

# Orange-Red Emitting Phosphors Sm<sup>3+</sup>-Activated Borosilicate for near UV-based White LEDs

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**Abstract**—A new phosphor Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> has been synthesized via solid-state reaction process. Emission/excitation spectra and photoluminescence decay behaviors were investigated in detail. The phosphors Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> can be excited under the excitation of 405 nm, Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> could show orange-red emitting light which cover the region from 450 to 700 nm. The intensity of Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> phosphor increases with Sm<sup>3+</sup> ions adding, then gradually decreases as the doping concentration becomes higher than 0.03, it occurs concentration quenching the possibility of energy transfer between Sm<sup>3+</sup> ions increases, we can roughly estimate the critical distance of energy transfer (R<sub>c</sub>) according to the report of Blasse, after calculating, the R<sub>c</sub> value is about 12.6 Å. When the Sm<sup>3+</sup> at 0.03 mol, the chromaticity coordinates of Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> is (0.62, 0.34) which closed to the standard CIE of red light (0.67, 0.33). The results showed that Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> phosphors may be promising phosphor candidate in UV white LEDs.

**Keywords**-Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup>; Luminescence; Phosphor; Energy Transfer; Lifetime

## I. INTRODUCTION

White-light-emitting diodes (W-LEDs) have been paid more and more attention as the advantage of longer lifetime, higher rendering index, higher luminosity efficiency and lower energy consumption [1, 2]. The most common method is realized by combining the blue light of GaN chips and the yellow emission of YAG: Ce<sup>3+</sup> [3-5], however, the type of white color varies with the input power and a poor color rendering index (Ra < 80). Many efforts have been made to overcome these mention above disadvantages, novel phosphor materials can be effectively excited by ultraviolet or blue light which can emit strong blue, green, red light, gained importance [6-8]. Tricolor phosphors with high stability and intense absorption in UV spectral region are in demand to meet the optimum requirements of w-LEDs.

Red emitting phosphor is one of the tricolor luminescent materials for white LEDs. Up to now, many researchers have been done on red or reddish-orange phosphors doped by Eu<sup>3+</sup>, Sm<sup>3+</sup>, Bi<sup>2+</sup> and Mn<sup>4+</sup> ions, commonly doped are Eu<sup>3+</sup> and Sm<sup>3+</sup> ions, they all have sharp excitation peaks at around 400 nm and narrow emissions at 580~630 nm, due to characteristic

intraconfigurational 4f-4f transitions. As well known, the sharp 4f-4f transitions and the full width at half maximum are outmost filled 5s<sub>2</sub> and 5p<sub>6</sub> orbitals. Such an inert host dependence of Eu<sup>3+</sup> and Sm<sup>3+</sup> leads to the excellent reproduction quality of optical properties of red phosphor especially in the process of mass production. Therefore, it is strongly expected that Eu<sup>3+</sup> or Sm<sup>3+</sup> would be ideal activator for red phosphor for white LEDs.

Usually, the Sm<sup>3+</sup> ion has sharp excitation peak at ~400 nm and shows narrow emissions due to characteristic intraconfigurational 4f-4f transitions of Sm<sup>3+</sup> in the host. The luminescence signal of Sm<sup>3+</sup> ion doped materials shows characteristic lines determined by the peculiar electronic structure of Sm<sup>3+</sup> ion energy levels. Sm<sup>3+</sup>-doped materials have been intensively investigated due to its increasing application in various fluorescent devices, and the search for novel reddish orange emitting phosphors has stimulated a growing interest in Sm<sup>3+</sup> doped materials.

Borosilicate was selected as host due to its advantages, such as stable physical and chemical properties, excellent thermal stability and easy to acquire. Commonly, it used to be the glass substrate material, in borosilicate system, attribute to adding of the boric acid, therefore, it can reduce the synthesis temperature of preparation of silicate, in addition, in ultraviolet region, borosilicate also has better absorption, borosilicate can applied as fluorescent material for LED according to this characteristic[9]. Recently, less research reported about this aspect, the respect of this region is worth investigating. In the composition of borosilicate, there including two elements (B, Si), generally speaking, B coordinated in the form of BO<sub>3</sub> (triangle) and BO<sub>4</sub> (tetrahedron) and Si coordinated in the form of silicon oxygen tetrahedron, different patterns of the B-Si connection could cause borosilicate present diversified borosilicate structure, boron silicate has good chemical stability which dues to the existence of the structure of BO<sub>4</sub>.

