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# Enhanced red light emission from $LaBSiO_5:Eu^{3+}, R^{3+}$ (R = Bi or Sm) phosphors

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#### 1. Introduction

White light emitting diodes (LEDs) have high potential application for replacement of the conventional incandescent and fluorescent lamps due to their superior advantages such as high efficiency, low energy consumption, long lifetime, environmental benefit, and easy maintenance [1,2]. At present, the most common approach for fabricating the white LEDs is to combine a blue LED with yellow-emitting phosphor, such as  $Y_3Al_5O_{12}$ :Ce<sup>3+</sup> [3]. Although this type of white LEDs has high luminous efficiency, it exhibits a low color rendering index due to the deficient of red light component [4]. Alternatively, the white light can be generated to apply a near-ultraviolet InGaN chip (380-410 nm) with blue, green, and red phosphors [5,6]. To attain high color rendering white LEDs, the red-emitting phosphors are urgently required. However, the currently commercial available red-emitting phosphors such as Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> are low efficiency and chemically unstable [7]. Therefore, it is necessary to develop more efficient redemitting phosphors suitable for the fabrication of white LEDs. Recently, silicate-based phosphors have been investigated extensively because of their high quantum efficiency, excellent chemical and thermal stability, water resistance and low cost [8-12]. Moreover, interesting candidates for red phosphors include materials containing Eu<sup>3+</sup>, which is widely used as a red-emitting activator via the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition at about 614 nm. In order to enhance the red emission intensity of Eu<sup>3+</sup>, rare earth or transition metal ions usually are codoped as sensitizers [13,14].

#### ABSTRACT

Polycrystalline LaBSiO<sub>5</sub>:Eu<sup>3+</sup>,R<sup>3+</sup> (R=Bi or Sm) phosphors have been synthesized by a facile sol-gel method. The phosphors have been characterized by thermogravimetric analysis/different scanning calorimeter, scanning electron microscopy, X-ray diffractometer and fluorescence measurements. It was found that the emission intensity of LaBSiO<sub>5</sub>:Eu phosphors increases clearly and reaches a maximum at 30 mol% with increasing of Eu<sup>3+</sup> concentration. The incorporation of Bi<sup>3+</sup> ions and/or Sm<sup>3+</sup> ions have greatly enhanced the emission intensity of Eu<sup>3+</sup> upon excitation with 391 nm light. The possible sensitization mechanisms of Sm<sup>3+</sup> and/or Bi<sup>3+</sup> on Eu<sup>3+</sup> emission intensity have been investigated and discussed. The high brightness and short luminescence decay times make it promising red-emitting candidates for white light-emitting diodes.

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Herein, the main objective of this work is to carry out a detailed study on the structural and luminescent properties of LaBSiO<sub>5</sub>: $Eu^{3+}$ , $R^{3+}$ (R=Bi or Sm) phosphors by sol-gel synthesis method. The high brightness red light has been obtained from La<sub>0.68</sub>BSiO<sub>5</sub>: $Eu_{0.30}$ , $Sm_{0.02}$ , suggesting that the as-prepared phosphors are promising red luminescent materials for white LEDs.

#### 2. Experimental

Red phosphors of LaBSiO<sub>5</sub>:Eu<sup>3+</sup>,R<sup>3+</sup> (R = Bi or Sm) were synthesized by sol-gel method. The starting materials were Eu<sub>2</sub>O<sub>3</sub> (99.99%), Bi<sub>2</sub>O<sub>3</sub> (99.99%), Sm<sub>2</sub>O<sub>3</sub> (99.99%), La<sub>2</sub>O<sub>3</sub> (99.99%), H<sub>3</sub>BO<sub>3</sub> (A.R.), Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS) (A.R.), nitric acid and citric acid. Firstly, La(NO<sub>3</sub>)<sub>3</sub>, Eu(NO<sub>3</sub>)<sub>3</sub>, Sm(NO<sub>3</sub>)<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> solutions were made by dissolving their oxides completely in nitric acid. Then, stoichiometric amounts of nitrate solutions were added into the beaker together with citric acid. Finally, the tetraethyl orthosilicate was added dropwise under vigorous stirring to form transparent sols which turned to yellow gels after drying at oven. The gels were calcined at 700 °C for 4 h and then 950 °C for 4 h in air. After cooling to room temperature, the phosphors were obtained.

