



# A new single-host white-light-emitting BaSrMg(PO<sub>4</sub>)<sub>2</sub>: Eu<sup>2+</sup> phosphor for white-light-emitting diodes

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## ABSTRACT

A single-host white-light-emitting phosphor, Eu<sup>2+</sup> doped BaSrMg(PO<sub>4</sub>)<sub>2</sub> (BSMP: Eu<sup>2+</sup>), was prepared by solid-state reaction. BSMP: Eu<sup>2+</sup> shows two main emission bands peaking at 447 and 536 nm, respectively. The emission band peaking at 447 nm is attributed to the 4f<sup>6</sup>5d<sup>1</sup>–4f<sup>7</sup> transition of Eu<sup>2+</sup> substituting Sr<sup>2+</sup>, while the emission band peaking at 536 nm originates from the 4f<sup>6</sup>5d<sup>1</sup>–4f<sup>7</sup> transition of Eu<sup>2+</sup> replacing Ba<sup>2+</sup> in host lattice. A white light-emitting diode (WLED) was fabricated by combination of a 380 nm emitting InGaN chip and the prepared white phosphor BSMP: Eu<sup>2+</sup>. In comparison with commercial GaN-pumped YAG: Ce<sup>3+</sup> phosphor, BSMP: Eu<sup>2+</sup> shows higher color stability against input forward-bias current and excellent color rendering index.

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## 1. Introduction

In recent years, studies on RGB phosphors suitable for NUV light excitation have been attracting more and more attention for fabricating WLEDs [1–6]. Compared with the commercial WLEDs fabricated with blue chip and yellow phosphor YAG: Ce<sup>3+</sup>, the WLEDs fabricated with NUV chip around 350–420 nm and corresponding phosphors have higher color rendering index [7,8] because all the colors are determined by the phosphors. However, re-absorption of emission colors leads to low luminous efficiency of WLEDs fabricated with NUV chip and three different host phosphors [7,8]. Furthermore, several mixed phosphors increased process difficulties for fabricating WLEDs. In order to solve these problems, it is necessary to develop single-host full-color emitting phosphors for NUV-pumped WLEDs.

Up to now, several white phosphors suitable for NUV-pumped WLEDs have been reported [7–15], such as Ba<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>: Eu<sup>2+</sup>, Mn<sup>2+</sup> [7], Sr<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>: Eu<sup>2+</sup>, Mn<sup>2+</sup> [8], CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>: Eu<sup>2+</sup>, Mn<sup>2+</sup> [9], La<sub>0.827</sub>Al<sub>1.19</sub>O<sub>19.09</sub>: Eu<sup>2+</sup>, Mn<sup>2+</sup> [10], Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>: Eu, Mn [11], Sr<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Ce<sup>3+</sup>, Eu<sup>2+</sup> [12], Mg<sub>0.1</sub>Sr<sub>1.9</sub>SiO<sub>4</sub>: Eu<sup>2+</sup> [13], Sr<sub>3</sub>Al<sub>2</sub>O<sub>5</sub>Cl<sub>2</sub>: Ce<sup>3+</sup>, Eu<sup>2+</sup> [14], Ba<sub>2</sub>MgSi<sub>2-x</sub>Al<sub>x</sub>O<sub>7</sub>: 0.1Eu<sup>2+</sup>, 0.1Mn<sup>2+</sup> [15], LaTiNbO<sub>6</sub>: Pr<sup>3+</sup> [16]. Most of these white phosphors are silicate or aluminate, which were prepared in high temperature. Phosphate is considered an excellent host for preparing phosphor due to its low sintering

temperature and good stability. However, there are few reports on the research of phosphate system as host for a white phosphor. Recently, a yellow-emitting phosphor Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>: Eu<sup>2+</sup> and a blue-emitting phosphor SrMg<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>: Eu<sup>2+</sup> used for NUV-pumped WLEDs have been reported one after the other [17–19]. The studies indicate that Eu<sup>2+</sup> occupying Ba<sup>2+</sup> sites in Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub> exhibits a broad yellow emission band peaking at 576 nm, while Eu<sup>2+</sup> substituting Sr<sup>2+</sup> in SrMg<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> shows a broad blue emission band peaking at 424 nm. Based on above results, white-light emission may be acquired by Eu<sup>2+</sup> ions substituting not only Ba<sup>2+</sup> ions but also Sr<sup>2+</sup> ions in phosphate host lattice. Therefore, in this paper, tunable white-light-emitting phosphors, Eu<sup>2+</sup> doped BaSrMg(PO<sub>4</sub>)<sub>2</sub> (BSMP: Eu<sup>2+</sup>), were prepared by solid-state method and investigated by photoluminescence. Finally, a WLED was fabricated by combining an NUV InGaN chip (λ<sub>em</sub> = 380 nm) with the prepared phosphor and its luminescent properties were also investigated.

