High Sensitivity Thermometry and Optical Heating Bi-function of $\text{Yb}^{3+}/\text{Tm}^{3+}$ Co-doped $\text{BaGd}_2\text{ZnO}_5$ Phosphors

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Abstract

$\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors have been effectively synthesized by traditional sol-gel method. The graph of X-ray diffraction (XRD) exhibited that the obtained phosphors were pure orthorhombic phase. The morphology and composition of the samples were obtained by field emission-scanning electron microscope (FE-SEM) and the energy dispersive spectrometry (EDS). From upconversion luminescence (UCL) emission spectra, the two strong blue emissions were obviously observed at 478 and 485 nm under the excitation of 980 nm. The possible energy diagram and UC mechanism were explained in detail. Optical temperature (T) sensing performances were evaluated in the temperature ranging 313 K - 573 K. And the highest sensor sensitivity calculated was 0.0055 K^{-1} at 323 K. Additionally, the laser excitation heating effect was also explored. The results indicated that $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors could be applied on optical temperature sensors and optical heater.

Keyword: Sol-gel method; XRD; UCL; Optical temperature sensing; Optical heater

1. Introduction

Lanthanide (Ln^{3+})-doped luminescent materials which have interesting and unique optical properties have already attracted extensive attention and been used to light, display and communicate, and so on [1-3]. Due to the high conversion efficiency, abundant metastable energy levels, and narrow emission band, rare earth (RE) ions are closely related to the UCL process under appropriate excitation wavelength [4-6]. Therefore, many couples of RE ions have been investigated deeply, such as Er^{3+} - Yb^{3+} [6-9], Nd^{3+} - Yb^{3+} [10, 11], Tb^{3+} - Yb^{3+} [12, 13], and Pr^{3+} - Yb^{3+} [14].

Temperature that is a unique unit in thermodynamics and accurately measuring the T of the materials has great influence on scientific research and practical production. Owing to the absorption and emission spectra of RE ions showing temperature sensitivity, Kusama et al. firstly put forward measuring temperature according to fluorescence intensity ratio (FIR) [15]. The FIR technique has many advantages comparing with traditional measurement method. Firstly, it is not constrained by the temperature condition, and increases the accuracy of measurement. Secondly, it utilizes the thermally coupled energy levels with thermal stability and chemical durability [16]. Consequently, FIR technique can be used to measure optical temperature sensitively and also plays a great role in controlling the temperatures of special situations, for example power station, coal mine and oil refinery, etc [17].

Representatively, Tm^{3+} ion can emit blue and red light under 980 nm excitation, Yb^{3+} ion generally absorbs 980 nm photons and enhances emission intensities of Tm^{3+} ion as sensitizer [18, 19]. And the Tm^{3+} ion which includes thermally coupled energy

levels is appropriate for FIR technique with preferable sensitivity and accuracy [20-23]. Recently, so many researches have reported that the properties of host materials that contain structure, phonon energy, stability and functionality decide the exploring ranges and sensitivities of optical temperature sensors based on the FIR technique [24-27]. However, the oxide chemical stability is good but processes high phonon energy and low upconversion efficiency. $\text{BaGd}_2\text{ZnO}_5$ as a new host material has overcome above mentioned defects. During the process of preparing $\text{BaGd}_2\text{ZnO}_5$, ZnO as a kind of raw materials, which contains some special properties of large free-exciton binding energy, non-noxious nature, and optical characteristic features at room temperature, is often used to synthesize new materials for photonics, solar cells and spin-transport electronics (spintronics) [28, 29]. Therefore, Etchart et al. reported that $\text{BaGd}_2\text{ZnO}_5$ was so far the most efficient UCL materials and UC efficiency was higher than NaYF_4 previously [30]. The phonon energy of this material only is 360 cm^{-1} [31, 32]. In this paper, the $\text{Tm}^{3+}/\text{Yb}^{3+}$ doped $\text{BaGd}_2\text{ZnO}_5$ phosphors were effectively got via sol-gel ways. The UCL excited by 980 nm diode laser has been investigated in $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors. The FIR from $^1\text{G}_{4(2)}$ and $^1\text{G}_{4(1)}$ levels to $^3\text{H}_6$ of Tm^{3+} was used to investigate the optical temperature sensing properties. Moreover, the heating effect was also explored. All the experimental results indicated that the $\text{BaGd}_2\text{ZnO}_5: \text{Yb}^{3+}/\text{Tm}^{3+}$ phosphors can be applying on optical temperature sensing and optical heater.

