

Short communication

A novel high color purity blue-emitting phosphor: $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Tm}^{3+}$ Jiangong Li^{a,*}, Huifang Yan^b, Fengmei Yan^c^a Department of Electronic Science and Engineering, Huanghuai University, Zhumadian 463000, China^b Department of Foreign Languages and Literature, Huanghuai University, Zhumadian 463000, China^c Department of Chemistry and Chemical Engineering, Huanghuai University, Zhumadian 463000, China

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ABSTRACT

A series of Tm^{3+} -doped $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Tm}^{3+}$ ($0.02 \leq x \leq 0.12$) blue-emitting phosphors with high color purity were prepared by solid-state reaction method. The crystal structure and luminescence properties of the as-prepared phosphors were studied. This phosphor shows a satisfactory blue performance (peak at 453 nm) due to the $^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition of Tm^{3+} excited by 357 nm light. Investigation of Tm^{3+} content dependent emission spectra indicates that $x=0.04$ is the optimum doping content of Tm^{3+} ions in the $\text{CaBi}_2\text{B}_2\text{O}_7$ host. The critical distance and the concentration quenching mechanism were also investigated. In particular, the color purity of as prepared sample was analyzed and the result shows that the color purity of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Tm}^{3+}$ is higher than the commercial blue phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM:Eu²⁺) and the latest reported Tm^{3+} doped blue phosphors. The present work suggests that the $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Tm}^{3+}$ phosphor is a potential blue-emitting candidate for the application in the near-UV WLEDs.

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1. Introduction

Currently, trivalent aldehydium (Tm^{3+}) rare-earth ion as an important activator of blue luminescence materials has drawn great attention for the applications in the white light emitting diodes (WLEDs) and field-emission display (FED) devices [1–4]. For example, $\text{NaBaBO}_3:\text{Tm}^{3+}$ and $\text{Sr}_2\text{B}_2\text{O}_5:\text{Tm}^{3+}$ have been proposed as a promising candidate as blue-emitting for the near-ultraviolet (near-UV) pumped WLEDs [5,6]. And an efficient $\text{La}_2\text{O}_3:\text{Tm}^{3+}$ phosphor was reported and shows excellent performance in the FED application [6]. In general, Tm^{3+} doped inorganic compounds always feature satisfying blue-emitting performance due to their blue transition of $^1\text{D}_2 \rightarrow ^3\text{F}_4$ under near-UV light excitation [7–9]. Hence, it is important to investigate the novel Tm^{3+} doped phosphors for possible applications in the industry especially in the solid state lighting area.

Rare earth doped borate phosphors have been widely investigated in the application in the near-UV WLEDs for their superiorities of a low synthesis temperature, good chemical and physical stability [10–15]. The investigations in Tm^{3+} doped borate phosphors were emerged in large numbers in recent years, such as $\text{NaBaBO}_3:\text{Tm}^{3+}$, $\text{Sr}_2\text{B}_2\text{O}_9\text{Cl}:\text{Tm}^{3+}$ and $\text{Sr}_2\text{B}_2\text{O}_5:\text{Tm}^{3+}$ [5,6,16]. Kargin et al. firstly published that the crystal structure of $\text{CaBi}_2\text{B}_2\text{O}_7$ single

phase of an orthorhombic structure with a space group of Pna (21) in 2008, and the corresponding lattice parameters is $a=8.937 \text{ \AA}$, $b=5.477 \text{ \AA}$, $c=12.591 \text{ \AA}$ and $V=616.33 \text{ \AA}^3$ [17]. However, to the best of our knowledge, there is no study on the luminescent properties of rare earth doped $\text{CaBi}_2\text{B}_2\text{O}_7$ phosphors except the investigation on the luminescent properties of Eu^{3+} doped $\text{CaBi}_2\text{B}_2\text{O}_7$: in our previous work [18].

In this paper, we synthesized a novel blue emitting phosphor $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Tm}^{3+}$ by solid state reaction method. Its crystal structure, crystal morphology, luminescence properties of $\text{CaBi}_2\text{B}_2\text{O}_7:\text{Tm}^{3+}$ were investigated. The critical distance, concentration quenching mechanism and color purity performance were also investigated in detail.

