

# Growth and optical properties of Er<sup>3+</sup>-doped BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystal

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## Introduction

With the development of high power diode lasers, there has been increasing research interest in diode pumped solid-state laser materials [1–3]. It is well-known that, Er<sup>3+</sup> is a suitable diode-pumped laser ion with optical transitions in the infrared region as well as in the visible wavelength range. Er<sup>3+</sup> ions can emit 1.55 μm fluorescence through the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition. The infrared emission of Er<sup>3+</sup> around 1.55 μm has gained the attention of researchers due to its important applications in laser radar, eye-safe light detection, optical communications and the medical field [4–7]. Therefore, Er<sup>3+</sup>-doped crystal materials have been widely investigated.

Monoclinic double molybdate crystals with the formula BaRe<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> (Re = rare earth) were investigated as host materials for solid-state lasers. The BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystal has a perfect (010) cleavage plane, and the cleavage character makes the crystal suitable as a gain medium for microchip lasers because it can be easily cleaved into wafers with sub-millimeter thickness [8]. In previous work, spectroscopic characterization was made and 1.06 μm laser operation was demonstrated in Nd<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> [9, 10]. Laser performance has also been demonstrated in Tm<sup>3+</sup> and Yb<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystals [8, 11]. In addition, we reported on the growth and spectroscopic characterization of BaNd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystals [12].

In this paper, we report on the crystal growth and spectroscopic characterization of Er<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub>. In this work, the concentration of Er<sup>3+</sup> is at about a 1% at substitution level for Gd<sup>3+</sup>.

## 2. Experimental

### 2.1. Crystal growth

Since the BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystal melts congruently, the Er<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystal can be grown by the Czochralski method using a platinum crucible that is 70 mm in diameter and 40 mm in height. The heating apparatus is a 2 kHz intermediate frequency furnace that was used to heat the crucible.

Polycrystalline Er<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> material was synthesized by a solid-phase reaction with 99.99% pure Er<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>. The raw materials, with composition BaEr<sub>0.02</sub>Gd<sub>1.98</sub>(MoO<sub>4</sub>)<sub>4</sub>, were weighed. A 1.5 wt% excess amount of MoO<sub>3</sub> was added to the mixture to compensate for the volatilization of MoO<sub>3</sub> during synthesis of the polycrystal and crystal growth. The weighed materials were ground, mixed and heated at 800°C for 12 h in a platinum crucible. After the crucible cooled down to room temperature, the mixture was remixed, pressed into pellets and reheated at 850°C for 12 h to allow the polycrystalline compounds to react completely.

Initially, a Pt wire with 0.5 mm diameter was used as a crystal seed. Then a seed cut from the crystal grown with the Pt wire seed was used to grow a large sized single crystal. The pulling rate was varied from 0.7 to 2 mm/h and the crystal rotation speed was kept between 6 and 8 rpm. After growth was completed, the crystal

was cooled to room temperature at a rate of 10 °C/h. The Er<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> crystal tends to crack during the annealing process due to spontaneous cleavage. Figure 1 shows the unpolished cleaved microchips that were obtained.

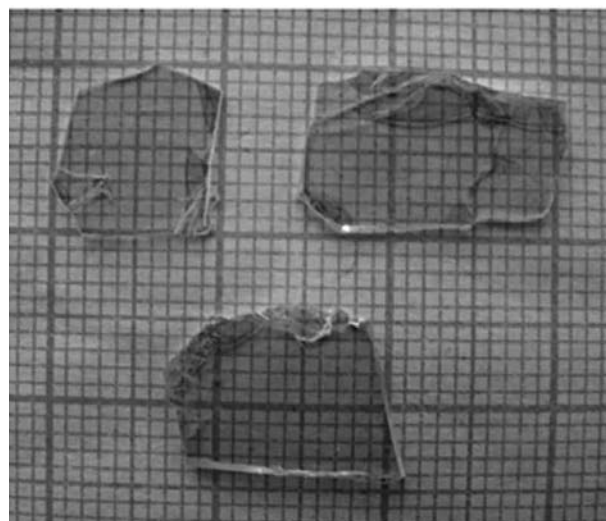


Fig. 1. Cleaved microchip without polishing of Er<sup>3+</sup>: BaGd<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub>

### 2.2. Effective segregation coefficient

X-ray fluorescence analysis was used to measure the concentration of elemental Er, Ba, Gd, and Mo in the crystal. The specimen measured was cut from the as-grown crystal and ground into powder. The polycrystalline material used for growing the crystal was referenced as a comparison standard. Based on the measurement results, the effective segregation coefficients of Er, Ba, Gd, and Mo in the grown crystal were calculated.