Therefore, boron silicate as substrate of luminescent material is a good choice as the result of its excellent chemistry and thermal stabilization, facile synthesis and cheap raw materials (H<sub>3</sub>BO<sub>3</sub>), so it has been extensively applied to phosphor for LED, since it can be efficiently excited by LED chips, there have been a few reports recently about this materials applied in phosphors for white LED, as is known to all, Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub> as a stable

boron silicate host, the luminescence property with Sm<sup>3+</sup> have not yet been investigated in detail. Therefore, in the present work, in this paper, we utilize the advantages of borosilicate and choose Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub> as substrate of luminescent material, and doped with trivalent rare earth Sm<sup>3+</sup> to analyze the luminescence properties under ultraviolet excitation conditions.

## II. EXPERIMENTAL

### A. Preparation of Sr<sub>3-x</sub>B<sub>2</sub>SiO<sub>8</sub>: xSm<sup>3+</sup> ( $x=0.01\sim0.09$ ) samples

Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup>-phosphors were prepared by a solid-state reaction technique. Analytical reagent grade (99.90%) SrCO<sub>3</sub>、H<sub>3</sub>BO<sub>3</sub>、SiO<sub>2</sub>, spectrographically pure (99.99%) Sm<sub>2</sub>O<sub>3</sub> were employed as reactants. Reactant samples were first quantified by the stoichiometric ratio and then thoroughly mixed by grinding them in an agate mortar for 2 hours, and then transferred the samples into the corundum crucible and placed in a muff furnace at 600°C for 1h, then get out and grinding them in an agate mortar for 1 hour again, subsequently, firing at 1000°C for 3h. Finally, corundum crucibles were cooled to room temperature and the phosphor samples were obtained.

### B. Apparatus and measurements

The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), the operation voltage and current were maintained at 40 kV and 40 mA, respectively, a scan rate of 2 %/min was applied to record the patterns in the range of  $2\theta = 10\sim60^\circ$ . The excitation and emission spectra were measured by a Spectrofluorophotometer RF-5301PC series equipped with a 150W Xenon lamp. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz). All the experiments were performed at room temperature.

## III. RESULTS AND DISCUSSION

### A. Characteristic analysis of XRD

The phase purities and the crystal structures of the as-prepared powder samples were characterized by XRD at room temperature. The XRD patterns of Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub>: Sm<sup>3+</sup> phosphor samples with the Sm<sup>3+</sup> concentrations are seen in Figure 1. All of the diffraction peaks are accord with Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub> (JCPDS card No.32-1224). The samples are of single phase without any impurities. This indicates that doping of Sm<sup>3+</sup> in Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub> host with such a small concentration has no other phase specific changes, the radii of Sm<sup>3+</sup> ion is close to the radius of Sr<sup>2+</sup>, it preferably occupy the Sr<sup>2+</sup> ion [10].

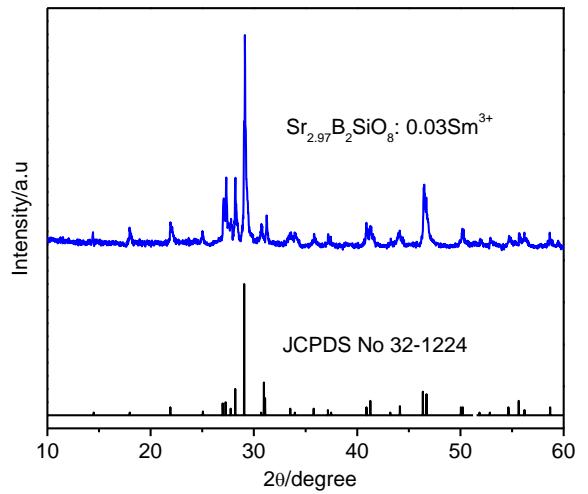


Figure 1. Typical XRD pattern of Sr<sub>2.97</sub>B<sub>2</sub>SiO<sub>8</sub>:0.03Sm<sup>3+</sup>