2. Experimental

2.1 Synthesis of $\text{BaGd}_2\text{ZnO}_5: x \text{Tm}^{3+}, y \text{Yb}^{3+}$ phosphors

$\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors were successfully synthesized by sol-gel ways with variation of doping concentration. All chemical reagent can be directly used without further purification and commercially available. We will describe the process of synthesis in details. 0.3947 g BaCO_3 , 0.1628 g ZnO , certain amount $\text{Tm}(\text{NO}_3)_3$, $\text{Gd}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3$ were dissolved in deionized water (18 Mohm·cm) to form transparent solution A. Then, weighting 3.3622 g citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was also dissolved in deionized water with stirring to get transparent solution B. And, solution B was dropped slowly in solution A with continuously stirring. After a few minutes, the prepared transparent solution was dried at 90°C for 24 h to obtain the brown dried gels. After grinding in an agate mortar, the phosphors were fired in air at 500 °C for 2 h. Finally, the preheated samples were annealed to 1200°C and kept for 2 h to obtain the $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors.

2.2 Characterization

The analysis of the structure and crystalline phase was recorded on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 15 °/min in the 2θ range from 10° to 80° using Cu K α radiation ($\lambda = 0.15405$ nm). The field emission-scanning electron microscope (FE-SEM, XL30, Philips) examined morphology and size of the obtained samples. The chemical element analysis was measured by the energy dispersive spectrometry (EDS) coupled with FE-SEM. The Andor Shamrock SR-750 fluorescence spectrometer measured the UCL spectra. The signals of obtained samples were collected from 400 to 750 nm by A CCD detector combined with a monochromator. A 980 nm diode which was coupled to a fiber (the core diameter 200

mm, numerical aperture 0.22) laser was used as the pump source. Andor SR-500i spectrometer (Andor Technology Co, Belfast, UK) was used to record the luminescence spectra by exciting the samples with 980 nm. The Yb³⁺/Tm³⁺ co-doped BaGd₂ZnO₅ samples were loaded in an iron sample cell and the temperature of the samples increased from 313 K to 573 K heated by resistive wire elements.

3. Results and discussion

3.1 XRD

The phase purity and crystal structure of BaGd₂ZnO₅: xTm³⁺, yYb³⁺ phosphors have been measured by XRD. The XRD patterns of BaGd₂ZnO₅: xTm³⁺, yYb³⁺ ((a) y = 4%, x = 0.1%, 0.3%, 0.5%, 0.7% and 0.9%; (b) x = 0.1%, y = 6%, 8%, 10%, 12%, 15% and 20%) are showed in Figure 1. The results shows that all diffraction peaks location of phosphors conform to the standard card of BaGd₂ZnO₅ (JCPDS No. 49-0518). Experimental data reveals that obtained samples are pure orthorhombic phase and Yb³⁺ and Tm³⁺ have also successfully doped in substrate. The morphology, size and elemental composition of BaGd₂ZnO₅: 0.1% Tm³⁺, 12% Yb³⁺ sintered at 1200⁰C were revealed by FE-SEM image and EDS data in Figure 2 (a) and (b). From the Figure 2 (a), we can see that the particles present nearly uniform distribution and slightly agglomerate approximate spherical morphology with the size of about 1μm. According to the EDS data of Tm³⁺ /Yb³⁺ co-doped BaGd₂ZnO₅ exhibited in Figure 2 (b), the atomic percentages of the samples were found to be Ba:Zn = 3.14:3.24, which was also shown in Table 1. And the percentage of Rare Earth element (namely Gd:Tm:Yb = 86.15:2.70:11.15), which was relative to the total quantities of Rare

Earth ions, was consistent with expected value in general. However, the atomic percentage ratio of O was higher than the estimated value because of the environmental trace and combustible gases evolved during the reaction [33].