### 2.3. Specific heat measurement

Specific heat was measured using a differential scanning calorimeter (NETZSCH model STA 449C) over the temperature range of 25–300°C at a heating rate of 5°C/min.

### 2.4. Absorption spectrum measurement

The absorption spectrum was recorded on a Jasco model V-570 UV/visible/ near IR spectrophotometer over the range of 200–1800 nm at room temperature.

### 2.5. Fluorescence spectrum and fluorescence decay curves measurement

The fluorescence spectrum was measured using Xenon lamp excitation over the range of 850–1700 nm at room temperature. The excitation wavelength was 522 nm. The fluorescence decay curves at 1536 and 998 nm, corresponding to the respective transitions <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, were measured.

### 3. Results and discussion

#### 3.1. Doped concentration

The effective segregation coefficients  $k$  of  $\text{Er}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Mo}^{6+}$  in the  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  crystal was calculated using the equation  $k = c_1/c_2$ , where  $c_1$  and  $c_2$  are the respective concentrations of the ions in the crystal and raw materials. The effective segregation coefficients of  $\text{Er}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Mo}^{6+}$  are determined to be 0.973, 0.988, 1.039, 0.966, respectively.

#### 3.2. Specific heat

Specific heat is an important factor that influences the damage threshold of laser crystals. It is generally expected that a material with higher specific heat will have more resistance to laser damage. The dependence of the specific heat of the obtained crystal on temperature is shown in Figure 2. From this Figure, we can see that the specific heat increases almost linearly with temperature, and it ranges from 0.471 to 0.642  $\text{J g}^{-1} \text{K}^{-1}$  over the temperature range from 25 to 300°C. The specific heat is 0.502  $\text{J g}^{-1} \text{K}^{-1}$  at 50°C, a value that is slightly larger than that of  $\text{Nd}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  [9] and  $\text{Er}^{3+}:\text{LiLa}(\text{MoO}_4)_2$ , and slightly lower than that of  $\text{Er}^{3+}:\text{NaY}(\text{MoO}_4)_2$  [6]. Therefore,  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  should exhibit a higher laser damage threshold than  $\text{Nd}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  and  $\text{Er}^{3+}:\text{LiLa}(\text{MoO}_4)_2$  and a lower one than  $\text{Er}^{3+}:\text{NaY}(\text{MoO}_4)_2$ .

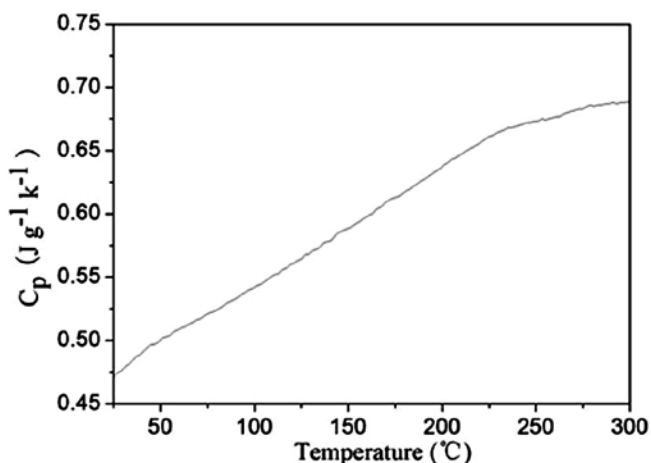


Fig. 2. Dependence of the specific heat of  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  on temperature

