



Preparation, characterization and photoluminescence properties of BaB₂O₄: Eu³⁺ red phosphor

Jie Liu, Xiang-De Wang, Zhan-Chao Wu*, Shao-Ping Kuang*

Key Laboratory of Eco-chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China

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ABSTRACT

A new red emitting BaB₂O₄: Eu³⁺ phosphor was synthesized by solid-state reaction method. X-ray powder diffraction (XRD) analysis confirmed the monoclinic formation of BaB₂O₄. Field-emission scanning electron-microscopy (FE-SEM) observation indicated that the microstructure of the phosphor consisted of irregular grains with heavy agglomerate phenomena. Upon excitation with 394 nm light, the BaB₂O₄: Eu³⁺ phosphor shows bright red emissions with the highest photoluminescence (PL) intensity at 611 nm due to ⁵D₀ → ⁷F₂ transitions of Eu³⁺ ions. The CIE chromaticity coordinates are calculated from the emission spectrum to be $x = 0.64$, $y = 0.35$. The effects of the Eu³⁺ concentration on the PL were investigated. The results showed that the optimum concentration of Eu³⁺ in BaB₂O₄ host is 6 mol% and the dipole–dipole interaction plays the major role in the mechanism of concentration quenching of Eu³⁺ in BaB₂O₄: Eu³⁺ phosphor. The effect of charge compensation on the emission intensity was also studied. The charge compensations of Li⁺, Na⁺ and K⁺ anions all increased the luminescent intensity of BaB₂O₄: Eu³⁺. K⁺ anion gave the best improvement to enhance the intensity of the emission, indicating K⁺ is the optimal charge compensator. All properties show that this phosphor could serve as a potential candidate for application as a red phosphor for NUV chip LED.

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1. Introduction

White light-emitting diodes (WLED) have already been used widely in many areas and have several promising features such as high luminous efficiency, low power consumption, maintenance and environmental protection [1,2]. Near-ultraviolet (NUV) conversion is the most available method which can achieve WLED [3,4]. In this method, red/green/blue tricolor phosphors are pumped by NUV-InGaN chips (~400 nm) to generate white light. So phosphors play a crucial role in these solid-state lighting devices. However, the main tricolor phosphors for NUV InGaN-based LEDs are still some classical phosphor, such as BaMgAl₁₀O₁₇: Eu²⁺ for blue, ZnS: (Cu⁺, Al³⁺) for green, and Y₂O₂S: Eu³⁺ for red [5]. Especially, the efficiency of the Y₂O₂S: Eu³⁺ red phosphor is about eight times less than that of the blue and green phosphors. Furthermore, the sulfide-based phosphors have low chemical stabilities against strong irradiation from InGaN chip and cause some environmental problems both in preparation and in application as they contain toxic elements. Therefore, it is urgent to find novel red phosphors, which exhibit intense red emission with strong excitation band at around 400 nm

for NUV LED chips. The red phosphor is also required to have high chemical stability and good chromaticity coordinates near the National Television Standard Committee (NTSC) standard values for red.

Borate is excellent matrices for Eu³⁺-activated phosphors due to several advantages such as low synthetic temperature, high stability and high luminescence efficiency. During the past few years, a number of red-emitting borate phosphors have been synthesized and studied extensively which can be used for fabricating WLEDs [6–10]. In this paper, a new phosphor of Eu³⁺ doped monoclinic BaB₂O₄ is synthesized by solid stated method. The optimum Eu³⁺ doped concentration, the critical distance of the concentration quenching, the mechanism of concentration quenching, and effect of charge compensation on luminescence intensity are also investigated.

2. Experimental

2.1. Synthesis

A series samples, Ba_{1-x}B₂O₄: Eu³⁺_x ($x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10$) were synthesized by a conventional solid-state reaction technique. The appropriate amount of BaCO₃ (A.R. grade), H₃BO₃ (A.R. grade) and Eu₂O₃ (99.99%) were firstly ground, and

* Corresponding authors. Tel.: +86 532 84023653; fax: +86 532 84023927.

E-mail addresses: wuzhan_chao@163.com (Z.-C. Wu), qustks@126.com (S.-P. Kuang).

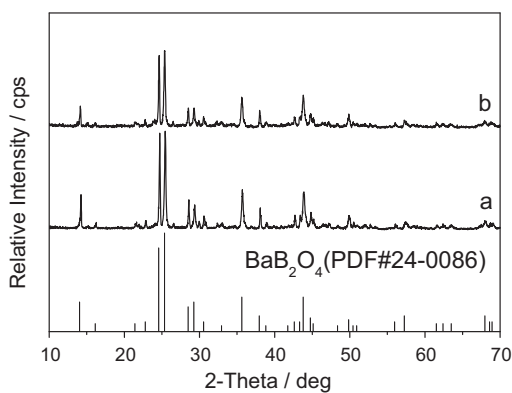


Fig. 1. XRD patterns of the samples (a: $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ and b: BaB_2O_4).

then burned in an electric furnace at 800°C for 4 h. In some cases, appropriate amount of Li_2CO_3 (A.R. grade), Na_2CO_3 (A.R. grade) or K_2CO_3 (A.R. grade) were added as the charge compensators.

2.2. Measurements

Crystal phase identification was carried out on an X-ray diffractometer (D-MAX2500/PC, RIGAKU Corporation of Japan) using 40 kV, 20 mA, and $\text{Cu } K_\alpha$ radiation (1.5406 \AA). Morphology and size of the calcined particles were observed by Field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Corporation of Japan). Excitation and emission spectra of the powdered phosphors were measured on a Fluorolog-3-21 spectrometer (JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source. All measurements were made at room temperature unless otherwise stated.