3.2 UCL of BaGd₂ZnO₅: xTm³⁺, yYb³⁺

Under pump power 980 nm, Figure 3 illustrates UCL emission spectra of Yb³⁺/Tm³⁺ co-doped BaGd₂ZnO₅ samples with different doping concentrations. Two blue emissions and red emission are observed at 478 nm (¹G₄₍₂₎→³H₆), 485 nm (¹G₄₍₁₎→³H₆) and 655 nm (¹G₄₍₂₎→³F₄), respectively. We can see that one of the bands is divided into two sections in the blue region because of interactions among electrons and spin-orbit coupling. In the Figure 3(a), the room-temperature UC emission intensities hold Yb³⁺ ions concentration at fixed 4%, Tm³⁺ concentrations change from 0.1% to 0.9%. At the same time, Figure 3(b) shows the concentrations of Yb³⁺ ions in the co-doped BaGd₂ZnO₅ phosphors vary from 6% to 20%, the Tm³⁺ ions concentration is set at 0.1%. As shown in Figure 3(a) and (b), it is observed that the spectral properties and UCL intensities vary with the changes of doping concentrations and the location of emission peak shows no changes. In addition, it can be found that the UCL emission intensities of BaGd₂ZnO₅: x Tm³⁺, 4% Yb³⁺ decrease gradually with the concentration of Tm³⁺ more than 0.1% as a result of concentration quenching in Figure 3(a). Furthermore, the concentration quenching may result from energy transfer between the nearest Tm³⁺ and Yb³⁺ ions. When the concentration of Tm³⁺ is above 0.1%, the distance between Tm³⁺ and Yb³⁺ ions will be reduced, which strengthens nonradiative relaxation and causes the decrease in UCL intensity [34]. The

Figure 3(b) indicates the UCL intensities decrease extraordinarily with the increasing Yb^{3+} above 12%. Therefore, we can concluded that the better luminous one of these $\text{BaGd}_2\text{ZnO}_5$ phosphors is doped 0.1% Tm^{3+} and 12% Yb^{3+} .

3.3 Energy Diagram and Pump Power Study

In Figure 4 and Figure 5, UC processes and related mechanism can be explained in detail. Figure 4 displays possible double logarithmic relationship between emission intensities and excitation power by experiment fitting, and the relationship of the UCL intensity (I_{UC}) and the pump power (P_{pump}) obey following relationship:

$$I_{UC} \propto (P_{pump})^n,$$

where n represents the number of photons used to jump to the excited state, I_{UC} and P_{pump} are respectively the UCL intensity and power [35-37]. It can be found that the slopes of the two fitted lines corresponding to 478 nm and 485 nm blue emission are 2.86 and 2.63, respectively. Therefore, the n values reveal that blue UC emission is three-photon process and three NIR excitation photons are absorbed to emit one blue UC photon in the $\text{BaGd}_2\text{ZnO}_5:\text{Tm}^{3+}/\text{Yb}^{3+}$ samples.

UC mechanism is shown in Figure 5. The $^2\text{F}_{7/2}$ level of Yb^{3+} ions are excited to $^2\text{F}_{5/2}$ under the 980 nm excitation. And then, the $^3\text{H}_5$ which is metastable energy level of Tm^{3+} ions is populated by energy transfer (ET) or ground state absorption (GSA) process. The population of lower level $^3\text{F}_4$ is populated by a multiphonon relaxation. After through the process of ET an excited state absorption (ESA), the population of the $^3\text{F}_4$ state to higher $^3\text{F}_{2,3}$ states then from the $^3\text{F}_{2,3}$ to $^3\text{H}_4$ level takes place by non-radiative relaxation. Due to jumping from $^3\text{H}_4$ (Tm^{3+}) to $^1\text{G}_4$ (Tm^{3+}), thermally

coupled levels $^1G_{4(2)}/^1G_{4(1)}$ of the 1G_4 state relax to 3H_6 to emit blue lights. The population at the 1G_4 state returned to the 3F_4 level and transition from the $^3F_{2,3}$ levels to the lowest state 3H_6 gives the red emissions at around 655 and 695 nm, correspondingly.

