,22)</sup> According to the Judd-Ofelt theory, the calculated absorption line strength  $S_{cal}$  of electric dipole transition from the initial state  $|4f^N SLJ\rangle$  to the final state  $|4f^N S'L'J'\rangle$  can be expressed as:

$$S_{cal} = \sum_{t=2,4,6} \Omega_t \left| \langle 4f^N SLJ | U^{(t)} | 4f^N S'L'J' \rangle \right|^2 \quad (3)$$

where  $S, L, J$  are spin angular momentum, orbit angular momentum, and total angular momentum of the initial state, and  $S', L',$  and  $J'$  are those of the final state,  $|\langle 4f^N SLJ | U^{(t)} | 4f^N S'L'J' \rangle|$  is the reduced matrix element of unit tensor operators for each absorption line, which is considered to be dependent on the rare earth dopant ion

only and can be quoted from Ref. [23]. The experimental absorption line strength  $S_{\text{exp}}$  can be obtained from the absorption spectrum by the equation:

$$S_{\text{exp}} = \frac{3hc}{8\pi^3 e^2 \lambda N_c} \frac{9n}{(n^2 + 2)^2} (2J + 1) \int \alpha(\lambda) d\lambda \quad (4)$$

where  $h$  is the Plank constant,  $c$  is the light velocity,  $e$  is the electron charge,  $\lambda$  is the mean wavelength of the absorption band,  $n$  is the refractive index,  $J$  is the total angular momentum of the initial state  $^{2S+1}L_J$  ( $J = 8$  for the  $^5I_8$  level of Ho<sup>3+</sup>),  $\int \alpha(\lambda) d\lambda$  is the integration of the absorption coefficient in the corresponding absorption band.  $N_c$  is determined to be  $5.20 \times 10^{19} \text{ cm}^{-3}$  for Ho<sup>3+</sup> in the grown crystal. The refractive index used here is the average of ordinary refractive index and extraordinary refractive index.

The Judd-Ofelt intensity parameters  $\Omega_t$  ( $t = 2, 4, 6$ ) can be obtained by means of least square fitting between Eqs. (3) and (4). The root mean square (*rms*) deviation between the experimental and calculated line strengths can evaluate the accuracy of the fitting process, which is defined as follow:

$$rms\Delta S = \sqrt{\sum_{i=1}^N (S_{\text{exp}} - S_{\text{cal}})^2 / (N - 3)} \quad (5)$$

where  $N$  is the number of absorption bands.

The experimental and calculated absorption line strengths and the *rms*  $\Delta S$  are listed in Table I. The root mean square deviation value is  $rms \Delta S = 0.25855 \times 10^{-20}$ , and the value is rather small compared with the values in other references, which indicates a better fitting result.<sup>(14, 24-31)</sup> The Judd-Ofelt intensity parameters  $\Omega_t$  ( $t = 2, 4, 6$ ) obtained are  $\Omega_2 = 17.425 \times 10^{-20}$ ,  $\Omega_4 = 5.407 \times 10^{-20}$ ,  $\Omega_6 = 1.523 \times 10^{-20} \text{ cm}^2$ . As is shown in Table II, the values of Judd-Ofelt intensity parameters of Ho<sup>3+</sup> in Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal are close to those of different molybdate or tungstate crystals. The slight difference between the intensity parameters of Ho<sup>3+</sup> in various hosts might be caused by the Judd-Ofelt theoretical error and the influence of different host crystals and co-doping

**Table I.** Mean wavelength, experimental and calculated absorption line strengths of Ho<sup>3+</sup> in Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal.

Transition	$\lambda$ (nm)	$\int \alpha(\lambda) d\lambda$ (nm/cm)	$S_{\text{exp}}$ (10 <sup>-20</sup> cm <sup>2</sup> )	$S_{\text{cal}}$ (10 <sup>-20</sup> cm <sup>2</sup> )
$^5I_8 \rightarrow ^5G_5, ^3G_5$ (Ho <sup>3+</sup> )	419	7.099	2.663	2.886
$^5I_8 \rightarrow ^5G_6, ^5F_1$ (Ho <sup>3+</sup> )	452	88.250	31.257	31.249
$^5I_8 \rightarrow ^3K_8$ (Ho <sup>3+</sup> )	469	1.148	0.395	0.783
$^5I_8 \rightarrow ^5F_2$ (Ho <sup>3+</sup> )	475	0.891	0.303	0.293
$^5I_8 \rightarrow ^5F_3$ (Ho <sup>3+</sup> )	487	1.317	0.439	0.527
$^5I_8 \rightarrow ^5F_4, ^5S_2$ (Ho <sup>3+</sup> )	539	8.866	2.712	2.37
$^5I_8 \rightarrow ^5F_5$ (Ho <sup>3+</sup> )	643	12.715	3.322	3.164
$^5I_8 \rightarrow ^5I_6$ (Ho <sup>3+</sup> )	1157	10.077	1.506	1.409
$^5I_8 \rightarrow ^5I_7$ (Ho <sup>3+</sup> )	1953	36.471	3.276	3.480