3. Results and discussion

3.1. XRD of phosphor powders

The XRD patterns of the obtained BaB_2O_4 and $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ are given in Fig. 1. It can be found that the XRD patterns of BaB_2O_4 and $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ are consistent with JCPDS card (PDF#24-0086), indicating that doping of a small content of Eu^{3+} ion had little influence on the lattice structure of luminescence materials. The crystal structure of the prepared BaB_2O_4 can be refined to be monoclinic, space group $C2/c$ with $a = 11.133$, $b = 12.67$ and $c = 8.381$. It is different from the reported $\beta\text{-BaB}_2\text{O}_4$, which is rhombohedral, space group $R3c$ with $a = b = 12.532$ and $c = 12.726$ (PDF#38-0722) [10]. According to the calculated Hinchley index (crystallinity index) [11,12], $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ has a better crystallinity than BaB_2O_4 .

3.2. FE-SEM images of phosphor powders

Fig. 2 shows the FE-SEM image of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ powders prepared at 800°C . It was observed that the microstructure of the phosphor consisted of irregular grains with heavy agglomerate phenomena. The average size of the $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ powders is about $2\text{--}6 \mu\text{m}$. The results show that $\text{BaB}_2\text{O}_4:\text{Eu}^{3+}$ phosphor has a good crystallinity and a relatively low sinter temperature, which is also consistent with the requirements of energy saving for products in today's society.

3.3. Photoluminescence properties

For the device application, overlap between the excitation spectra of phosphor and the emission spectrum of InGaN chip is required

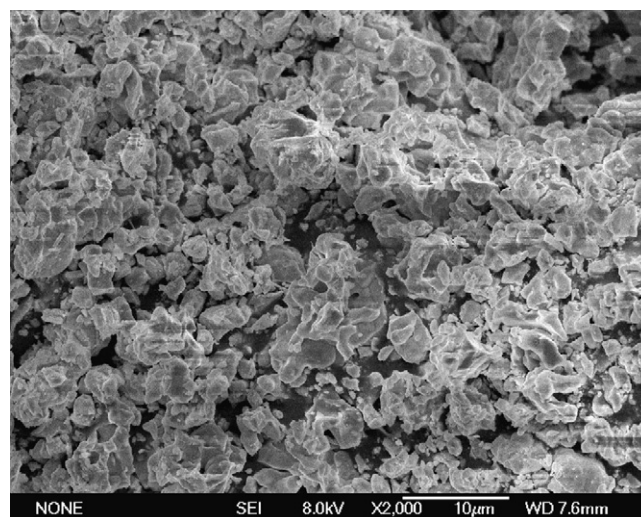


Fig. 2. FE-SEM images of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$.

to obtain high luminescence efficiency. The excitation (curve a) and emission (curve b) spectra of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ are shown in Fig. 3. The broad excitation band at $\sim 300 \text{ nm}$ is attributed to the $\text{O} \rightarrow \text{B}$ charge transfer (CT) transition and the sharp lines in $360\text{--}480 \text{ nm}$ range are intra-configurational $4f\text{--}4f$ transitions of Eu^{3+} in the host lattices. It is found that the excitation intensity at 394 nm is the highest in the excitation spectrum, which is attributed to the ${}^7F_0 \rightarrow {}^5L_6$ transition and matches the emission spectrum of the InGaN chip. The excitation peak at 465 nm is corresponding to the transition of ${}^7F_0 \rightarrow {}^5D_2$. The main emission peak in curve (b) is a ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 611 nm . Other transitions for the 5D_j excited levels to 7F_j ground states, such as ${}^5D_0 \rightarrow {}^7F_j$ lines in $570\text{--}720 \text{ nm}$ range are relatively weak, which is advantageous to obtain the good CIE chromaticity coordinates. The results imply that Eu^{3+} ions occupy the lattice sites without inversion symmetry, which is in good agreement with the structural results. The CIE chromaticity coordinates are calculated from the emission spectrum to be $x = 0.64$, $y = 0.35$. Compared with the NTSC standard CIE chromaticity coordinate values for red ($x = 0.67$, $y = 0.33$), it is found that the CIE chromaticity coordinates of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ are close to the NTSC standard values. These results imply that the luminescent property of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$ is good when it is applied in LED.

The effect of doped- Eu^{3+} concentration on the emission of $\text{BaB}_2\text{O}_4:\text{Eu}^{3+}$ phosphor was also investigated. The emission spectra

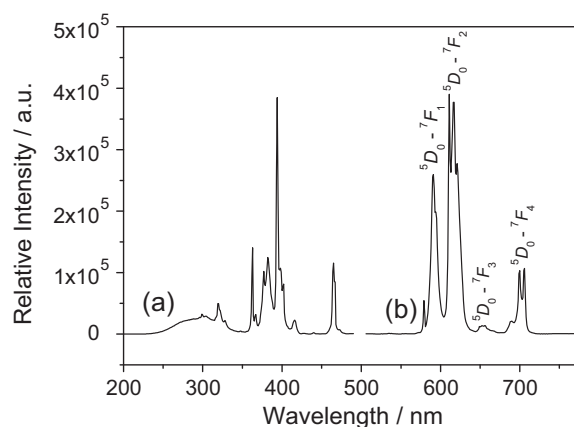


Fig. 3. Photoluminescence spectra of $\text{Ba}_{0.94}\text{B}_2\text{O}_4:\text{Eu}^{3+}_{0.06}$. (a) Excitation spectrum ($\lambda_{\text{em}} = 611 \text{ nm}$) and (b) emission spectrum ($\lambda_{\text{ex}} = 394 \text{ nm}$).

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