## 2. Experimental procedures

### 2.1. Synthesis

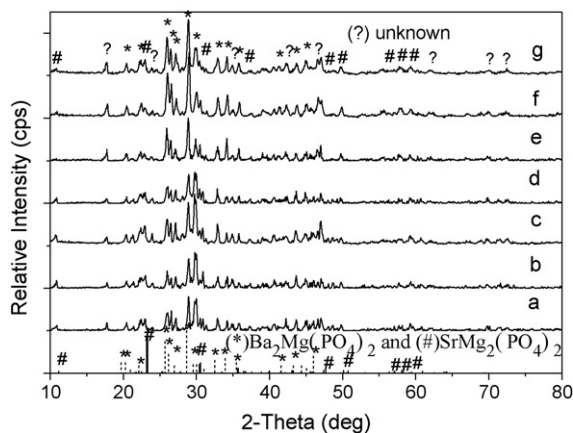
Ba<sub>0.97</sub>Sr<sub>1-m</sub>Mg(PO<sub>4</sub>)<sub>2</sub>: Eu<sup>2+</sup><sub>0.03+m</sub> system (BSMP1: m = 0.01, 0.03, 0.05, 0.07) and Ba<sub>1-n</sub>Sr<sub>0.97</sub>Mg(PO<sub>4</sub>)<sub>2</sub>: Eu<sup>2+</sup><sub>0.03+n</sub> system (BSMP2: n = 0.01, 0.05, 0.07) were synthesized by a conventional solid-state reaction technique. The starting materials SrCO<sub>3</sub> (A.R. grade), BaCO<sub>3</sub> (A.R. grade), (MgCO<sub>3</sub>)<sub>4</sub>Mg(OH)<sub>2</sub>·5H<sub>2</sub>O (A.R. grade), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (A.R. grade), and Eu<sub>2</sub>O<sub>3</sub> (99.99% purity) with stoichiometric molar ratio were firstly ground, and then burned in an electric furnace at 1150 °C for 3 h under a reducing CO atmosphere.

### 2.2. Characterization

Crystal phase identification was carried out on an X-ray diffractometer (D/max-III A, RIGAKU Corporation of Japan) using 40 kV, 20 mA, and Cu Kα radiation

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**Fig. 1.** XRD patterns of BSMP1 system (a:  $m=0.01$ , b:  $m=0.03$ , c:  $m=0.05$ , and d:  $m=0.07$ ) and BSMP2 system (e:  $n=0.01$ , f:  $n=0.05$ , and g:  $n=0.07$ ).

(1.5406 Å). Excitation and emission spectra of the powdered phosphors were measured on a JOBIN YVON Fluorolog-3-21 spectrometer at room temperature and a 450 W xenon lamp was used as the excitation source.

### 2.3. LED measurements

To fabricate WLED, the phosphor BSMP:  $\text{Eu}^{2+}$  was mixed with epoxy resin in order to be pre-coated on the 380-nm LED chip. Another type of transparent epoxy resin was used to protect and fix the whole device, and the subsequent curing was done at 120 °C for 1 h. Emission spectra, chromaticity coordinates and correlated color temperature ( $T_c$ ) of the fabricated WLED were measured by PMS-50 LED spectrophotocolorimeter (EVERFINE, China).