**Table II.** Judd-Ofelt parameters of Ho<sup>3+</sup> in various molybdate hosts.

Hosts	$\Omega_2$ (10 <sup>-20</sup> cm <sup>2</sup> )	$\Omega_4$ (10 <sup>-20</sup> cm <sup>2</sup> )	$\Omega_6$ (10 <sup>-20</sup> cm <sup>2</sup> )	Reference
NaGd(WO <sub>4</sub> ) <sub>2</sub>	9.12	4.73	0.86	[25]
KGd(WO <sub>4</sub> ) <sub>2</sub>	10.14	3.09	1.99	[26]
KGd(WO <sub>4</sub> ) <sub>2</sub>	15.35	3.79	1.69	[27]
Tm <sup>3+</sup> /Ho <sup>3+</sup> : LiGd(MoO <sub>4</sub> ) <sub>2</sub>	18.9	5.99	1.41	[28]
NaLa(MoO <sub>4</sub> ) <sub>2</sub>	16.19	4.21	1.00	[29]
NaY(MoO <sub>4</sub> ) <sub>2</sub>	12.53	4.81	1.24	[30]
NaGd(MoO <sub>4</sub> ) <sub>2</sub>	22.44	5.83	1.03	[31]
Yb <sup>3+</sup> /Ho <sup>3+</sup> : NaGd(MoO <sub>4</sub> ) <sub>2</sub>	17.425	5.407	1.523	This work

ions. It is generally acknowledged that the  $\Omega_2$  parameter is related to the covalence of rare earth-ligand bonding and symmetry of the ligand field in the rare earth site of the hosts. In our case, a larger value of  $\Omega_2$  is believed to be the result of strong covalence of Ho–O bond in the molybdate crystal. The other two parameters  $\Omega_4$  and  $\Omega_6$  are important parameters to calculate the spectroscopic quality factor ( $\Omega_4/\Omega_6$ ), which is critically important in predicting the stimulated emission of laser medium. The calculated spectroscopic quality factor of Ho<sup>3+</sup> in Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal is 3.55, which is larger than that of many laser medium,<sup>(32)</sup> indicating that Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal is a promising material for efficient laser output.

The magnetic dipole transitions between the states of  $4f^N$  configuration are allowed when the selection rules are satisfied. The selection rules are  $\Delta l = \pm 1$ ,  $\Delta S = 0$ ,  $\Delta L \leq 2l$ ,  $\Delta J \leq 2l$  for allowed electric dipole transitions and  $\Delta \alpha = \Delta S = \Delta L = 0$ ,  $\Delta J = 0, \pm 1$  for allowed electric dipole transitions, where  $l = 3$  for lanthanide series ions.<sup>(33)</sup> Taking the contribution of the magnetic dipole transitions into account, the spontaneous transition probability  $A_{JJ'}$  is given by equations:

$$A_{JJ'} = A_{JJ'}^{\text{ed}} + A_{JJ'}^{\text{md}} \quad (6)$$

$$A_{JJ'}^{\text{ed}} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \frac{n(n^2+2)^2}{9} \times \sum_{t=2,4,6} \Omega_t |\langle 4f^N SLJ || \mathbf{U}^{(t)} || 4f^N S'L'J' \rangle|^2 \quad (7)$$

$$A_{JJ'}^{\text{md}} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} n^3 |\langle 4f^N SLJ || \mathbf{L} + 2\mathbf{S} || 4f^N S'L'J' \rangle|^2 \quad (8)$$

where  $|\langle 4f^N SLJ || \mathbf{L} + 2\mathbf{S} || 4f^N S'L'J' \rangle|$  is the reduced matrix element of magnetic dipole operator  $\mathbf{L} + 2\mathbf{S}$ . ( $\mathbf{L}$  is the orbital angular momentum operator and  $\mathbf{S}$  is the spin angular momentum operator). The values of the reduced matrix elements of unit tensor operators  $|\langle 4f^N SLJ || \mathbf{U}^{(t)} || 4f^N S'L'J' \rangle|$  for the spontaneous radiative transitions from different initial states are given in Ref. [33], and the values of the reduced matrix elements of magnetic dipole operator in LS coupling scheme can be calculated according to the formulas in Ref. [34].

Furthermore the fluorescence branching ratios  $\beta_{JJ'}$  and radiative lifetime  $\tau_r$  can be calculated using

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \quad (9)$$

$$\tau_r = \frac{1}{\sum_{J'} A_{JJ'}} \quad (10)$$

The calculated spontaneous transition probabilities  $A_{JJ'}$ , branching ratios  $\beta_{JJ'}$  and radiative lifetimes  $\tau_r$  are tabulated in Table III.