### B. Photoluminescence of Sr<sub>2.97</sub>B<sub>2</sub>SiO<sub>8</sub>:0.03Sm<sup>3+</sup> phosphors

PL excitation and emission spectra of Sm<sup>3+</sup> doped Sr<sub>3</sub>B<sub>2</sub>SiO<sub>8</sub> phosphor samples with 3mol% concentration are presented in Figure 2. Figure 2-a shows the excitation spectrum of the sample that monitored at the emission of 600 nm which consists the band in the range of 300 to 500 nm with the maximum at 405 nm which attributed the 6H5/2→4K11/2 of Sm<sup>3+</sup>. Figure 2-b presents the emission spectrum of the sample excited by 405nm, which covers the region from 450 to 700 nm consisting of the characteristic transitions of Sm<sup>3+</sup>, namely, 4G5/2→6H5/2 (565 nm), 4G5/2→6H7/2 (600 nm) and 4G5/2→6H9/2 (647 nm), among these characteristic peaks of Sm<sup>3+</sup>, the emission of 4G5/2→6H5/2 (565 nm) and 4G5/2→6H7/2 (600 nm) are predominant.

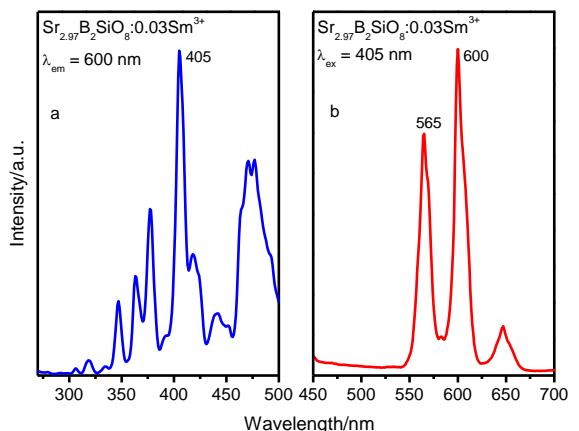


Figure 2. Photoluminescence excitation (a,  $\lambda_{\text{em}} = 600 \text{ nm}$ ) and emission (b,  $\lambda_{\text{ex}} = 405 \text{ nm}$ ) spectra of Sr<sub>2.97</sub>B<sub>2</sub>SiO<sub>8</sub>: 0.03Sm<sup>3+</sup>

Figure 3 shows the emission intensity of  $\text{Sr}_3\text{B}_2\text{SiO}_8$ : Sm<sup>3+</sup> ( $x = 0.01 \sim 0.09$ ) with different concentration under the excitation of 405nm. The emission intensities of all of the emission are enhanced significantly with the Sm<sup>3+</sup> concentration increasing, then gradually decreases as the doping concentration becomes higher than 0.03, it occurs concentration quenching, therefore, the optimum doping concentration of Sm<sup>3+</sup> is fixed at 3 mol%. The concentration quenching may be induced by cross relaxation processes in close Sm<sup>3+</sup>-Sm<sup>3+</sup>. When the Sm<sup>3+</sup> concentration increases, the possibility of energy transfer between Sm<sup>3+</sup> ions will also increase. According to the report of Blasse, we can roughly estimate the critical distance of energy transfer (Rc), and calculated as follows[11]:

$$Rc \approx 2 \left( \frac{3V}{4\pi XcN} \right)^{1/3} \quad (1)$$

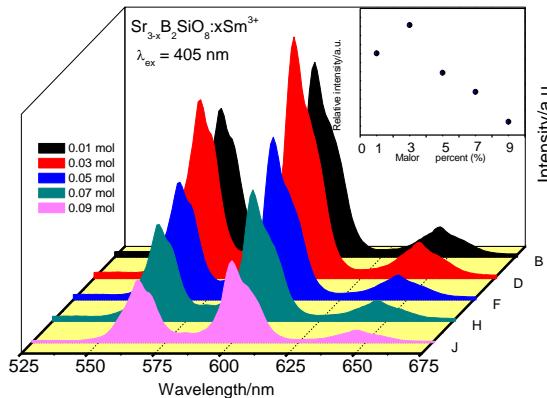


Figure 3. Photoluminescence emission spectra of  $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8$ : xSm<sup>3+</sup> with different Sm<sup>3+</sup> concentration under the excitation of 405 nm

Here V is the unit cell volume, Xc is the critical concentration, and N is the number of the ions in a unit cell. In  $\text{Sr}_3\text{B}_2\text{SiO}_8$ ,  $V=125 \text{ \AA}^3$ ,  $N=4$ , and the critical concentration Xc is about 0.03 in our system. The Rc value is about  $12.6 \text{ \AA}$  by using eq 1.

