Experimental investigation of refractive index and Judd-Ofelt parameters of BaGd$_2$ZnO$_5$:Eu^{3+} microcrystalline powder

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Eu^{3+} doped BaGd$_2$ZnO$_5$ microcrystalline powder are prepared through high-temperature solid-state method, XRD analysis indicates that the prepared powder sample has a good and pure crystal phase and belongs to orthorhombic crystallographic system. Emission spectra under 360 nm excitation is measured and five emission peaks are discovered, corresponding to transitions from energy level $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$. Refractive index of BaGd$_2$ZnO$_5$:Eu^{3+} microcrystalline powder sample is calculated through obtained lifetime of energy level $^5D_0$ in Eu^{3+} ions. At last, Judd-Ofelt calculation is executed for the prepared powder sample and spectral intensity parameters Ω_2 and Ω_4 are obtained, material property of BaGd$_2$ZnO$_5$ host is analyzed.

1. Introduction

Rare-earth (RE) doped fluorescent materials are extensively applied in such fields as solid-state laser [1-3], white-light LED [4, 5], light frequency transformation [6-8] and solar cell [9-12]. Nowadays, one of the most important research purpose for RE doped fluorescent materials is to improve its luminescence quantum efficiency.

Non-radiation transitions caused by multi-phonon relaxation is a main factor for influencing luminescence quantum efficiency of RE doped fluorescent materials [13-14]. Normally, the lower phonon energy the host material has, the lower multiple-phonon relaxation probability and the higher luminescence quantum efficiency there are. Fluoride and halide host materials have lower phonon energy, but their chemical properties are unstable. Pursuing A kind of host material with not only lower phonon energy but also stable chemical properties is always an important goal for researchers in the luminescence field.

In 2010, Etchart et. al. [15] reported up-conversion efficiency (emission power / absorbed power) of Yb^{3+}/Er^{3+} co-doped BaGd$_2$ZnO$_5$ phosphor and confirmed that its green light up-conversion efficiency can be achieved to 5%, which is the highest up-conversion efficiency to this day. BaGd$_2$ZnO$_5$ is a kind of host material with both stable chemical structure and lower phonon energy (360 cm^{-1}) [16], and has good application prospect. Eu^{3+} ion is a type of RE ions with simple energy level structure, and its transition characteristic between two energy levels is affected by surrounding environment obviously. Moreover, Eu^{3+} ion has similar ion radius and crystallization properties to other trivalent rare earth ions, so it can be taken as probe for detecting local microcosmic environment of RE ions.

Judd-Ofelt (J-O) theory [17, 18] provides a new method for analyzing crystal field structure, J-O intensity parameters Ω_t (t=2, 4, 6) can be used to evaluate performance of laser medium and luminescence material, thereinto, parameter Ω_2 reflects local crystal field structure and covalence degree of RE ions, but parameters Ω_4 and Ω_6 depend on long range effect and reflect whole characteristic of host material. However, traditional J-O analysis method is limited to crystal, glass and solution host with RE ions doping, but cannot be used to analyze RE doped powder material. One reason is that refractive index of powder host material is difficult to be obtained using common Abbe index measurement method, the other reason is that transmitted spectrum of powder sample cannot be measured due to strong diffuse effect, so the absorbing spectrum of powder sample is hard to get.

For the above questions, this article introduces one kind of new method for performing J-O calculation of RE doped powder materials, and luminescence characteristic of Eu^{3+} doped BaGd$_2$ZnO$_5$ powder material is analyzed.

In this article, Eu^{3+} doped BaGd$_2$ZnO$_5$ microcrystalline powder sample is prepared through high-temperature solid-phase method firstly. Then, lifetime of $^5D_0$ energy level of Eu^{3+} ions is measured and refractive index of the prepared powder sample is

calculated using method introduced in Ref. [19]. Furthermore, J-O analysis is performed through obtained emission spectra of Eu^{3+} ions and J-O intensity parameters Ω_2 and Ω_4 are calculated, based on calculated results, luminescence properties about Eu^{3+} doped $BaGd_2ZnO_5$ microcrystalline powder is analyzed.