#### 3.3. Optical spectrum analysis

The absorption spectrum of the  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  crystal is shown in Figure 3. The profile of the absorption spectrum is similar to that of other  $\text{Er}^{3+}$ -doped crystals, such as  $\text{Er}^{3+}:\text{Sr}_3\text{Y}(\text{BO}_3)_3$  [4],  $\text{Er}^{3+}:\text{LiLa}(\text{MoO}_4)_2$  [6], and  $\text{Er}^{3+}:\text{LiGd}(\text{MoO}_4)_2$  [7]. From this Figure, it is observed that there are several absorption peaks from 360 to 1800 nm. The wavelengths centre at 380, 452, 490, 522, 656, 802, 980 and 1534 nm. They respectively relate to transitions from the  $\text{Er}^{3+}$  ground states,  $^4\text{I}_{15/2}$ , to the excited states  $^4\text{G}_{11/2}$ ,  $^4\text{F}_{5/2} + ^4\text{F}_{3/2}$ ,  $^4\text{F}_{7/2}$ ,  $^2\text{H}_{11/2}$ ,  $^4\text{F}_{9/2}$ ,  $^4\text{I}_{9/2}$ ,  $^4\text{I}_{11/2}$  and  $^4\text{I}_{13/2}$ . The interesting feature in the absorption spectrum is the strong broad absorption band with a full width at half maximum (FWHM) of about 13 nm at 522 nm and of 10 nm at 380 nm. As a consequence, the pumping wavelength was chosen to be 522 nm.

Upon excitation of the  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  crystal at 522 nm, the luminescence emission spectrum of the crystal was measured and is shown in Figure 4. From this Figure, it can be seen that the emission intensity at 1450–1600 nm corresponding to the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition is stronger than that in the wavelength range 950–1000 nm corresponding to the  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$  transition. The most intense emission band at 1536 nm, can potentially be used for eye-safe lasers. It also can be found that there are small peaks near 1536 nm, which is the result of energy levels splitting of  $\text{Er}^{3+}$  ion because of the effect of crystal field.

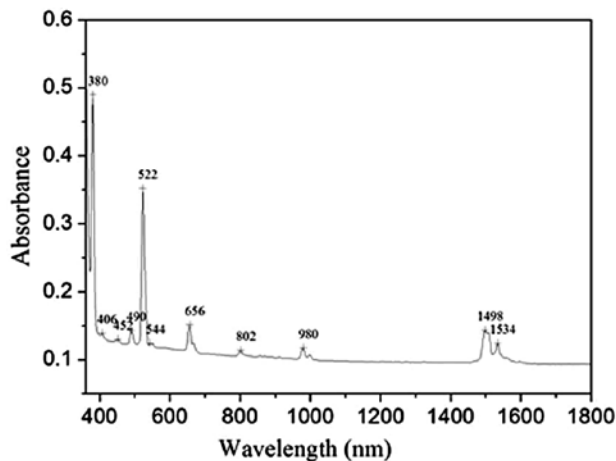


Fig. 3. Absorption spectrum of  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  at room temperature

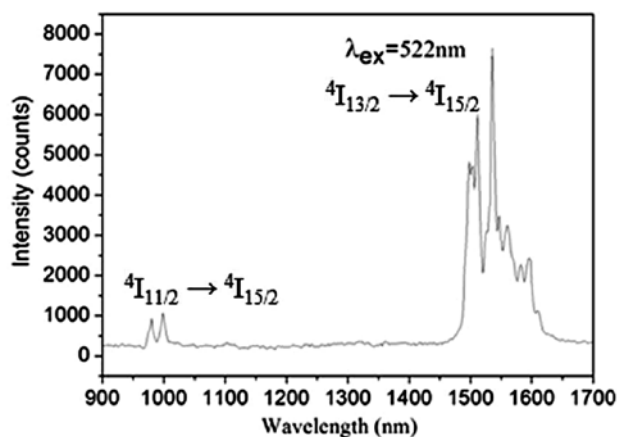


Fig. 4. Fluorescence spectrum of  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  at room temperature