The crystallization and phase transformation behavior of the obtained phosphors were monitored by both thermogravimetric analysis (TGA)/different scanning calorimeter (DSC) (Netzsch STA449C, at a heating rate of 10 K/min) and X-ray powder diffraction (XRD) (Philips Model PW1830 diffractometer, Cu K $\alpha$ ). The morphology and size of the synthesized phosphors were characterized by a scanning electron microscope (SEM) (JEOL-JSM-5610LV). Room temperature excitation and emission spectra were recorded on a TRIAX320 spectrofluorimeter (Jobin-Yvon Co.) with a 450 W xenon lamp as the excitation source.

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Fig. 1. TG/DSC curves of the LaBSiO<sub>5</sub>:Eu precursor. The inset presents SEM image of the LaBSiO<sub>5</sub>:Eu phosphor.

#### 3. Results and discussion

Fig. 1 presents TG/DSC curves of the LaBSiO<sub>5</sub>:Eu precursor. It indicates the weight loss takes place in the TG curve from room temperature to 550 °C and decomposition process can be divided into two processes. The first weight loss step below 200 °C accompanied by a strong endothermic peak around 116 °C is attributed to dehydration of physical adsorbed water. The second weight loss process from 200 °C to 550 °C corresponds to the burning of the citrate acid ligand and the decomposition of metal nitric. The exothermic peak at about 813 °C is related to the crystallization of LaBSiO<sub>5</sub>. Therefore, the calcination temperature of 950 °C was adopted to ensure the prepared LaBSiO<sub>5</sub> phosphor with both a high chemical homogeneity and a fine particle size. The inset illustrates SEM image of the LaBSiO<sub>5</sub>:Eu phosphor. The average size of the phosphor is about 1  $\mu$ m.

The XRD patterns of the samples  $La_{0.7}BSiO_5:Eu_{0.3}$ ,  $La_{0.68}BSiO_5:Eu_{0.3},Bi_{0.02}$  and  $La_{0.68}BSiO_5:Eu_{0.3},Sm_{0.02}$  are shown in Fig. 2. The patterns agree well with Joint Committee on Powder Diffraction Standards (JCPDS) 87-2172. In addition, it can be visualized that the limited doped Eu<sup>3+</sup> ions do not cause any significant changes in the host structure. The lanthanum borosilicate LaBSiO<sub>5</sub>



**Fig. 2.** XRD patterns of: (a) JCPDS 87-2172; (b)  $La_{0.7}BSiO_5:Eu_{0.3}$ ; (c)  $La_{0.68}BSiO_5:Eu_{0.3},Bi_{0.02}$ ; and (d)  $La_{0.68}BSiO_5:Eu_{0.3},Sm_{0.02}$ . The inset shows the crystal structure of  $LaBSiO_5$ .



Fig. 3. Excitation ( $\lambda_{em}$  = 614 nm) and emission spectra ( $\lambda_{ex}$  = 391 nm) of La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>.

has a triclinic crystal structure with a space group of P31 and the cell parameters are a=b=6.874 Å, c=6.717 Å. As shown in the inset of Fig. 2, two different tetrahedral groups, namely BO<sub>4</sub> and SiO<sub>4</sub>, are interlinked by corner-sharing with each other to form a six-membered ring system [15].