2. Material preparation and test

2.1. Preparation process and test method

Weigh a share of raw material with mass of 10 grams according to mole ratio as $BaCO_3$: ZnO: Gd_2O_3: Eu_2O_3 = 1: 1.05: 0.99: 0.01, respectively. Here, redundant 5% ZnO is added for compensating Zn^{2+} ion loss due to decomposed ZnO in high temperature. In these raw material, Eu_2O_3 is spectroscopic reagent, $BaCO_3$, ZnO and Gd_2O_3 are analytical reagent. These raw material are grinded and mixed in an agate mortar successively, then placed in a ceramic crucible, outside which a bigger ceramic crucible is inverted over for insulating air. The two ceramic crucibles are put into a muffle furnace and calcined at 1300°C for four hours, then are taken out and cooled to room temperature naturally. Cooled samples are grinded again and enclosed in a sample sack for next measurement.

X-ray diffraction (XRD) pattern of the prepared sample is measured using Hitachi DMAX-3A equipment, whose scanning scope are from 20 ° to 70 ° (Copper target, λ=0.154 nm). Stimulated emission spectrum and fluorescence lifetime are obtained by adopting fluorescence spectrometer with FLS980 type.

2.2. Test results and analysis

Measured XRD pattern is shown in Fig. 1. It can be seen from Fig. 1 that main X-ray diffraction peaks are in accordance with XRD peaks of $BaGd_2ZnO_5$ in PDF 49-0518, which means that $BaGd_2ZnO_5$ compound has been generated from the raw materials through chemical reaction as follows

$$BaCO_3 + ZnO + Gd_2O_3 \rightarrow BaGd_2ZnO_5 + CO_2\uparrow \qquad (1)$$

The prepared Eu^{3+} doped $BaGd_2ZnO_5$ sample belongs to orthorhombic system and Pbnm space group, and the unit cell parameters are: a = 0.7162nm, b = 1.2489nm, c = 0.5775nm; $\alpha = \beta = \gamma = 90°$.
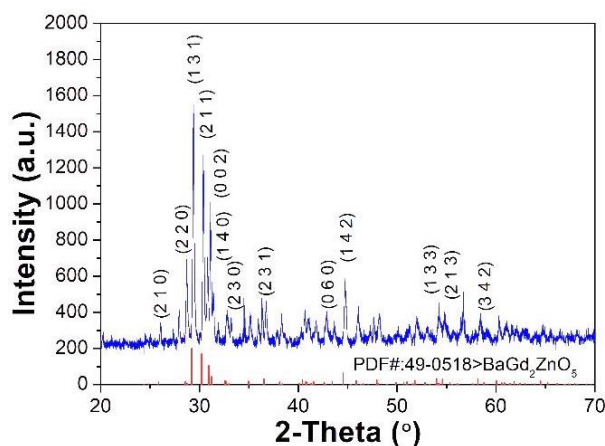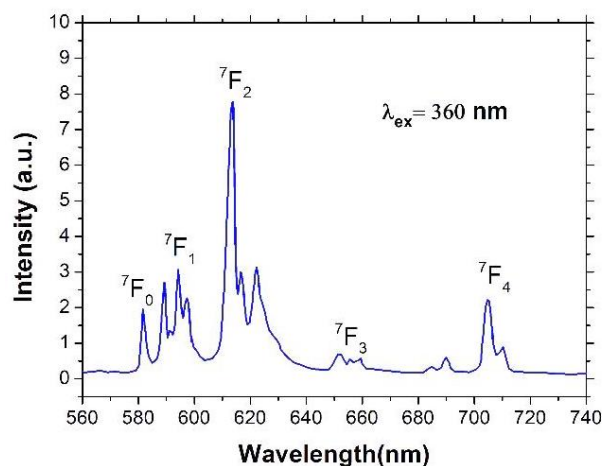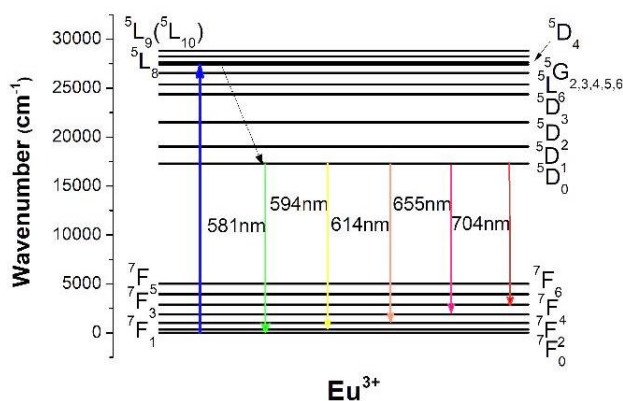