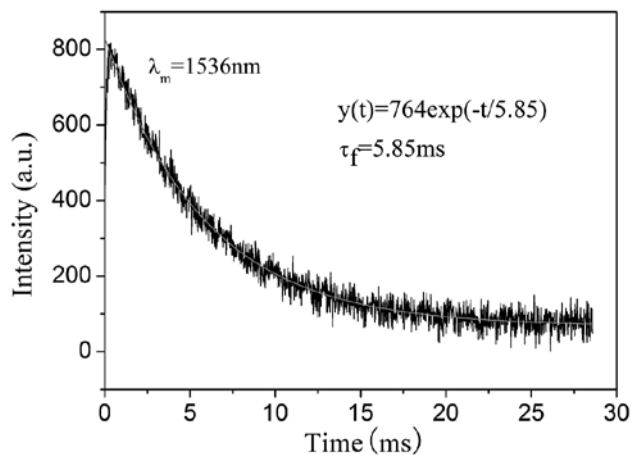


Fig. 5. Fluorescence decay curves of  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  at 1536 nm

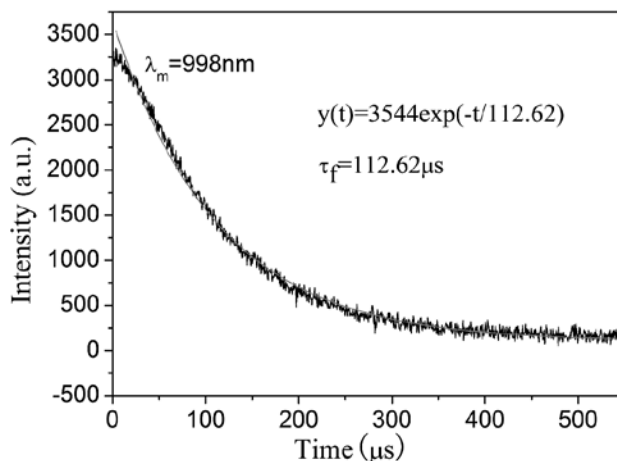


Fig. 6. Fluorescence decay curves of  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  at 998 nm

The fluorescence lifetime of the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition of  $\text{Er}^{3+}$ :  $\text{BaGd}_2(\text{MoO}_4)_4$  at room temperature is shown in Figure 5. The lifetime (5.85 ms) determined by fitting to a single exponential is longer than the radiative lifetime (4.89 ms) seen from Table 2. This phenomenon has also existed in some other  $\text{Er}^{3+}$ -doped hosts, such as  $\text{Er}^{3+}$ : $\text{NaGd}(\text{WO}_4)_2$  [13],  $\text{Er}^{3+}$ : $\text{NaY}(\text{MoO}_4)_2$  [14],  $\text{Er}^{3+}$ : $\text{LiNbO}_3$  [15]. This may be resulted from excitation trapping and emission reabsorption [16, 17].

The fluorescence decay curve at 998 nm for  $\text{Er}^{3+}$ :  $\text{BaGd}_2(\text{MoO}_4)_4$  is shown in Figure 6. The lifetime of the  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  transition of the crystal was measured to be 112.62  $\mu\text{s}$ , which is close to the corresponding value for  $\text{Er}^{3+}$ : $\text{LiGd}(\text{MoO}_4)_2$  [7].

### 3.4. Judd–Ofelt analysis

Judd–Ofelt theory is the most effective theory for the analysis of optical properties of rare earth ions doped in the crystals and glasses [18].

The integrated absorption coefficient  $\int K(\lambda)d\lambda$ , the transition-line intensity  $S_{\text{exp}}(J \rightarrow J')$ , the oscillator strength for the absorption  $P_{\text{exp}}(J \rightarrow J')$  and the differential absorption cross section  $\sigma_a(\lambda)$  may be written [19]

$$\sigma_a(\lambda) = \frac{D(\lambda)}{N_0 L \lg e} \quad (1)$$

$$\int K(\lambda)d\lambda = N_0 \frac{8\pi^3 e^2 \bar{\lambda} (n^2 + 2)^2}{3hc} \frac{1}{9n} \frac{1}{(2J+1)} S_{\text{exp}}(J \rightarrow J') \\ = N_0 \frac{\pi \bar{\lambda}^2 e^2}{mc^2} P_{\text{exp}}(J \rightarrow J') \quad (2)$$