In general, there are three mechanisms for nonradiate energy transfer, including exchange interaction, radiation reabsorption and electric multipolar interactions. The Rc obtained above indicate the little possibility of exchange interaction since the exchange interaction is predominant only for about  $5\text{-}8 \text{ \AA}$ [12]. The mechanism of radiation is only efficacious when the fluorescence and absorption spectra are widely overlapping, which also does not applied in these cases. As a result, we can infer that the electric multipolar interactions would be responsible for the energy transfer mechanisms between the Sm<sup>3+</sup> ions. As described by Dexter's energy transfer expressions of multipolar interaction and Reisfeld's approximation, the following relationship can be attained[13]:

$$\frac{\eta s_0}{\eta s} \propto C^{\alpha/3} \quad (2)$$

where  $\eta s_0$  and  $\eta s$  represent the luminescence quantum efficiencies of the host with the absence and presence of Sm<sup>3+</sup> ions. The value for  $\alpha = 6, 8$  and  $10$  corresponds to dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively. While, the value of  $\eta s_0/\eta s$  is hard to obtain, it can be approximately calculated used by the value of  $I_{s0}/I_s$ , where  $I_{s0}$  and  $I_s$  on behalf of the luminescence intensity of the host without and with the Sm<sup>3+</sup> ions, respectively, therefore, the following relationship can be attained:

$$\frac{I_{s0}}{I_s} \propto C^{\alpha/3} \quad (3)$$

The relationship between  $I_{s0}/I_s$  and  $C^{\alpha/3}$  based on the above equation can be illustrated, the best linear relationship could be obtained when  $\alpha = 6$ , indicating that the mechanism of energy transfer between Sm<sup>3+</sup> ions is d-d interaction.

### C. Photoluminescence lifetimes of $\text{Sr}_3\text{B}_2\text{SiO}_8$ : Sm<sup>3+</sup> phosphors

Experiment tests the fluorescence lifetime of different concentrations of Sm<sup>3+</sup> in  $\text{Sr}_3\text{B}_2\text{SiO}_8$  system. The Figure 4 shows the fluorescence decay curves and simple orbit transition of Sm<sup>3+</sup>, after fitting, the values A1, t1, A2, t2 listed in TABLE1, their decay curves can be well fitted by a double exponential function:

$$I = A1\exp(-t/t1)+A2\exp(-t/t2) \quad (4)$$

where t1 and t2 are two components of the luminescence lifetime, A1 and A2 are the fitting parameters. The lifetime could be evaluated by  $t = (A1t1+A2t2)/(A1t1+A2t2)$ , where t is defined as the average lifetime, the luminescence lifetime after fitting show in TABLE1. The luminescence lifetime of 0.01~0.09mol of Sm<sup>3+</sup> are 6.985 E-7, 8.972 E-7, 6.116 E-7, 6.111 E-7 and 5.370 E-7 s.

A schematic diagram for Sm<sup>3+</sup> -activated  $\text{Sr}_3\text{B}_2\text{SiO}_8$  is displayed in the inset of Figure 4, under the excitation of 405 nm, Sm<sup>3+</sup> ions are excited from the  $6H5/2$  ground state to the  $4F7/2$  excited state and then to the  $4G5/2$  energy level by non-radiative relaxation, then, transfer occurs from  $4G5/2$  to the level of  $6H5/2$ ,  $6H7/2$  and  $6H9/2$ , emitting 565, 600 and 647 nm, respectively, the 600 nm is obviously stronger, which could also leading to the orange-red visible light.