3.4 Temperature Sensing Behavior

According to the different intensities ratio from two closely thermally coupled levels, the UCL properties which is connected with temperature of $BaGd_2ZnO_5: Tm^{3+}$, Yb^{3+} phosphor has been surveyed to utilize in optical temperature sensing. It can also been seen that the population obeys Boltzmann distribution in the thermally coupled levels [24, 38]. Figure 6 exhibits the UC emission spectra of 0.1% Tm^{3+} , 12% Yb^{3+} codoped $BaGd_2ZnO_5$ sample ranging 313 K - 573 K and the pump power is set up at 0.5W. We can find interestingly that the FIR (I_{478}/I_{485}) varies with the increase of temperature. Because the level of $^1G_{4(2)}$ can be populated obviously from $^1G_{4(1)}$ by a thermal excitation, which will lead to the relative variation of intensity between the two thermally coupled levels to ensure a quasi-thermal equilibrium according to the Boltzmann distribution. It is well known that the population of each energy level are linked with the emission intensities, so the FIR from two blue emissions can be defined in this way [39-41].

$$FIR = \frac{N(^1G_{4(2)})}{N(^1G_{4(1)})} = \frac{I_{478}}{I_{485}} = \frac{g_2 \sigma_{2j} \omega_{2j}}{g_1 \sigma_{1j} \omega_{1j}} \exp\left[\frac{-\Delta E}{K_B T}\right] = B \exp\left[\frac{-\Delta E}{K_B T}\right], \quad (1)$$

where

$$B = \frac{g_2 \sigma_{2j} \omega_{2j}}{g_1 \sigma_{1j} \omega_{1j}}, \text{ N, g, } \sigma, \omega \text{ represent ions, the degeneracy, the emission cross-section,}$$

the angular frequency of fluorescence two transitions. I_{2j} and I_{1j} are the intensities of the ${}^1G_{4(2)} \rightarrow {}^3H_6$ (455 nm-482 nm) and ${}^1G_{4(1)} \rightarrow {}^3H_6$ (482 nm-509 nm), respectively. ΔE is the energy difference between the ${}^1G_{4(2)}$ and ${}^1G_{4(1)}$ levels, k_B represents the Boltzmann constant and T shows the absolute temperature [41].

As shown in Figure 7(a), the logarithm of FIR and T^{-1} are fitted to straight line which the slope is 575.2 according to experimental data. And the 575.20 is equal to the value of $\frac{-\Delta E}{k_B}$. The Figure 7(b) exhibits the distinction of FIR with different temperature, in which the FIR values increased from 1.00 to 2.17 from 313 K to 573 K. The calculated value of B was 5.81.

The sensitivity is the most significant parameter for detecting temperature and has the relation with the rate of FIR varying with different temperature and the expression was be written as on the basis of equation (1) [42]:

$$S = \frac{dFIR}{dT} = FIR \left[\frac{\Delta E}{k_B T^2} \right] = B \frac{\Delta E}{k_B T^2} \exp \left[\frac{-\Delta E}{k_B T} \right]. \quad (2)$$

The Figure8 illuminates the relationship between sensitivity and temperature. It can be obviously got that the maximum sensitivity is about 0.0055 K^{-1} at 323 K and maintains decreasing with the temperature enhancement in experiment. Meanwhile, the measurement error that is a significant parameter for estimating temperature sensing can be calculated by this Equation according to the standard deviation FIR and sensitivity (3) [43]:

$$\Delta T = \Delta FIR \times \frac{K_B T^2}{FIR \Delta E} \quad (3)$$

where the ΔT is the error in the measured temperature and the ΔFIR is varied with FIR.

