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High sensitivity thermometry and optical heating Bi-function of Yb^{3+}/Tm^{3+} Co-doped $BaGd_2ZnO_5$ phosphors

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ABSTRACT

Yb^{3+}/Tm^{3+} co-doped $BaGd_2ZnO_5$ 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 luminance (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 Yb^{3+}/Tm^{3+} co-doped $BaGd_2ZnO_5$ phosphors could be applied on optical temperature sensors and 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. $BaGd_2ZnO_5$ as a new host material has overcame above mentioned defects. During the process of preparing $BaGd_2ZnO_5$, 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

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electronics (spintronics) [28,29]. Therefore, Etchart et al. reported that $BaGd_2ZnO_5$ 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 Tm^{3+}/Yb^{3+} doped $BaGd_2ZnO_5$ phosphors were effectively got via sol-gel ways. The UCL excited by 980 nm diode laser has been investigated in Tm^{3+}/Yb^{3+} co-doped $BaGd_2ZnO_5$ phosphors. The FIR from $^1G_{4(2)}$ and $^1G_{4(1)}$ levels to $^3H_6$ 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 $BaGd_2ZnO_5$: Yb^{3+}/Tm^{3+} phosphors can be applying on optical temperature sensing and optical heater.

2. Experimental

2.1. *Synthesis of $BaGd_2ZnO_5$: x Tm^{3+}, y Yb^{3+} phosphors*

Yb^{3+}/Tm^{3+} co-doped $BaGd_2ZnO_5$ 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 $Tm(NO_3)_3$, $Gd(NO_3)_3$ and $Yb(NO_3)_3$ were dissolved in deionized water (18 MΩ·cm) to form transparent solution A. Then, weighting 3.3622 g citric acid ($C_6H_8O_7$) 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 Yb^{3+}/Tm^{3+} co-doped $BaGd_2ZnO_5$ 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 Kα radiation (λ = 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 Yb^{3+}/Tm^{3+} co-doped $BaGd_2ZnO_5$ 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.

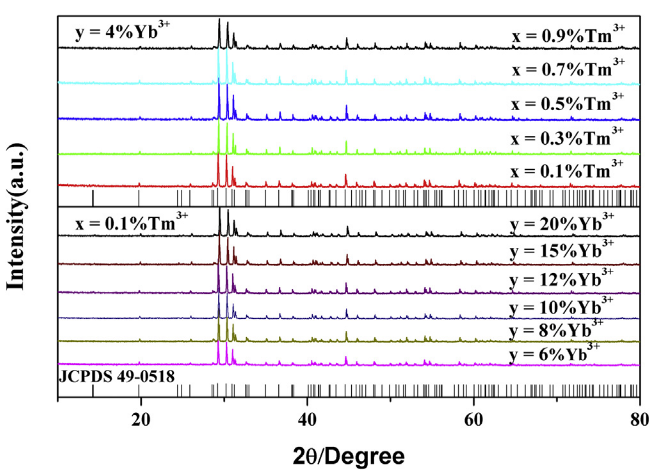

Fig. 1. The X-ray diffraction patterns of $BaGd_2ZnO_5$: xTm^{3+}, yYb^{3+} phosphors: (a) y = 4%, x = 0.1%, 0.3% 0.5%, 0.7% and 0.9%; (b) x = 0.1%, y = 6%, 8%, 10%, 12%, 15% and 20%. and reference date JCPDS 49-0518.

3. Results and discussion

3.1. *XRD*

The phase purity and crystal structure of $BaGd_2ZnO_5$: xTm^{3+}, yYb^{3+} phosphors have been measured by XRD. The XRD patterns of $BaGd_2ZnO_5$: xTm^{3+}, yYb^{3+} ((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 Fig. 1. The results show that all diffraction peaks location of phosphors conform to the standard card of $BaGd_2ZnO_5$ (JCPDS No. 49-0518). Experimental data reveals that obtained samples are pure orthorhombic phase and Yb^{3+} and Tm^{3+} have also successfully doped in substrate. The morphology, size and elemental composition of $BaGd_2ZnO_5$: 0.1% Tm^{3+}, 12% Yb^{3+} sintered at 1200 °C were revealed by FE-SEM image and EDS data in Fig. 2 (a) and (b). From Fig. 2 (a), we can see that the particles present nearly uniform

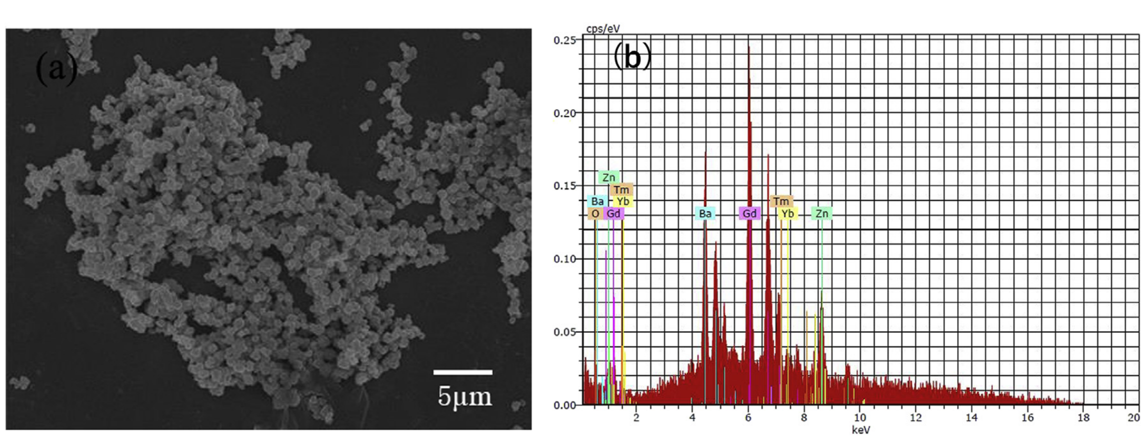

Fig. 2. (a) The FE-SEM image of $BaGd_2ZnO_5$: 0.1% Tm^{3+}, 12% Yb^{3+} sintered at 1200 °C. (b) EDS spectrum of the sample for $BaGd_2ZnO_5$: 0.1% Tm^{3+}, 12% Yb^{3+} as a function of energy.