### 3.5. Fluorescence Spectrum

The fluorescence spectrum of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal around 2.0  $\mu\text{m}$  at room temperature excited by 980 nm radiation is shown in Figure 4. The peak at 1960 nm is caused by the second order diffraction of the exciting light at 980 nm by optical grating in the spectrometer. As is shown in the figure, a broad and strong emission band around 2045 nm attributed to the transition from level <sup>5</sup>I<sub>7</sub> to <sup>5</sup>I<sub>8</sub> is observed. The full width at half maximum of the emission band is 118 nm. This suggests that the Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal can be used as a broadly tunable laser crystal. Under the absorption of the exciting light at 980 nm, the Yb<sup>3+</sup> ions is excited to the upper laser level <sup>2</sup>F<sub>5/2</sub>, from which the energy can be transferred to the nearby <sup>5</sup>I<sub>6</sub> level of Ho<sup>3+</sup>. The non-radiative relaxation

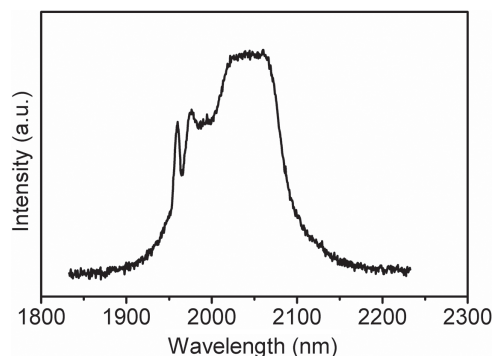


Fig. 4. Fluorescence spectrum around 2.0  $\mu\text{m}$  of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal excited by 980 nm radiation at room temperature.

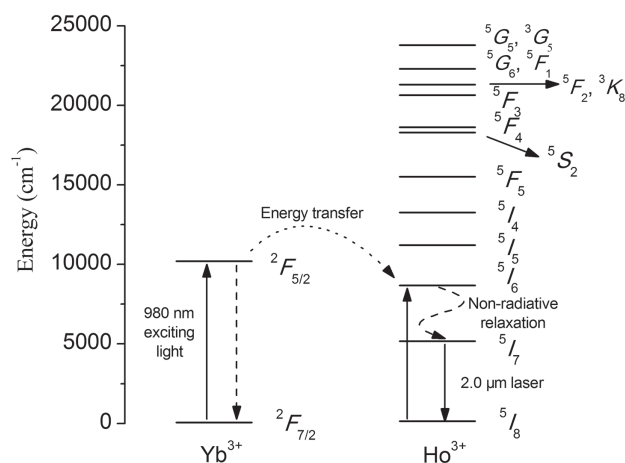
from <sup>5</sup>I<sub>6</sub> level to <sup>5</sup>I<sub>7</sub> level of Ho<sup>3+</sup> populates the upper laser level <sup>5</sup>I<sub>7</sub> of Ho<sup>3+</sup>. Then 2.0  $\mu\text{m}$  laser radiation can be emitted via the transition from level <sup>5</sup>I<sub>7</sub> to <sup>5</sup>I<sub>8</sub> of Ho<sup>3+</sup> (see “Energy level scheme” in Fig. 5). A similar energy transfer process has been found in Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped YAG crystal, yttrium aluminum tetraborate crystal, fluorophosphate glass, tellurite glass, and germanate glass.<sup>(8,35–38)</sup>

The stimulated emission cross section can be derived by the Füchtbauer-Ladensburg equation:

$$\sigma_e(\lambda) = \frac{A_{JJ'}\lambda^4}{8\pi cn^2} \frac{\lambda \cdot I(\lambda)}{\int \lambda \cdot I(\lambda) d\lambda} \quad (11)$$

Table III. Calculated spontaneous transition probabilities, branching ratios and radiative lifetimes of Ho<sup>3+</sup> in Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal.