Fig. 3 gives the excitation and emission spectra of the La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub> phosphor. The band extending from 250 to 325 nm is associated with  $O^{2-}-Eu^{3+}$  charge-transfer (CT) transition while the sharp lines ascribe to transitions of Eu<sup>3+</sup>:<sup>7</sup>F<sub>0</sub>  $\rightarrow$  <sup>5</sup>L<sub>9</sub> (358 nm), <sup>5</sup>G<sub>3</sub> (380 nm), <sup>5</sup>L<sub>6</sub> (391 nm), <sup>5</sup>D<sub>3</sub> (442 nm), <sup>5</sup>D<sub>2</sub> (462 nm). Under the excitation of 391 nm, the emission bands are caused by the 4f–4f transitions of Eu<sup>3+</sup> corresponding to <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>0</sub> (574 nm), <sup>7</sup>F<sub>1</sub> (582 nm), <sup>7</sup>F<sub>2</sub> (600, 606, 614, 620 nm), <sup>7</sup>F<sub>3</sub> (641, 651 nm), and <sup>7</sup>F<sub>4</sub> (684, 694 nm), respectively [16]. The <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> emission line of Eu<sup>3+</sup> splits into four peaks, which is determined by the energy-level splitting of the <sup>7</sup>F<sub>2</sub> state [17]. In Eu<sup>3+</sup> doped LaBSiO<sub>5</sub> phosphor, the lack of inversion symmetry and the break of parity selection rules make the <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> electric dipole transition dominated among all these transitions [18]. The result is beneficial to obtain the red phosphor with good color purity.



Fig. 4. Eu<sup>3+</sup> concentration dependence of the emission intensity of  $La_{1-x}Eu_xBSiO_5$  ( $\lambda_{ex}$  = 391 nm) phosphor.



**Fig. 5.** (a) Excitation spectra of LaBSiO<sub>5</sub>:Eu<sup>3+</sup> and LaBSiO<sub>5</sub>:Bi<sup>3+</sup>,Eu<sup>3+</sup> phosphors, the inset shows the enlarged figure of excitation band from 225 to 350 nm. (b) Emission spectra of La<sub>0.7-x</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Bi<sub>x</sub> ( $\lambda_{ex}$  = 391 nm) phosphors.

Fig. 4 exhibits the relationship between emission intensity and concentration of  $Eu^{3+}$  ion. With increasing  $Eu^{3+}$  concentration, the photoluminescence intensities are gradually enhanced up to the critical concentration of 30 mol% and then decrease due to concentration quenching. When the concentration of  $Eu^{3+}$ ion increases, the distance between the  $Eu^{3+}$  luminescent centers becomes smaller which results in the nonradiative energy transfer from one  $Eu^{3+}$  to another  $Eu^{3+}$  ion takes place easily. With respect to the mechanism of energy transfer in phosphors, Blasse has pointed out that the critical transfer distance ( $R_C$ ) at which the probability of transfer is equal to the probability of radiative emission, can be calculated using the formula [19]:

$$R_{\rm c} \approx 2 \left[ \frac{3V}{4\pi x_c N} \right]^{1/3}$$

where *V* is the volume of the unit cell,  $x_c$  is the critical concentration of the activator ion, and *N* is the number of cations in the unit cell. By taking the experimental and analytic values of *V*,  $x_c$ , and *N* (274.9 Å<sup>3</sup>, 0.3, 3, respectively [15]), the critical transfer distance of Eu<sup>3+</sup> in LaBSiO<sub>5</sub> is calculated to be about 8.4 Å.

For enhancing the red emission intensity of  $Eu^{3+}$ ,  $Bi^{3+}$  and/or  $Sm^{3+}$  was codoped into LaBSiO<sub>5</sub> as sensitizers. Fig. 5(a) shows the excitation spectra of LaBSiO<sub>5</sub>: $Eu^{3+}$  and LaBSiO<sub>5</sub>: $Bi^{3+}$ , $Eu^{3+}$  phosphors. After introducing  $Bi^{3+}$  into the phosphor, a rather broad band due to the absorption of  $Bi^{3+}$  was observed in the excitation band from 240 to 340 nm which almost overlap with charge transfer band of O–Eu<sup>3+</sup>. The changes can be visualized clearly from the