Where  $l$  is the thickness of the sample,  $e$  is the electron charge,  $D(\lambda)$  is the absorbance,  $(J \rightarrow J')$  represents the transition from the ground multiplet  $4I_{15/2}$  to an excited  $J'$ -multiplet,  $n$  is the refractive index of the crystal,  $c$  is the speed of light,  $h$  is Planck's constant,  $m$  is the electron mass,  $N_0$  is the average  $\text{Er}^{3+}$  in the lattice structure. Owing to the cleavage nature of the  $\text{BaGd}_2(\text{MoO}_4)_4$ , it is difficult to measure its refractive index and then obtain its Sellmeier equations. So, an approximate refractive index of 2.02 is generally adopted for the  $\text{BaGd}_2(\text{MoO}_4)_4$  crystal in spectral analysis [10]. Line intensities and optical parameters of  $\text{Er}^{3+}$ :  $\text{BaGd}_2(\text{MoO}_4)_4$  crystal are listed in Table 1.

**Table 1**  
**Line intensities and optical parameters of the  $\text{Er}^{3+}$ :  $\text{BaGd}_2(\text{MoO}_4)_4$  crystal**

Transition final state $4f^n \psi' J'$	Central wavelength (nm)	$\sigma_a$ ( $\times 10^{-20} \text{cm}^2$ )	$\int K(\lambda)d\lambda$ ( $\times 10^{-7}$ )	$S_{\text{exp}}(J \rightarrow J')$ ( $\times 10^{-20} \text{cm}^2$ )	$P_{\text{exp}}(J \rightarrow J')$ ( $\times 10^{-6} \text{cm}^2$ )
${}^4G_{11/2}$	380	7.6172	45.3436	16.6101	59.3047
${}^2H_{9/2}$	407	0.2045	1.1394	0.3897	1.2991
${}^4F_{3/2}, {}^4F_{5/2}$	452	0.1534	1.1303	0.3481	1.0449
${}^4F_{7/2}$	490	0.9623	0.5349	0.1519	0.4207
${}^2H_{11/2}$	522	6.328	38.3557	10.2282	26.5845
${}^4S_{3/2}$	544	0.1749	1.345	0.3441	0.8583
${}^4F_{9/2}$	656	1.1932	6.5789	1.3960	2.8873
${}^4I_{9/2}$	802	0.2404	1.4457	0.2509	0.4245
${}^4I_{11/2}$	980	0.4603	4.6177	0.6559	0.9080
${}^4I_{13/2}$	1498	1.109	19.1011	1.7749	1.6076

According to the J–O theory, the line strength of the electric-dipole transitions can also be expressed as

$$S_{\text{cal}}(J'' \rightarrow J') = \sum_{t=2,4,6} \Omega_t \left| \langle 4f^n \psi'' J'' \| U^{(t)} \| 4f^n \psi' J' \rangle \right|^2 \quad (3)$$

Where  $U^{(t)}$  ( $t=2, 4$  and  $6$ ) are the matrix elements of unit tensor operators and their values can be found from [20–21]. By a least-root-mean-square fitting between Eqs. (2) and (3), the J–O intensity parameters  $\Omega_t$  ( $t=2, 4$  and  $6$ ) were obtained and fitted as  $\Omega_2 = 15.66465 \times 10^{-20} \text{cm}^2$ ,  $\Omega_4 = 1.82670 \times 10^{-20} \text{cm}^2$ ,  $\Omega_6 = 0.89712 \times 10^{-20} \text{cm}^2$ .