2. Experimental

In the Tm^{3+} ions doped $\text{CaBi}_2\text{B}_2\text{O}_7$ system, the coordinate number (CN) of Bi^{3+} and Ca^{2+} is 6 [15]. The ionic radii of Tm^{3+} , Ca^{2+} , Bi^{3+} is 0.88, 1.00 and 1.03 Å for CN=6, respectively [19]. Although the ionic radii of Bi^{3+} and Ca^{2+} are almost the same, we believe that Tm^{3+} could replace the Bi^{3+} due to the matched charge of two ions. Hence, the samples with formula $\text{CaBi}_{2-x}\text{B}_2\text{O}_7:x\text{Tm}^{3+}$ ($x=0, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.10$ and 0.12) were prepared by solid state reactions at a high temperature. CaCO_3 (analytical reagent grade), Bi_2O_3 (analytical reagent grade), H_3BO_3 (analytical reagent grade) and Tm_2O_3 (99.99% purity) were used as starting materials. The stoichiometric materials were weighted and ground together

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in an agate mortar (the amount of H_3BO_3 was added in excess about 5% to compensate its evaporation losses during the high temperature synthesis process.). Thereafter, the mixture was transferred to a corundum crucible and precalcined at $400^\circ C$ for 1 h, and then subsequently further sintered at $800^\circ C$ for 3 h in the air atmosphere.

The purities of samples were tested by X-ray diffraction (XRD) patterns using Rigaku Ultima IV Advanced X-ray diffractometer with a $Cu K\alpha$ (40.0 kV, 30.0 mA) radiation ($\lambda = 1.5418 \text{ \AA}$). A scan rate of $6^\circ/\text{min}$ was applied to record the patterns in the 2θ range of 10° – 60° . The crystal size and the crystal morphology of prepared samples were observed by Hitachi S-4800 scanning electron microscope (SEM). Photoluminescence excitation (PLE) and emission (PL) spectra were measured by Hitachi F-4600 spectrofluorometer equipped with a 150 W Xenon lamp as an excitation source. All the measurements were performed at room temperature.

3. Results and discussion

The XRD patterns of $CaBi_{2-x}B_2O_7:xTm^{3+}$ ($x = 0, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.10$ and 0.12) samples are shown in Fig. 1(a). It can be observed that all of the diffraction peaks from the $CaBi_2B_2O_7$ and Tm^{3+} doped $CaBi_2B_2O_7$ samples can be well indexed to the standard card ICSD#245016, consistent with a $CaBi_2B_2O_7$ phase of above mentioned orthorhombic structure with a space group of Pna (21) and lattice parameters of $a = 8.937 \text{ \AA}$, $b = 5.477 \text{ \AA}$, $c = 12.591 \text{ \AA}$ and $V = 616.33 \text{ \AA}^3$ (the detailed crystal structure of $CaBi_2B_2O_7$ is shown in Fig. 2). Moreover, the zoomed XRD patterns of all samples recorded in the 2θ ranging from 33.5° to 35° . It can be found that the diffraction angle of (120) diffraction peak shifted slightly to a higher angle when Tm^{3+} ions content increases. The phenomena can be explained that the ionic radii of Tm^{3+} ion (CN = 6, $r = 0.880 \text{ \AA}$) is smaller than the ionic radii of Bi^{3+} ion (CN = 6, $r = 1.03 \text{ \AA}$) and cause the shrinkage of crystal distortion of $CaBi_2B_2O_7:Tm^{3+}$ when the content of Tm^{3+} ions increases. The results confirm that Tm^{3+} ions have successfully substituted Bi^{3+} ions.

To investigate the crystal size and the crystal morphology, Fig. 3 illustrates the SEM image of a typical $CaBi_{1.96}B_2O_7:0.04Tm^{3+}$ sample. One can see that the typical sample shows the irregular powder size and morphology structure. The average grain size of $CaBi_{1.96}B_2O_7:0.04Tm^{3+}$ sample are about 2–8 μm . The experimental result indicates that the obtained sample shows a good crystallinity and the grain size is a suitable candidate for the application in the solid state lighting application.

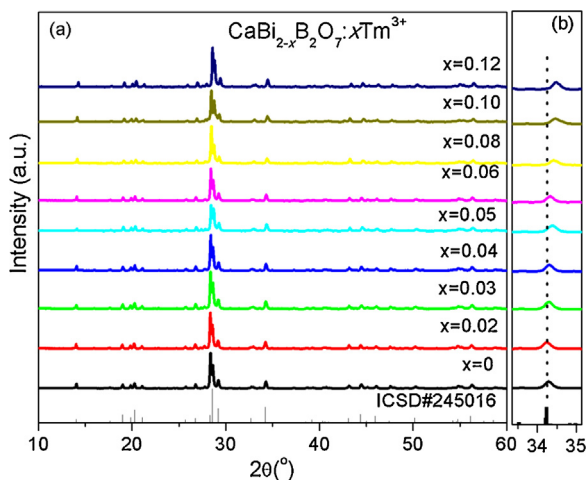


Fig. 1. (a) XRD patterns of $CaBi_{2-x}B_2O_7:xTm^{3+}$ ($x = 0, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.10$ and 0.12) samples (the standard data card ICSD#245016 for $CaBi_2B_2O_7$ is provided as a reference). (b) Zoomed XRD patterns of all samples recorded in the 2θ ranging from 33.5° to 35° .