Initial state	Final state	Wavelength (nm)	$A_{JJ'}^{\text{cd}}$ (s <sup>-1</sup> )	$A_{JJ'}^{\text{md}}$ (s <sup>-1</sup> )	$\beta_{JJ'}$ (%)	$\tau_r$ (ms)
<sup>5</sup> I <sub>7</sub>	<sup>5</sup> I <sub>8</sub>	1988	159.68	118.42	100	3.596
<sup>5</sup> I <sub>6</sub>	<sup>5</sup> I <sub>7</sub>	2858	46.52	70.25	23.79	2.038
<sup>5</sup> I <sub>6</sub>	<sup>5</sup> I <sub>8</sub>	1173	373.97	–	76.21	
<sup>5</sup> I <sub>5</sub>	<sup>5</sup> I <sub>6</sub>	3925	19.15	28.80	13.59	
<sup>5</sup> I <sub>5</sub>	<sup>5</sup> I <sub>7</sub>	1654	167.16	–	47.36	2.834
<sup>5</sup> I <sub>5</sub>	<sup>5</sup> I <sub>8</sub>	903	137.81	–	39.05	
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>5</sub>	4864	11.79	11.84	12.08	
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>6</sub>	2172	70.11	–	35.85	5.113
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>7</sub>	1234	84.58	–	43.24	
<sup>5</sup> I <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	761	17.27	–	8.83	
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>4</sub>	4472	0.20	–	~ 0	
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>5</sub>	2276	21.32	–	0.26	
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>6</sub>	1461	25.34	–	3.17	0.124
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>7</sub>	967	1568.26	–	19.42	
<sup>5</sup> F <sub>5</sub>	<sup>5</sup> I <sub>8</sub>	651	6227.64	–	77.13	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> F <sub>5</sub>	3602	1.42	–	0.03	0.216
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> I <sub>4</sub>	1995	28.31	–	0.61	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> I <sub>5</sub>	1415	72.21	–	1.56	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> I <sub>6</sub>	1040	347.00	–	7.48	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> I <sub>7</sub>	762	1637.42	–	35.31	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> I <sub>8</sub>	551	2550.61	–	55.01	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> S <sub>2</sub>	–	–	–	–	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> F <sub>5</sub>	3214	67.29	23.25	0.66	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>4</sub>	1870	48.32	–	0.35	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>5</sub>	1351	362.09	–	2.65	0.073
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>6</sub>	1005	1035.74	–	7.59	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>7</sub>	743	1773.84	–	12.99	
<sup>5</sup> F <sub>4</sub>	<sup>5</sup> I <sub>8</sub>	541	10341.75	–	75.75	



**Fig. 5.** Energy level and energy transfer scheme of Yb<sup>3+</sup> and Ho<sup>3+</sup> in Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal.

where  $\lambda$  is the emission wavelength,  $I(\lambda)$  is the fluorescence emission intensity at wavelength  $\lambda$ .<sup>(39)</sup> The stimulated emission cross section for the transition from  $^5I_7$  to  $^5I_8$  (Ho<sup>3+</sup>) of Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal was calculated to be  $1.2320 \times 10^{-20} \text{ cm}^{-2}$  at 2060 nm, which is larger than that of fluorophosphate glass, germanate glass, lanthanum aluminum germinate glass, silicate glass, Y<sub>2</sub>O<sub>3</sub> ceramic, and YAG crystal.<sup>(36, 38, 39–42)</sup> All these results indicate that Yb<sup>3+</sup>/Ho<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal may be a suitable laser host material for  $\sim 2.0 \mu\text{m}$  tunable laser operation.

#### 4. CONCLUSION

A Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal with dimensions of  $\Phi 15 \times 40 \text{ mm}^3$  was successfully grown by the Czochralski method. The powder XRD analysis revealed its tetragonal structure. The room temperature absorption spectrum and fluorescence spectrum was measured. The absorption cross section of Yb<sup>3+</sup> at 977 nm is  $0.461 \times 10^{-19} \text{ cm}^{-2}$  with the full width at half maximum of 49 nm. The intensity of typical absorption band of Yb<sup>3+</sup> is not very strong on account of low doping concentration of Yb<sup>3+</sup> in the grown crystal. The Judd-Ofelt intensity parameters of Ho<sup>3+</sup> in the crystal were calculated to be  $\Omega_2 = 17.425 \times 10^{-20}$ ,  $\Omega_4 = 5.407 \times 10^{-20}$ ,  $\Omega_6 = 1.523 \times 10^{-20} \text{ cm}^2$ . The root mean square (*rms*) deviation between the experimental and calculated line strengths is rather small, which indicates high accuracy of the fitting process. The spontaneous transition probability, fluorescence branching ratios and radiative lifetime were calculated as well. A broad emission band around  $2.0 \mu\text{m}$  was observed in the fluorescence spectrum corresponding to the transition from level  $^5I_7$  to  $^5I_8$  of Ho<sup>3+</sup> and the full width at half maximum is 118 nm. The stimulated emission cross section for the transition from  $^5I_7$  to  $^5I_8$  of Ho<sup>3+</sup> is  $1.2320 \times 10^{-20} \text{ cm}^{-2}$ . Results indicate that

the Yb<sup>3+</sup>/Ho<sup>3+</sup> co-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal may be a promising candidate for diode pumped tunable laser operating around  $2.0 \mu\text{m}$ .

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Received: 11 April 2015. Revised/Accepted: 1 June 2015.