enlarge figure in the inset of Fig. 5(a). Therefore, it is indicated that an effective energy transfer from  $Bi^{3+}$  to  $Eu^{3+}$  ions was happened. The emission spectra for  $La_{0.7-x}BSiO_5:Eu_{0.3},Bi_x$  phosphors under 391 nm excitation were presented in Fig. 5(b). Compared with  $La_{0.7}BSiO_5:Eu_{0.3}$  phosphor, the luminescence intensity of  $La_{0.68}BSiO_5:Eu_{0.3},Bi_{0.02}$  phosphor has increased by 2.5 times. However, with increasing  $Bi^{3+}$  concentration, the emission intensity starts decreasing due to the sensitization effect of the  $Bi^{3+}$  ion on the  $Eu^{3+}$  emission varies with the  $Bi^{3+}$  concentration. For higher concentration of  $Bi^{3+}$  ions,  $Bin^{3+}$  aggregates may be formed which act as trapping centers and dissipate the absorbed energy nonradiatively, instead of transferring it to the  $Eu^{3+}$  activator ions [13]. The possible energy transfer process from  $Bi^{3+}$  to  $Eu^{3+}$  in  $La_{0.7-x}BSiO_5:Eu_{0.3}Bi_x$  phosphors has been illustrated in the energy level scheme as presented in Fig. 6.

Fig. 7(a) shows the excitation spectra of LaBSiO<sub>5</sub>:Eu, LaBSiO<sub>5</sub>:Sm and LaBSiO<sub>5</sub>:Eu,Sm. It is exhibited that the excitation spectrum of LaBSiO<sub>5</sub>:Eu,Sm including both the excitation band of LaBSiO<sub>5</sub>:Eu and LaBSiO<sub>5</sub>:Sm, where the new peaks located at 346, 375, 404, and 480 nm corresponding to the transitions  ${}^{6}\text{H}_{5/2} \rightarrow {}^{3}\text{H}_{7/2}$ ,  ${}^{6}\text{P}_{7/2}$ ,  ${}^{4}K_{11/2}$  and  ${}^{4}F_{5/2} + {}^{4}I_{13/2}$  of Sm<sup>3+</sup>, respectively. The emission spectra of La<sub>0.7-x</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>x</sub> under 391 nm excitation were investigated and displayed in Fig. 7(b). The intensities of the emission spectra of the Eu<sup>3+</sup>-Sm<sup>3+</sup> co-doped systems are much stronger than that of the single Eu<sup>3+</sup>-doped systems. It indicates that the Sm<sup>3+</sup> ions can absorb and transfer energy to Eu<sup>3+</sup> ions efficiently. The luminescence reaches the strongest intensity at  $x = 2 \mod 8$ . Higher doping concentration of Sm<sup>3+</sup> can cause concentration quenching of Sm<sup>3+</sup> emission, and results in the decreasing of emission intensity of  $Eu^{3+}$ . As displayed in Fig. 8, the energy of the  ${}^{4}G_{5/2}$  state of  $Sm^{3+}$  ions is a little higher than that of the  ${}^{5}D_{0}$  state of the Eu<sup>3+</sup> ions, which supposed that energy transfer from Sm<sup>3+</sup> to Eu<sup>3+</sup> dominated by resonance takes place [14].

The decay curves for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (614 nm) transition of Eu<sup>3+</sup> ions in the phosphors are presented in Fig. 9. The values can be fitted well into single-exponential function as  $I = I_{0}\exp(-t/\tau)$ , in which  $\tau$  is the decay lifetime. The lifetime  $\tau$  values for La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>, La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Bi<sub>0.02</sub>, and La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>0.02</sub> phosphors are determined to 2.79 ms, 2.54 ms and 2.17 ms, respectively. After the introducing of Bi<sup>3+</sup> or Sm<sup>3+</sup> ions, the faster decay time of Eu<sup>3+</sup> may



Fig. 6. Energy level diagrams of  $Bi^{3+}$  and  $Eu^{3+}.$  Energy transfer process from  $Bi^{3+}$  to  $Eu^{3+}$  is indicated.