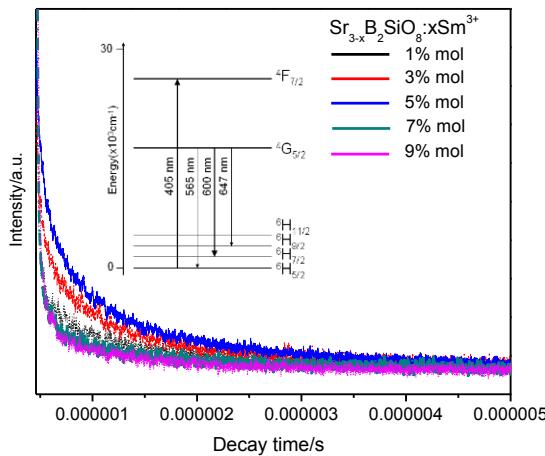


Figure 4. Photoluminescence decay curves of  $\text{Sm}^{3+}$  in  $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:\text{xSm}^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09$ ) phosphors

TABLE I. THE FITTING PARAMETERS OF FLUORESCENCE LIFETIME OF  $\text{Sr}_3\text{xB}_2\text{SiO}_8:\text{xSm}^{3+}$

$\text{Sm}^{3+}(x/\text{mol})$	$A_1$	$t_1$	$A_2$	$t_2$	$t$
0.01	0.0002	1.220E-6	0.0016	1.379E-7	6.985E-7
0.03	0.0005	1.239E-6	0.1238	9.378E-7	8.972E-7
0.05	0.0005	1.247E-6	0.1240	9.482E-7	6.116E-7
0.07	0.0011	1.025E-6	0.0473	1.172E-7	6.111E-7
0.09	0.0012	1.209E-6	0.0301	1.479E-7	5.370E-7

#### D. Chromaticity coordinates of $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$ phosphors

The chromaticity coordinates of different molar (0.01–0.09 mol) of  $\text{Sm}^{3+}$ -activated  $\text{Sr}_3\text{B}_2\text{SiO}_8$  are presented in Figure 5. From Figure 5, we can observed that with the  $\text{Sm}^{3+}$  ions added (0.01–0.09 mol), the color moved to the red region, the chromaticity coordinates of  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$  are 1:(0.55, 0.28), 2: (0.62, 0.34), 3:(0.61, 0.32), 4:(0.59, 0.30) and 5:(0.57, 0.29), respectively. When the intensity of  $\text{Sm}^{3+}$  reach the maximum, it is close to the

standard CIE of red light (0.67, 0.33), this result indicates that the  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$  may act as phosphors for the development of W-LEDs under UV/NUV excitation.

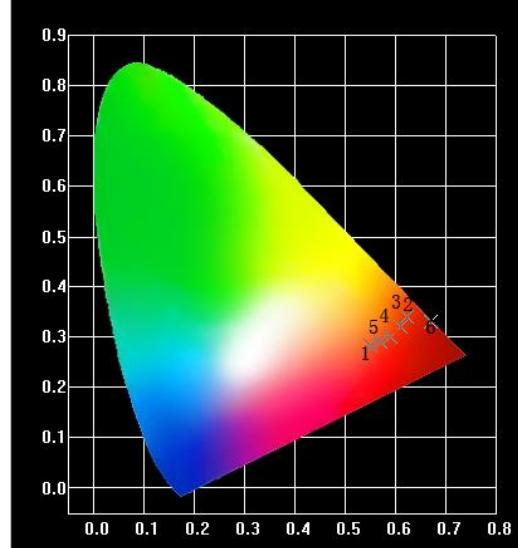


Figure 5. Chromaticity coordinates of  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$  (1:(0.55, 0.28), 2: (0.62, 0.34), 3:(0.61, 0.32), 4:(0.59, 0.30), 5:(0.57, 0.29), 6: (0.67, 0.33))

#### IV. CONCLUSIONS

In summary, a series of  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$  phosphors have been synthesized by thaditional high temperature solid state reaction. The phosphors  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$  excited under the UV region and show orange-red emitting light extended from 550 nm to 650 nm. In addition, the mechanism of energy transfer between  $\text{Sm}^{3+}$  ions is d-d interaction, according to the study results based on Dexter's formula and Reisfeld's approximation. The CIE coordinate of  $\text{Sr}_3\text{B}_2\text{SiO}_8: 0.03\text{Sm}^{3+}$  was calculate to be ( $x = 0.62, y = 0.34$ ), which is close to the standard CIE of red light (0.67, 0.33). The results showed that  $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Sm}^{3+}$ -phosphors may be promising phosphor candidate in UV white LEDs.

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