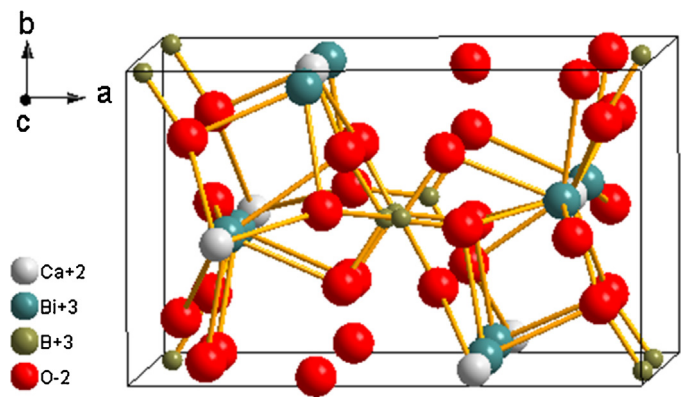


Fig. 2. Crystal structure of the $CaBi_2B_2O_7$ host.

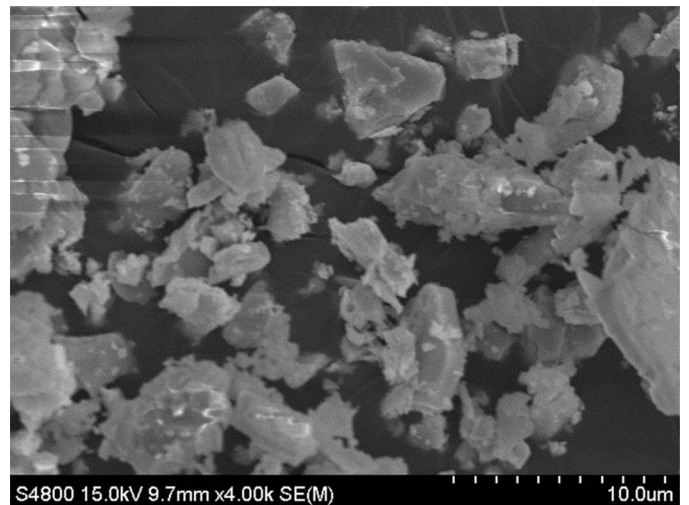


Fig. 3. SEM image of a typical $CaBi_{1.96}B_2O_7:0.04Tm^{3+}$ sample.

The excitation spectrum monitored at 453 nm of typical sample $CaBi_{1.96}B_2O_7:0.04Tm^{3+}$ is shown in Fig. 4 curve 1. It can be found that the excitation spectrum dominated at 357 nm, which is assigned to the typical $4f-4f$ transition of Tm^{3+} from ground state 3H_6 to excited state 1D_2 [20]. Fig. 4 curve 2 depicts the emission

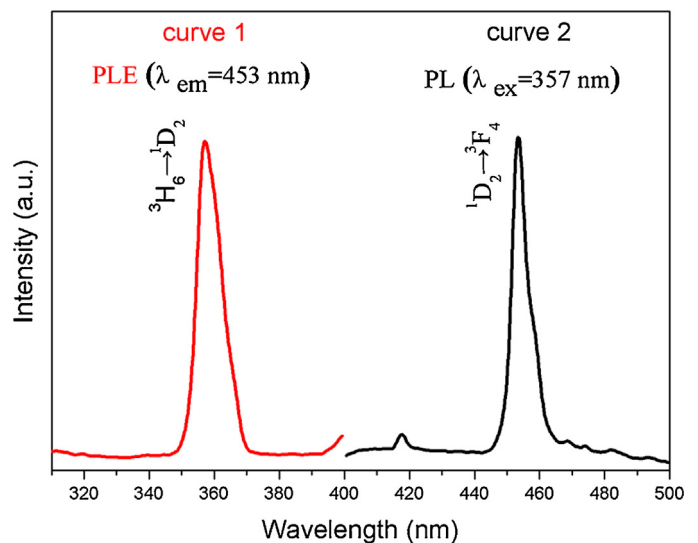


Fig. 4. Excitation spectrum ($\lambda_{em} = 453 \text{ nm}$) and emission spectrum ($\lambda_{ex} = 357 \text{ nm}$) of $CaBi_{1.96}B_2O_7:0.04Tm^{3+}$ phosphor.

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