**Fig. 7.** (a) Excitation spectra of LaBSiO<sub>5</sub>:Eu<sup>3+</sup>, LaBSiO<sub>5</sub>:Sm<sup>3+</sup> and LaBSiO<sub>5</sub>:Sm<sup>3+</sup>,Eu<sup>3+</sup> phosphors. (b) Emission spectra of La<sub>0.7-x</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>x</sub> ( $\lambda_{ex}$  = 391 nm) phosphors.

be ascribed to the more impurities which provides more nonradiative recombination centers.

The Commission Internationale de l'Eclairage (CIE) 1931 chromaticity coordinates were calculated based on the corresponding PL spectra and summarized in Table 1, and represented also in Fig. 10. The CIE chromaticity coordinates of La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub> are



Fig. 8. Energy level diagrams of  $\rm Sm^{3+}$  and  $\rm Eu^{3+}.$  Energy transfer process from  $\rm Sm^{3+}$  to  $\rm Eu^{3+}$  is indicated.



**Fig. 9.** The luminescence decay curves of the 614 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) emissions of: (a) La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>; (b) La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Bi<sub>0.02</sub>; and (c) La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>0.02</sub> phosphors ( $\lambda_{ex}$  = 391 nm).



**Fig. 10.** CIE color coordinates of La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>0.02</sub> ( $\lambda_{ex}$  = 391 nm)(G, R, B: CRTs coordinates). The inset presents the picture of La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub> phosphor under a UV source.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### Table 1

The CIE chromaticity coordinates and  $^5D_0 \rightarrow {}^7F_2$  relative intensity of phosphors ( $\lambda_{ex}$  = 391 nm).

Sample no.	Phosphor compositions	CIE chromaticity coordinates		${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ relative intensity (a.u.) $\lambda_{ex}$ = 391 nm
		x	y	
а	La <sub>0.7</sub> BSiO <sub>5</sub> :Eu <sub>0.3</sub>	0.624	0.375	1.0
b	La <sub>0.68</sub> BSiO <sub>5</sub> :Eu <sub>0.3</sub> ,Bi <sub>0.02</sub>	0.623	0.377	2.5
С	La <sub>0.68</sub> BSiO <sub>5</sub> :Eu <sub>0.3</sub> ,Sm <sub>0.02</sub>	0.623	0.376	3.6

(x=0.624, y=0.375) under the excitation of 391 nm, the codoped Bi<sup>3+</sup> or Sm<sup>3+</sup> ions has made no big change to the CIE coordinates. The inset of Fig. 10 presents the picture of La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub> phosphor with bright red emission from its surface under a UV-source. Table 1 also lists the comparison of relative emission intensity of the samples. It is indicated that La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>0.02</sub> phosphor with CIE chromaticity coordinates of (x=0.623, y=0.376) is the best candidate for the application of white LEDs due to the 3.6 times higher emission intensity than that of La<sub>0.7</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>.

#### 4. Conclusions

In summary, LaBSiO<sub>5</sub>:Eu<sup>3+</sup>,R<sup>3+</sup> (R=Bi or Sm) phosphors have been synthesized by a facile sol-gel process. Their structural and spectroscopic properties have been investigated. Upon excitation with UV light of 391 nm, these phosphors have shown bright red emissions centered at 614 nm due to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup>. It was worthy of mention here that the red emission of Eu<sup>3+</sup> is enhanced by a factor of 2.5 and 3.6 by co-doping 2 mol% Bi<sup>3+</sup> and/or 2 mol% Sm<sup>3+</sup>, respectively. A bright red light has been obtained from La<sub>0.68</sub>BSiO<sub>5</sub>:Eu<sub>0.3</sub>,Sm<sub>0.02</sub> phosphor with CIE chromaticity coordinates of (x = 0.623, y = 0.376), indicating the phosphor has potential application as the red components in white LEDs.

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