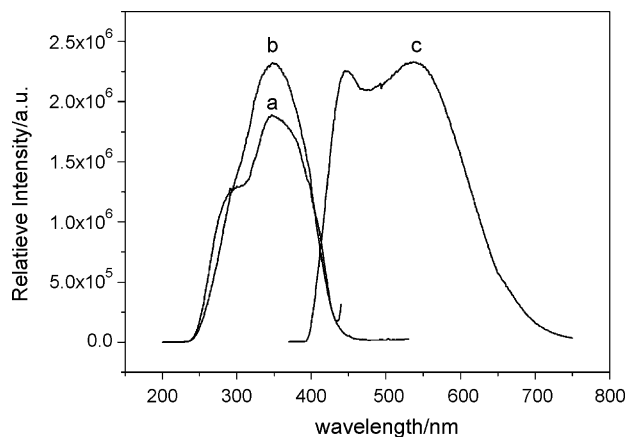
## 3. Results and discussion

### 3.1. XRD

The XRD patterns of BSMP1 and BSMP2 are shown in Fig. 1. Compared with standard cards of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  (PDF#16-0556, the Powder Diffraction File of the Joint Committee on Powder Diffraction Standards) and  $\text{SrMg}_2(\text{PO}_4)_2$  (PDF#52-1590) carefully, it is observed that some diffraction peaks of the prepared samples can be indexed to the phases of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  (PDF#16-0556), while others can be indexed to the phases of  $\text{SrMg}_2(\text{PO}_4)_2$  (PDF#52-1590). However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds. These results imply that the prepared samples are not the simple physical mixtures of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$  and  $\text{SrMg}_2(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$ , but a new single-host phosphor (BSMP:  $\text{Eu}^{2+}$ ). The detailed structure of BSMP is still under investigation.

### 3.2. Photoluminescence properties

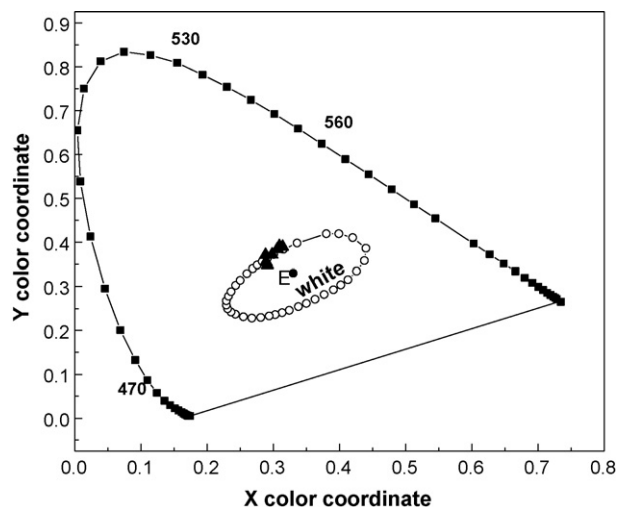
Fig. 2 is the photoluminescence spectra of the obtained phosphor  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}_{0.04}$ . Curves (a) and (b) are two different excitation spectra monitored at 447 and 536 nm, respectively. From Fig. 2, it can be observed that both of the excitation spectra are broad excitation bands ranged from 250 to 440 nm except for the difference of peak shapes and intensities, which means this phosphor can be well excited by NUV light around 380 nm and the doped- $\text{Eu}^{2+}$  ions may occupy two kinds of lattice sites. Since phosphate hosts exhibit absorption in the vacuum ultraviolet region (100–200 nm) [20–22], the excitation band in the range of 250–440 nm is originated from the  $4f^7$ – $4f^65d^1$  transition of the doped  $\text{Eu}^{2+}$  ions [23]. Curve (c) is the emission spectrum of  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}_{0.04}$  excited by 350 nm NUV light. The emission spectrum is very broad, which almost extends through the



**Fig. 2.** Excitation spectra (a:  $\lambda_{\text{em}}=447$ , b:  $\lambda_{\text{em}}=536$  nm) and emission spectra (c) ( $\lambda_{\text{ex}}=350$  nm) of  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}_{0.04}$  powder.