Given  $\Omega_t$  ( $t=2, 4$  and  $6$ ), the radiative lifetime of a given upper level and the branching ration of the fluorescence emission can also be calculated

$$A(J'' \rightarrow J') = \frac{64\pi^4 e^2}{3h\lambda^3} \frac{n(n^2 + 2)^2}{9} \frac{1}{(2J''+1)} S_{\text{cal}}(J'' \rightarrow J') \quad (4)$$

$$\tau_{\text{rad}} = \frac{1}{\sum_{J'} A(J'' \rightarrow J')} \quad (5)$$

$$\beta_{J''J'} = \frac{A(J'' \rightarrow J')}{\sum_{J'} A(J'' \rightarrow J')} \quad (6)$$

The calculated results are given in Table 2. The stimulated emission cross section  $\sigma_{\text{em}}$  can be calculated from

$$\sigma_{\text{em}} = \frac{\lambda^4}{8\pi \cdot c \cdot n^2 \cdot \Delta\lambda \cdot \tau_r} \quad (7)$$

Where  $\lambda$  is the wavelength of the fluorescence peak,  $n$  is the refractive index,  $\Delta\lambda$  is the frequency FWHM. The stimulated emission cross section at about 1536 nm for the transition  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  is  $4.50 \times 10^{-20} \text{cm}^2$ , which is beneficial to the realization of human security of the laser output.

**Table 2**  
**Luminescence parameters of the  $\text{Er}^{3+}$ :  $\text{BaGd}_2(\text{MoO}_4)_4$  crystal**

Final state	Radiation (nm)	$S_{\text{cal}}(J'' \rightarrow J')$ ( $\times 10^{-20} \text{cm}^2$ )	$P_{\text{cal}}(J'' \rightarrow J')$ ( $\times 10^{-6} \text{cm}^2$ )	$A(J'' \rightarrow J')$ ( $\text{S}^{-1}$ )	$\tau_{\text{rad}}$ (ms)	$\beta_{J''J'}$ (%)	$\sum(J'' \rightarrow J')$ ( $\times 10^{-18} \text{cm}^2$ )	
${}^4I_{13/2}$	${}^4I_{15/2}$	1536	1.8040	6.2449	204.484	4.89	100	1.6046
	${}^4I_{13/2}$	2777.8	1.8051	1.1753	40.5168	2.296	9.3029	1.0371
	${}^4I_{15/2}$	998	0.7969	1.4557	395.0111		90.697	1.2846
${}^4I_{11/2}$	${}^4I_{15/2}$	4651.2	0.2841	0.1326	1.6305	0.3691	0.1170	
	${}^4I_{13/2}$	1739.1	0.6681	0.8338	73.3470	2.263	16.6019	0.7359
${}^4I_{9/2}$	${}^4I_{15/2}$	800	0.3253	0.8824	366.8199	83.0289	0.7788	
	${}^4I_{9/2}$	3508.8	2.0395	1.2615	27.2561	0.8574	1.1132	
	${}^4I_{11/2}$	1980.2	2.2750	2.4935	169.1542	0.315	5.3212	2.2004
${}^4F_{9/2}$	${}^4I_{13/2}$	1156.1	0.5023	0.9429	187.6696		5.9036	0.8321
${}^4F_{9/2}$	${}^4I_{15/2}$	660.1	1.3924	4.5779	2794.794	87.9177	4.0398	
	${}^4F_{9/2}$	3125	0.0242	0.0421	1.1462	0.0432	0.0371	
${}^4I_{9/2}$	${}^4I_{9/2}$	1639.3	0.3719	1.2314	121.8919	4.6035	1.0866	
	${}^4S_{3/2}$	${}^4I_{11/2}$	1212.1	0.0740	0.3312	59.9588	0.3776	2.2644
${}^4I_{13/2}$	${}^4I_{13/2}$	863.6	0.3106	1.9516	696.0757	26.2886	1.7222	
	${}^4I_{15/2}$	545	0.1983	1.9750	1768.75	66.8002	1.7428	

#### 4. Conclusions

An  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  single crystal was grown by the Czochralski method. A spectroscopic characterization of the crystal was made. There are several strong absorption peaks over the range from 380 to 1600 nm and intense fluorescence peaks were observed. The intensity at 1450–1600 nm, attributed to the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition, is much larger than that at 950–1000 nm attributed to the  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  transition. The fluorescence lifetime of  ${}^4I_{13/2}$  and  ${}^4I_{11/2}$  is around 5.85 ms and 112.62  $\mu\text{s}$ , respectively. The results reveal that the  $\text{Er}^{3+}:\text{BaGd}_2(\text{MoO}_4)_4$  crystal can be regarded as a potential laser material.

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