The error in measured temperature is obtained to be ± 0.20 K. The result shows that the $\text{BaGd}_2\text{ZnO}_5$: 0.1% Tm^{3+} , 12% Yb^{3+} phosphor can be regarded as potential temperature sensing materials.

3.5 Analysis of Optical Heater

Thermal effect induced by laser has been analyzed carefully under different power excitation, the temperature of $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped $\text{BaGd}_2\text{ZnO}_5$ phosphors varies with the increase of pump power in Figure 9. At the same time, the blue emission spectra of samples and plot of the calculated FIR (I_{478}/I_{485}) are shown in Figure 10 and the calculated values are exhibited in Table 2. The temperature of phosphors rises obviously with the enhancement of power densities and the maximum value of T is 365 K at 14.86 W/cm^2 . At the same time the number of FIR rises ranging 0.9 to 1.2 when the power density increases from 4.25 to 14.86 W/cm^2 . Considering properties of the optical temperature sensing, FIR and temperature have a linear relationship, so under different pump powers, the substrate temperature heated under the 980 nm excitation can be written by following Eq. (3) which is rearranged from Equation (1) [44]:

$$T = \left[\frac{1}{\ln B - \ln \text{FIR}} \right] \left[\frac{\Delta E}{K_B} \right]. \quad (4)$$

Where all the terms have their usual implications as mentioned Eq. (1). The substrate temperature varies from 328 to 365 K with increasing of power density from 7.08 to 14.86 W/cm^2 as shown in Figure 9. According to above results, the generation of heat becomes prominent by non-radiative relaxation at pump power. In general, the charged mobile is induced by the laser electric field strongly inside the crystalline,

and the obtained energy transfer to heat by electron-phonon coupling. Heat produced spreads away from the crystalline and causes an increase in temperature of the nearby volume. At the same time, the enhanced electron-phonon interaction also occurs and leads to extra heating of crystalline in crystalline. With temperature enhancement, the electron-phonon interaction increases [45, 46]. In conclusion, $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ phosphors have been made the better use of in respect of optical heating.

4. Conclusion

In summary, temperature sensing and optical heater bi-applications of $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped $\text{BaGd}_2\text{ZnO}_5$ phosphors are productively synthesized by sol-gel technique. The strong two blue emissions locate at 478 and 485 nm under excitation of 980 nm in UCL emission spectra of $\text{BaGd}_2\text{ZnO}_5:\text{Tm}^{3+}, \text{Yb}^{3+}$ phosphors. The UCL intensities rely on doping concentration, the optimal UCL emissions can be observed in $\text{BaGd}_2\text{ZnO}_5: 0.1\% \text{ Tm}^{3+}, 12\% \text{ Yb}^{3+}$ phosphor. UCL emissions are three-photon processes, and related UC mechanism has been also discussed in detail. The FIR of blue bands are related with temperature to examine its temperature sensing behavior. The maximum sensitivity of the $\text{BaGd}_2\text{ZnO}_5:0.1\% \text{ Tm}^{3+}, 12\% \text{ Yb}^{3+}$ phosphors is 0.0055K^{-1} at 323 K. Moreover, the heating generated by laser and the temperature of sample raise from 328 to 365 K with power density increasing from 4.25 to 14.86 W/cm^2 . Therefore, zincate will be selected to apply on our production and living with high sensitivity and convenience in terms of experimental data and results.

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Figure captions

Figure 1. The X-ray diffraction patterns of $\text{BaGd}_2\text{ZnO}_5: x\text{Tm}^{3+}, y\text{Yb}^{3+}$ phosphors: (a) $y = 4\%$, $x = 0.1\%, 0.3\%, 0.5\%, 0.7\%$ and 0.9% ; (b) $x = 0.1\%$, $y = 6\%, 8\%, 10\%, 12\%, 15\%$ and 20% . and reference date JCPDS 49-0518.