Fig. 1. XRD pattern of sample

(a) Emission spectra

(b) energy level transitions

Fig. 2. Emission spectra and energy level transitions of $BaGd_2ZnO_5$:Eu^{3+}

Emission spectra of the prepared $BaGd_2ZnO_5$:Eu^{3+} sample under 360 nm excitation and energy level transitions of Eu^{3+} are given in Fig. 2. In Fig. 2(a), there are five primary emission peaks, located at 581 nm, 594 nm, 614 nm, 655 nm and 704 nm, respectively, which correspond to energy level transitions of Eu^{3+} from level

^{5}D$_0$ to levels ^{7}F$_0$, ^{7}F$_1$, ^{7}F$_2$, ^{7}F$_3$ and ^{7}F$_4$. Energy level transition process can be described as follows: an electron at ground state ^{7}F$_0$ of Eu^{3+} ion can jump to excitation level ^{5}D$_4$ when absorbing a photon with wavelength 360 nm, then, the electron mainly relax to level ^{5}D$_0$ through non-radiation transition due to the energy level difference between level ^{5}D$_4$ and its lower levels. Energy level difference between level ^{5}D$_0$ and its neighboring lower level ^{7}F$_6$ is about 12200 cm^{-1}, much larger than phonon energy of BaGd$_2$ZnO$_5$ host, so non-radiative transition can be neglected and the electron located in level ^{5}D$_0$ primarily transits to lower levels by releasing a photon with corresponding energy. Because released photons all locate at visible light region, Eu^{3+} is one type of ions with excellent luminescence performance.

3. Determination of refractive index of BaGd$_2$nO$_5$:Eu^{3+} sample

Energy transitions of Eu^{3+} ion from level ^{5}D$_0$ to levels ^{7}F$_j$ (j=0, 1, 2, 3, 4, 5, 6) have such characteristics as: 1) the smallest energy difference between level ^{5}D$_0$ and its lower levels is about 12200 cm^{-1}, non-radiative transitions can be neglected, so luminescence quantum efficiency from the upper level ^{5}D$_0$ can be considered as 100% within largish dopant scope of Eu^{3+} ion; 2) fluorescence intensity of the upper level ^{5}D$_0$ takes on exponential decay curve with luminescence time, so it is easy to fitting lifetime of level ^{5}D$_0$; 3) energy level transition from ^{5}D$_0$ to ^{7}F$_1$ belongs to pure magnetic dipole transition, whose transition probability is only related to refractive index of host material, but without relationship with crystal field symmetry.

According to above characteristics, refractive index of host material can be determined by adopting method in Ref. [19], which is described as follows:

1) Set magnetic transition probability of ^{5}D$_0 \rightarrow {}^7$F$_1$ as A$_1$, the other transitions (^{5}D$_0 \rightarrow {}^7$F$_j$ (j=0, 2, 3, 4, 5, 6)) can be expressed as

$$A_j = a_j A_1 \qquad (2)$$

here, $a_j = \frac{\int I_j(\nu)d\nu}{\int I_1(\nu)d\nu} \cdot \frac{\overline{\nu}_1}{\overline{\nu}_j}$ denotes proportional coefficient

and means ratio of integral intensity of spectral peaks.