whole visible light region from 400 to 700 nm. Obviously, the emission spectrum consists of two main emission bands peaking at 447 and 536 nm, respectively, and its CIE (Commission Internationale de L'Eclairage) chromaticity coordinates are calculated as ( $x=0.291$ ,  $y=0.349$ ) which locate in white light region in CIE-1931 chromaticity diagram [24]. It can be presumed that the two emission bands result from the  $4f^65d^1$ – $4f^7$  transitions of  $\text{Eu}^{2+}$  ions occupying  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  sites in host lattice, respectively. However, in comparison with the blue emission band peaking at 424 nm of  $\text{Eu}^{2+}$  in  $\text{SrMg}_2(\text{PO}_4)_2$  host [18,19] and the yellow emission band peaking at 576 nm of  $\text{Eu}^{2+}$  in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  matrix [17], the blue emission band of  $\text{Eu}^{2+}$  in BSMP host shows obvious red-shift about 23 nm, while the yellow emission band of  $\text{Eu}^{2+}$  in BSMP host exhibits remarkable blue-shift about 40 nm. These results also indicate that the obtained phosphor BSMP:  $\text{Eu}^{2+}$  is not the simple physical mixtures of the blue phosphor  $\text{SrMg}_2(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$  and the yellow phosphor  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$ , but a new single-host full-colors phosphor which could be applied potentially on NUV InGaN chips excitation phosphor-conversion WLEDs.

The dot E in CIE-1931 chromaticity diagram (see Fig. 3) shows the ideal white light chromaticity coordinates with  $x=0.333$  and  $y=0.333$ . Generally, the closer the CIE chromaticity coordinates to dot E, the higher the white-light-emitting quality. The chromaticity coordinates of emission bands can be adjusted through turning proportion of  $\text{Eu}^{2+}$  entering into two kinds of lattice sites in BSMP



**Fig. 3.** The chromaticity coordinates (the triangle symbols) of BSMP1 and BSMP2 systems in the CIE-1931 chromaticity diagram.

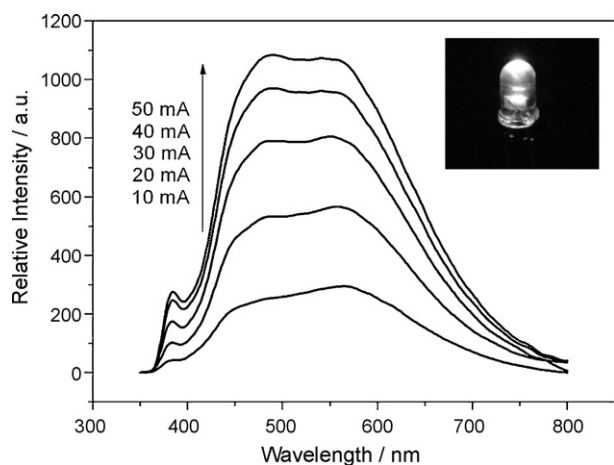
**Table 1**  
CIE chromaticity coordinates values of BSMP1 system and BSMP2 system.

BSMP1 BSMP2		$m=0.01$	$m=0.03$	$m=0.05$	$m=0.07$	$n=0.01$	$n=0.05$	$n=0.07$
CIE chromaticity coordinates values	(x)	0.291	0.289	0.298	0.306	0.314	0.309	0.288
	(y)	0.349	0.356	0.372	0.385	0.390	0.391	0.371

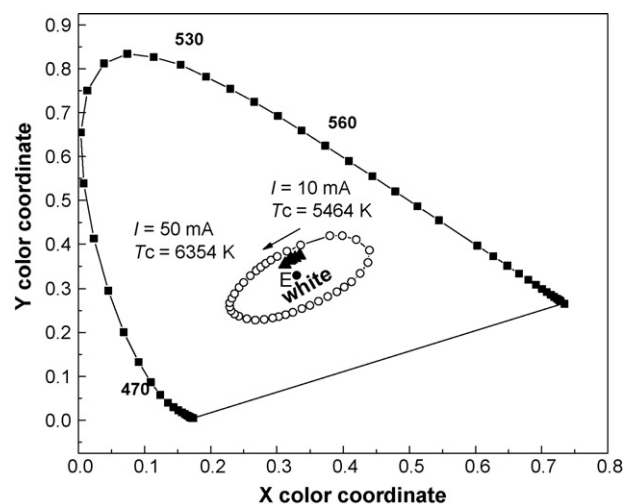
host. Thus, BSMP1 and BSMP2 were prepared. The changes of CIE chromaticity coordinates for the prepared samples are shown in Fig. 3 with the triangle symbols. It can be seen that the chromaticity coordinates of almost all the prepared samples locate in white light region in CIE-1931 chromaticity diagram. The CIE chromaticity coordinates values calculated from emission spectra of BSMP1 and BSMP2 phosphors are listed in Table 1. From Table 1, it can be seen that CIE chromaticity coordinates values increase basically with increasing  $m$ , whereas decrease basically with increasing  $n$ .

