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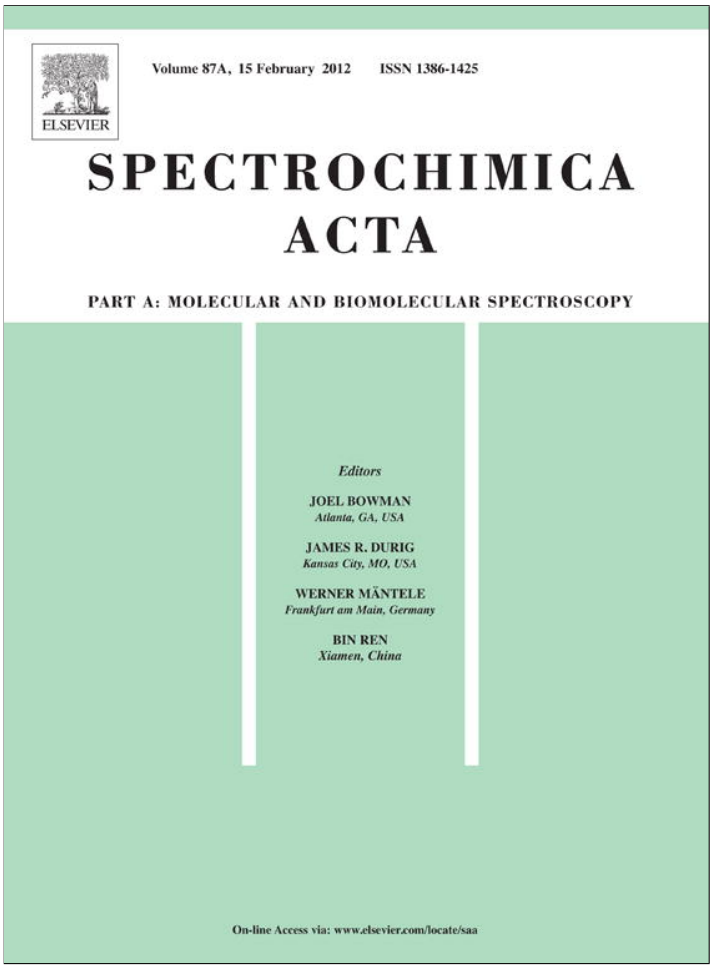

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Optimized photoluminescence of $SrB_2O_4:Eu^{3+}$ red-emitting phosphor by charge compensation

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ABSTRACT

A novel red-emitting phosphor, $SrB_2O_4:Eu^{3+}$, was synthesized by high temperature solid-state reaction and its photoluminescence properties were studied. The emission spectrum consists of four major emission bands. The emission peaks are located at 593, 612, 650 and 703 nm, corresponding to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ typical transitions of Eu^{3+}, respectively. The effects of Eu^{3+} doping content and charge compensators (Li^+, Na^+, K^+) on photoluminescence of $SrB_2O_4:Eu^{3+}$ phosphor were studied. The results show that the emission intensity can be affected by above factors and Na^+ is the optimal charge compensator for $SrB_2O_4:Eu^{3+}$. The photoluminescence of $NaSrB_2O_4:Eu^{3+}$ was compared with that of $Y_2O_2S:Eu^{3+}$. It implies that $SrB_2O_4:Eu^{3+}$ is a good candidate as a red-emitting phosphor pumped by near-ultraviolet (NUV) InGaN chip for fabricating white light-emitting diodes (WLEDs).

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1. Introduction

White light-emitting diodes (WLEDs) are promising for new generation solid-state lighting because of their advantages of high efficiency in converting electrical energy to light, long lifetime, good reliability and safety, low energy consumption and environment-friendly characteristics [1–3]. The WLED can be generated by two main ways. One is the combination of a blue LED with a yellow phosphor. The lighting efficiency of this type of WLED is pretty good in the low current condition, but the color rendering index is poor, for it only contains blue and yellow light and other colors' light is excluded [4]. The other is to mix the red/green/blue tricolor phosphors with a GaN/InGaN chip, which is the commonly used method at present. This type of WLED can offer superior color uniformity with high color rendering index and excellent light quality. However, the main tricolor phosphors for NUV InGaN-based LEDs are still some classical phosphor, such as $BaMgAl_{10}O_{17}:Eu^{2+}$ for blue, ZnS:(Cu^+, Al^{3+}) for green, and $Y_2O_2S:Eu^{3+}$ for red [5]. The red phosphor $Y_2O_2S:Eu^{3+}$ shows much lower efficiency than that of green and blue phosphors. Hence, the search for new red phosphors that can be efficiently excited by blue and near ultraviolet (NUV) light is urgent.

The optical properties of Eu^{3+} ion doped into matrices are important for the inorganic luminescent materials due to several advantages: (a) the pure red emission of the Eu^{3+} ion, (b) the Eu^{3+} ion is used as a general photo-luminescent probe, (c) the emitting level $^5D_0$ and the ground state $^7F_0$ are non-degenerate, (d) the magnetic dipole $^5D_0$–$^7F_1$ transition is allowed [6,7].