2) Total transition probability from level ^{5}D$_0$ to all its lower levels can be described as

$$A = \sum_{j=0}^{6} A_j = \sum_{j=0}^{6} a_j \cdot A_j = \left(\sum_{j=0}^{6} a_j\right) \cdot A_1 \qquad (3)$$

3) Measure lifetime τ_0 of energy level ^{5}D$_0$, there is a relationship between the total transition probability and the lifetime τ_0 as A = $1/\tau_0$, another equation can be

deduced as

$$A_1 = \frac{1}{\tau_0 \cdot \left(\sum_{j=0}^{6} a_j\right)} \qquad (4)$$

4) If the magnetic dipole transition probability of ^{5}D$_0 \rightarrow {}^7$F$_1$ transition of a host material with known refractive index n' is set as A'_1, the refractive index n of underdetermined host material can be expressed as
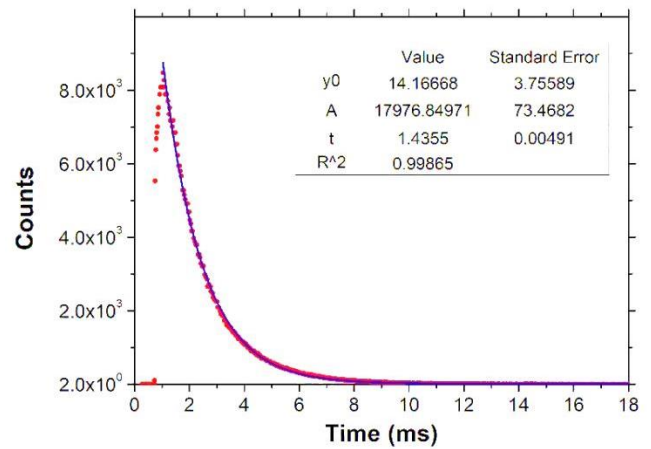
$$n = n' \cdot (A_1/A'_1)^{1/3} \qquad (5)$$

Fig. 3. Fluorescent decay curve

Fluorescence decay curve of monitoring wavelength 614 nm (corresponding to transition of ^{5}D$_0 \rightarrow {}^7$F$_2$) under excitation at wavelength 360 nm is displayed in Fig. 3, it is obvious that the decay curve obeys exponential dependence.

In order to obtain fluorescence lifetime, the decay curve is fitted according to equation as

$$y = A \cdot e^{-\frac{x}{t}} + y0 \qquad (6)$$

In Fig. 3, the dotted line denotes experimental data, the solid line is fitted data, it is clear that the fitted data curve is very agreement with the experimental data. The fitted parameters are A=17976.84, y0=14.16668, t=1.4355, respectively. Goodness of fit is equal to R^2=0.99865, means the good coincidence degree. The fitted lifetime of level ^{5}D$_0$ is $\tau_0 = 1.4355 ms$.

The relative transition probability calculated from Fig. 2(a), ^{5}D$_0$ level lifetime and obtained refractive index of BaGd$_2$ZnO$_5$ host powder are listed in Table 1.

Table 1. Relative transition probability, $^5D_0$ lifetime and calculated refractive index

Host material		LaF$_3$	BaGd$_2$ZnO$_5$
Relative transition probability	a_0	0.063	0.21
	a_1	1	1
	a_2	0.86	1.56
	a_3	0	0.30
	a_4	0.45	0.60
	a_5	0	0
	a_6	0	0
τ_0 (ms)		6.7	1.44
A_1 (sec^{-1})		60.3	189.8
Refractive index		1.58	2.31

According to introduced method and data of LaF$_3$ crystal in Ref. [19], refractive index of BaGd$_2$ZnO$_5$ host powder is equal to 2.31.