### 3.3. Fabricated WLEDs

The excitation band of  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  phosphor matches well with the NUV emitting of InGaN chip, implying a potential application of this phosphor in NUV-pumped WLEDs. It is necessary to investigate the luminescent properties of this phosphor in a WLED. For this purpose, a WLED was fabricated by combination of an NUV InGaN chip and the prepared phosphor  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$ . Emission spectra of the WLED were measured at different current ( $I=10, 20, 30, 40, 50$  mA), which are depicted in Fig. 4. The applied voltage was approximately 3.5 V. There are three main emission bands in emission spectrum of the WLED. The two strong broad emitting bands peaking at 454 and 541 nm are attributed to the  $4f^65d^1-4f^7$  transitions of  $\text{Eu}^{2+}$  ions substituting  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  ions in BSMP lattice, respectively, while the weak emission band peaking at 380 nm is due to part remains of the chip emission. As shown in Fig. 4, the NUV emission from InGaN-based chip has been almost absorbed completely and converted into visible light. In addition, the intensities of all emission bands increase with the increasing forward-bias current from 10 to 50 mA. This phenomenon can be explained as that more NUV emission from the InGaN chip is absorbed by  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  at higher current and converted into visible emission. The inset in Fig. 4 is a photograph of the lighting WLED with  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  under 20 mA current excitation. Bright white light from the LED is observed by naked eyes. When forward-bias current is 20 mA, CIE chromaticity coordinates are calculated as ( $x=0.3287, y=0.3638$ ) and  $T_c$  is 5620 K.



**Fig. 4.** The emission spectra of the WLED fabricated with  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  phosphor and an NUV InGaN chip with increasing forward-bias current. The inset shows photograph of the WLED under 20 mA current excitation.



**Fig. 5.** The chromaticity coordinates (the triangle symbols) of NUV-pumped white LED with  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  phosphor with increasing forward-bias current.

In our WLED, with increasing applied currents, the CIE chromaticity coordinates (shown with the triangle symbols in Fig. 5) shift slightly in the direction where color temperature increases from 5464 to 6354 K. However, in YAG:  $\text{Ce}^{3+}$ -based WLED reported previously [7], with increasing current, the CIE chromaticity coordinates shift significantly to the higher color temperature from 6500 to near 9000 K. These results indicate that the WLED fabricated with  $\text{Ba}_{0.97}\text{Sr}_{0.99}\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}_{0.04}$  phosphor and an NUV InGaN chip has higher color stability against input forward-bias current than YAG:  $\text{Ce}^{3+}$ -based WLED. The color rendering index ( $R_a$ ) of our WLED under 20 mA current excitation is 87, which is bigger than that of commercial YAG:  $\text{Ce}^{3+}$ -based WLED ( $R_a=82$ ) [7]. This may be due to a great amount of green light (500–530 nm) in emission spectra of our WLED, while this characteristic is lacking in a commercial YAG:  $\text{Ce}^{3+}$ -based WLED.

In view of application, each proper NUV-pumped WLED phosphor must meet the following necessary conditions. Firstly, the phosphor must efficiently absorb NUV light emitted from the InGaN chip. Secondly, the phosphor exhibits higher luminescent intensity under NUV light excitation. Thirdly, the phosphor should have high color stability. Since BSMP:  $\text{Eu}^{2+}$  meets all the conditions, it is considered to be a potential candidate as a single-host full-color phosphor for fabrication of WLEDs.

## 4. Conclusions

A single-host white phosphor BSMP:  $\text{Eu}^{2+}$  was prepared by high-temperature solid-state reaction. Furthermore, a bright WLED was fabricated by combination of an NUV InGaN chip and the prepared phosphor BSMP:  $\text{Eu}^{2+}$ . When forward-bias current is 20 mA, CIE chromaticity coordinates are calculated as ( $x=0.3287, y=0.3638$ ),  $T_c=5620$  K and  $R_a=87$ . Compared with commercial GaN-pumped YAG:  $\text{Ce}^{3+}$  phosphor, BSMP:  $\text{Eu}^{2+}$  phosphor shows higher color stability against input forward-bias current and excellent color rendering index. Thus, BSMP:  $\text{Eu}^{2+}$  is a good candidate as single-host white phosphor for fabrication of WLEDs.

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