Figure 2. (a) The FE-SEM image of $\text{BaGd}_2\text{ZnO}_5: 0.1\% \text{Tm}^{3+}, 12\% \text{Yb}^{3+}$ sintered at 1200°C . (b) EDS spectrum of the sample for $\text{BaGd}_2\text{ZnO}_5: 0.1\% \text{Tm}^{3+}, 12\% \text{Yb}^{3+}$ as a function of energy.

Figure 3. The UCL spectra of $\text{BaGd}_2\text{ZnO}_5: x\text{Tm}^{3+}, y\text{Yb}^{3+}$: (a) $y = 4\%$; $x = 0.1\%, 0.3\%, 0.5\%, 0.7\%, 0.9\%$. and (b) $x = 0.1\%$; $y = 4\%, 6\%, 8\%, 10\%, 12\%, 15\%$ and 20% .

Figure 4. The log-log plots of UCL intensity of $\text{BaGd}_2\text{ZnO}_5: 12\% \text{Yb}^{3+}, 0.1\% \text{Tm}^{3+}$ as a function of 980 nm pump power.

Figure 5. The energy level diagram of $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped $\text{BaGd}_2\text{ZnO}_5$ under excitation of 980 nm and possible UC processes.

Figure 6. Temperature evolution of the Tm^{3+} UC emission spectra excited by 980 nm laser for the $\text{BaGd}_2\text{ZnO}_5: 0.1\% \text{Tm}^{3+}, 12\% \text{Yb}^{3+}$ phosphor from 313 K to 573 K.

Figure 7. (a) The monolog plot of the FIR versus $1/T$ for the $\text{BaGd}_2\text{ZnO}_5$ phosphor; (b) FIR (I_{478}/I_{485}) of Tm^{3+} blue UC emissions for the $^1\text{G}_{4(2)}/^1\text{G}_{4(1)} \rightarrow ^3\text{H}_6$ transitions relative to the temperature range of 313-573 K.

Figure 8. The sensor sensitivity $S = d\text{FIR}/dT$ as a function of the temperature for $\text{BaGd}_2\text{ZnO}_5: 0.1\% \text{Tm}^{3+}, 12\% \text{Yb}^{3+}$ phosphor.

Figure 9. Comparison of temperature increase under 980 nm excitation for $\text{Yb}^{3+}/\text{Tm}^{3+}$

co-doped BaGd₂ZnO₅ phosphor.

Figure 10. The UCL spectra of the blue bands $^1G_{4(2)}/^1G_{4(1)} \rightarrow ^3H_6$ of Tm³⁺ with different pumping power for BaGd₂ZnO₅: 0.1% Tm³⁺, 12% Yb³⁺. Inset: R as a function of laser pump power.

Table captions

Table 1. EDS compositional analysis of the sample for BaGd₂ZnO₅: 0.1% Tm³⁺, 12% Yb³⁺.

Table 2. Calculated values of temperature at different pump power densities corresponding to different FIR values of BaGd₂ZnO₅: Tm³⁺/Yb³⁺ phosphors.

Figure 1

Figure 2(a)

Figure 2(b)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table 1. EDS compositional analysis of the sample for BaGd₂ZnO₅: 0.1% Tm³⁺, 12% Yb³⁺.

BaGd ₂ ZnO ₅ : 0.1% Tm ³⁺ , 12% Yb ³⁺			
Element	Weight %	Atomic %	Error %
Ba	14.42	3.14	0.5
Zn	7.09	3.24	0.3
O	46.95	87.7	7.2
Gd	26.85	5.10	1.0
Tm	0.90	0.16	0.3
Yb	3.80	0.66	0.3

Table 2. Calculated values of temperature at different pump power densities corresponding to different FIR values of BaGd₂ZnO₅: Tm³⁺/Yb³⁺ phosphors.

Power density(w/cm ²)	FIR	Temperature(K)
7.08	1.00	328
7.78	1.03	331
8.49	1.06	338
9.20	1.07	341
9.91	1.09	344
10.62	1.11	347
11.32	1.12	350
12.03	1.15	355
12.74	1.16	356
13.45	1.17	360