4. Determination and analysis of J-O parameters of BaGd$_2$nO$_5$:Eu^{3+} sample

Because transition $^5D_0 \rightarrow ^7F_1$ of Eu^{3+} ion belongs to pure magnetic dipole transition, whose transition probability can be expressed as

$$A_{md} = \frac{64\pi^4}{3h} \frac{\bar{v}_{md}^3}{2J'+1} n^3 S_{md} \qquad (7)$$

Here, h is Plank constant, J' is total angular quantum number, $\bar{v}_{md}$ denotes transition mean wavenumber, and S_{md} represents spectral line intensity of magnetic dipole transition, which generally is considered to be a certain value without relationship with host material and can be described as

$$S_{md} =$$
$$\frac{h^2}{16\pi^2 m^2 c^2} |< 4f^N \, \Psi \, J \, \|L + 2S\| \, 4f^N \, \Psi' J' >|^2,$$
$$\qquad (8)$$

where, m, c represent electron mass and light velocity, respectively, and $|< 4f^N \, \Psi \, J \, \|L + 2S\| \, 4f^N \, \Psi' J' >|^2$ is reduced matrix element for magnetic dipole reaction, when $J' = J + 1$,

$$|< 4f^N \, \Psi \, J \, \|L + 2S\| \, 4f^N \, \Psi' J' >|^2$$
$$= [(S + L + J + 2)(S + L - J)(J + S + 1 - L)(J + L + 1 - S)/4(J + 1)]^{1/2}$$
$$\qquad (9)$$

Here, S, L and J represent spin angular momentum, orbit angular momentum and total angular momentum, respectively.

According to optical transition selection rule of RE ions [21, 22], electrical dipole transitions of $^5D_0 \rightarrow ^7F_J$ (J=2, 4, 6) are allowable, whose radiative transition probability can be expressed as

$$A_{ed} = \frac{64\pi^4 e^2}{3h} \frac{\bar{v}^3}{2J'+1} \frac{n(n^2+2)^2}{9} \times \sum_{t=2,4,6} \Omega_t \langle \psi_J \| U^t \| \psi'_{J'} \rangle^2 \qquad (10)$$

where, e, n denote electron charge and refractive index of host material, respectively, $\bar{v}$ is transition mean wavenumber, $\langle \psi_J \| U^t \| \psi'_{J'} \rangle$ represents reduced matrix element of transition from original state ψ_J to ending state $\psi'_{J'}$.

The reduced matrix for $^5D_0 \rightarrow ^7F_J$ transitions of Eu^{3+} ions are listed in Table 2.

Table 2. The reduced matrix for $^5D_0 \rightarrow ^7F_J$ transitions of Eu^{3+} ions

	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_4$	$^5D_0 \rightarrow ^7F_6$
$U^{(2)}$	0.0032	0	0
$U^{(4)}$	0	0.0023	0
$U^{(6)}$	0	0	0.0002

In Table 2, only one reduced matrix element in each transition is nonzero value, and substituting these matrix elements into Equation (10) can obtain the expression as

$$A_J = \frac{64\pi^4 e^2}{3h} \frac{\bar{v}^3}{2J'+1} \frac{n(n^2+2)^2}{9} \times \Omega_J \langle \psi_J \| U^J \| \psi'_{J'} \rangle^2 \quad (11)$$

From Equations (7) and (10), ratio of spectral line intensity between electrical dipole transition and magnetic dipole transition can be expressed as

$$\frac{\int I_J(v)dv}{\int I_{md}(v)dv} = \frac{e^2}{S_{md}} \frac{v_J^3}{v_{md}^3} \frac{(n^2+1)^2}{9n^2} \Omega_J \times \langle \psi_J \| U^J \| \psi'_{J'} \rangle^2 \quad (12)$$

Values in the left of Equation (12) can be obtained from emission spectra, so the Judd-Ofelt parameters Ω_J can be deduced. Moreover, in Table 2, $U^{(6)}$ for transition $^5D_0 \rightarrow ^7F_6$ is very small, which means that luminescence intensity corresponding to transition $^5D_0 \rightarrow ^7F_6$ is often small and difficult to be observed, so that for most of Eu^{3+} doped phosphors, Judd-Ofelt parameters Ω_2 and Ω_4 can be obtained from emission spectra.

The calculated Judd-Ofelt parameters Ω_2 and Ω_4 of Eu^{3+} doped BaGd$_2$ZnO$_5$ microcrystalline powder are listed in Table 3, the two parameters of other host material are also given for comparision.

Table 3. Judd-Ofelt parameters Ω_2 and Ω_4 of Eu^{3+} ions in several host material

Material		$\Omega_2(\times 10^{-20}$cm$^2)$	$\Omega_4(\times 10^{-20}$cm$^2)$
LaF$_3$:Eu^{3+} [23]	Crystal	1.19	1.16
Gd$_2$O$_3$:Eu^{3+} [25]	135nm particle	7.74	5.66
Y$_2$O$_3$:Eu^{3+} [24]	Bulk material	6.31	0.66
YAlO$_3$:Eu^{3+}[23]	Crystal	2.66	6.32
PbF$_2$-H$_3$BO$_3$-Eu$_2$O$_3$ [20]	Glass (50% H$_3$BO$_3$)	$\approx$9	$\approx$0.5
BaGd$_2$ZnO$_5$:Eu^{3+}	Microcrystalline powder	3.82	1.23

It is well known that Judd-Ofelt intensity parameter Ω_2 depends on the asymmetry nature of the local environments around rare earth ions, which implies that it also depends on the covalence between rare earth ions and ligand anions. The higher Ω_2 value means the stronger covalent property and lower symmetrical characteristic of host material, otherwise, the host material has stronger ionic property and higher symmetrical characteristic. From Table 3, it can be seen that Ω_2 value of the prepared BaGd$_2$ZnO$_5$:Eu^{3+} microcrystalline powder is 3.82, which is less than these Ω_2 values of Gd$_2$O$_3$, Y$_2$O$_3$ host material and PbF$_2$-H$_3$BO$_3$-Eu$_2$O$_3$ oxyfluoride glass, and larger than that value of LaF$_3$ host material, but similar to Ω_2 value of YAlO$_3$ host. These results can be explained as that because oxidability of F$^-$ ion is larger than oxidability of O^{2-} ion, and easier to capture electron to form ionic bond with RE ions, so that fluoride host material has stronger ionic property and smaller Ω_2 value than oxide host material.

Determining Judd-Ofelt parameters through emission spectra of Eu^{3+} ions doped in host material can obtain structure information and covalence property of the host material. Therefore, Eu^{3+} ions can be taken as one kind of probe to be doped into host material and detect hos material characteristic. The method proposed in this article can not only analyze optical characteristic for host material with known refractive index, but also for host material with unknown refractive index, especially, for powder material, so it can be extensively used to evaluate luminescence performance of host material.

5. Conclusion

In this article, Eu^{3+} doped BaGd$_2$ZnO$_5$ microcrystalline powder are prepared through high-temperature solid-state method firstly, XRD pattern is measured and a good and pure crystal phase with orthorhombic structure is obtained. Then, emission spectra under 360nm excitation is measured and five emission peaks are discovered, corresponding to transitions from energy level ^{5}D$_0$ to ^{7}F$_0$, ^{7}F$_1$, ^{7}F$_2$, ^{7}F$_3$ and ^{7}F$_4$. Moreover, refractive index of BaGd$_2$ZnO$_5$: Eu^{3+} microcrystalline

powder sample is calculated through obtained lifetime of energy level ^{5}D$_0$ in Eu^{3+} ions. At last, Judd-Ofelt calculation is executed for the prepared powder sample and spectral intensity parameters Ω_2 and Ω_4 are obtained as 3.82 and 1.23, respectively, which means that BaGd$_2$ZnO$_5$ host material has higher covalence property and lower symmetrical characteristic, and is one kind of host material with good luminescence performance.

References

[1] X. L. Zhang, Y. Z. Wang, H. F. Shi, Acta Phys. Sin. **55**(4), 1787 (2006) (in Chinese).

[2] J. Liu, C. Liu, H. X. Shi, P. Wang, Acta Phys. Sin. **65**(19), 194209 (2016) (in Chinese).

[3] Y. B. Xing, B. Y. Ye, Z. W. Jiang, N. L. Dai, J. Y. Li, Acta Phys. Sin. **63**(1), 014209 (2014) (in Chinese).

[4] X. Huang, Nat. Photonics **8**(10), 748 (2014).

[5] C. H. Liang, Y. C. Chang, Y. S. Chang, Appl. Phys. Lett. **93**(21), 211902 (2008).

[6] F. Vetrone, J. C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, J. Phys. Chem. B **107**(5), 1107 (2003).

[7] J. Zhao, R. Hua, W. Zhang, Z. Feng, D. Tang, L. Na, B. Chen, J. Alloys Compd. **588**(5), 519 (2014).

[8] V. Babin, K. D. Oskam, P. Vergeer, A. Meijerink, Radiat. Meas. **38**(4-6), 767 (2004).

[9] B. M. Vander, L. Aarts, A. Meijerink, Phys. Chem. Chem. Phys. **11**(11), 11081 (2009).

[10] T. Trupke, M. A. Green, P. Würfel, J. Appl. Phys. **92**(3), 1668 (2002).

[11] K. M. Deng, L. Li, X. T. Wei, Y. H. Chen, C. X. Guo, M. Yin, J. Nanosci. Nanotechnol. **11**(11), 9489 (2011).

[12] Y. H. Wang, L. H. Xie, H. J. Zhang, J. Appl. Phys. **105**(2), 023528 (2009).

[13] S. Y. Xiang, B. J. Chen, J. S. Zhang, X. P. Li, J. S. Sun, H. Zheng, Z. L. Wu, H. Zhong, H. Q. Yu, H. P. Xia, Opt. Mater. Express **4**(9), 1966 (2014).

[14] B. Dong, D. P. Liu, X. J. Wang, T. Yang, S. M. Miao, C. R. Li, Appl. Phys. Lett. **90**(18), 181117 (2007).

[15] I. Etchart, A. Huignard, M. Berard, M. N. Nordin, I.

Hernandez, R. J. Curry, W. P. Gillin, A. K. Cheetham, J. Mater. Chem. **20**(3), 3989 (2010).

[16] C. F. Guo, X. Ding, Y. Yan, J. Am. Ceram. Soc. **93**(6), 1708 (2010).

[17] B. R. Judd, Phys. Rev. **127**(3), 750 (1962).

[18] G. S. Ofelt, J. Chem. Phys. **37**(3), 511 (1962).

[19] X. Y. Jiang, Z. L. Zhang, S. H. Xu, Chin. J. Lumin. **11**(2), 79 (1990) (in Chinese).

[20] B. J. Chen, H. Y. Wang, S. H. Huang, Chin. J. Lumin. **22**(2), 139 (2001) (in Chinese).

[21] M. J. Weber, Optical Properties of Ions in Crystals (New York: Wiley Interscience) 467 (1976).

[22] S. J. L. Ribeiro, R. E. O. Diniz, Y. Messaddeq, Chem. Phys. Lett. **220**(3-5), 214 (1994).

[23] S. Y. Zhang, Spectroscopy of Rare Earth Ions – Spectral Property ad Spectral Theory (Beijing: Science Press) 126 2008 (in Chinese).

[24] W. F. Krupke, Phys. Rev. **145**(1), 325 (1966).

[25] C. X. Liu, J. H. Zhang, S. Z. Lv, J. Y. Liu, Acta Phys. Sin. **53**(11), 3945 (2004) (in Chinese).

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