Borate is an excellent matrix material for Eu^{3+}-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 [8–12]. In Eu^{3+} doped alkaline earth borate phosphors, Eu^{3+} is expected to replace alkaline earth ion. It would be difficult to keep the charge balance in the crystallite sample. Hence, univalent charge compensator is necessary in order to keep the charge balance. However, little attention is paid to the effect of charge compensation on the luminescent properties of red-emitting borate phosphors.

In this paper, a novel red-emitting borate phosphor $SrB_2O_4:Eu^{3+}$ was synthesized by solid state method. The effects of Eu^{3+} doping content and charge compensators (Li^+, Na^+, K^+) on the luminescent properties were investigated.

2. Experimental

2.1. Preparation of $SrB_2O_4:Eu^{3+}$ phosphors

The $Sr_{1-x}B_2O_4:Eu^{3+}{}_x$ ($x = 0.02$, 0.04, 0.06, 0.08, 0.10) samples were prepared by a conventional solid-state reaction technique. Because trivalent Eu ions are located on divalent Sr ion sites and some charge-compensating defect is built into the lattices, Li^+,

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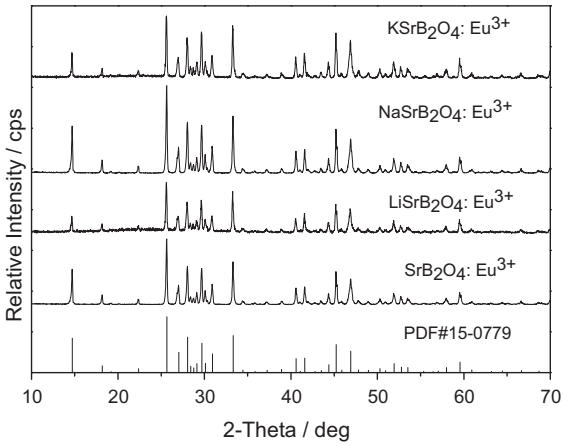

Fig. 1. XRD pattern of SrB_2O_4:Eu^{3+} and $MSrB_2O_4$:Eu^{3+} (M = Li, Na, K).

Na^+ or K^+ was added as charge compensator. Thus, a series of $M_xSr_{0.94-x}B_2O_4$:$Eu^{3+}_{0.06}$ (M = Li, Na, K) samples were also prepared by a conventional solid-state reaction technique. The starting materials are $SrCO_3$ (AR), Li_2CO_3 (AR), Na_2CO_3 (AR), K_2CO_3 (AR), H_3BO_3 (AR), and Eu_2O_3 (99.99%). The appropriate amount of starting materials was firstly ground, and then burned in an electric furnace at 750 °C for 4 h. $Y_{1.95}O_2S$:$Eu^{3+}_{0.05}$ was synthesized according to Ref. [13].

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 Cu K_α radiation (1.5406 Å). 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 analysis of the samples

The XRD patterns of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ and $M_{0.09}Sr_{0.82}B_2O_4$:$Eu^{3+}_{0.09}$ (M = Li, Na, K) are shown in Fig. 1. From Fig. 1, it can be observed that the four compounds have similar features and agree well with the Joint Committee on Powder Diffraction Standards (PDF 15-0779), indicating that the doped Eu^{3+} and the charge compensators had not caused obvious change in the host structure. SrB_2O_4 has an orthorhombic crystal structure with a space group of *pnca*(60), and its lattice parameter values are a = 6.589, b = 12.018 and c = 4.337 nm.

3.2. FE-SEM images of phosphor

Fig. 2 shows the FE-SEM image of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ powders prepared at 750 °C. It was observed that the microstructure of the phosphor consisted of irregular grains with some agglomerate phenomena. The average size of the $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ powders is about 3–5 μm. The results show that SrB_2O_4:Eu^{3+} phosphor has a relatively low sinter temperature, which is also consistent with the requirements of energy saving for products in today's society.

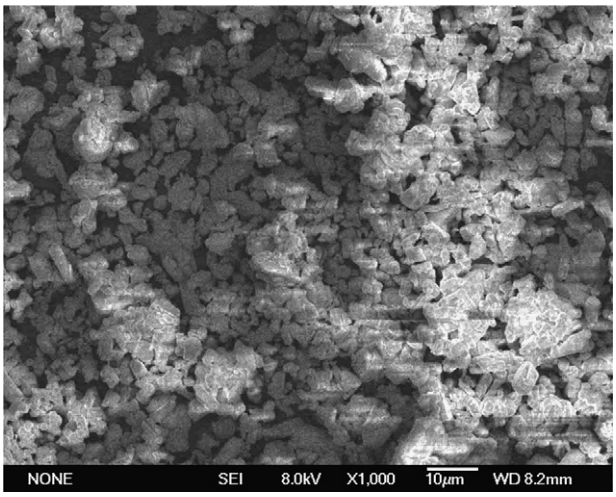

Fig. 2. FE-SEM image of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$.

3.3. Excitation and emission spectra of SrB_2O_4:Eu^{3+}

The excitation and emission spectra of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ phosphor are shown in Fig. 3. The broad excitation band at ~280 nm is attributed to the O → B charge transfer (CT) transition and the sharp lines in 360–480 nm range are intra-configurational 4*f*–4*f* 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 emission spectrum in curve (b) consists of four major emission bands. The highest emission peak is a $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 612 nm. Other emission peaks located at 593, 650 and 703 nm, corresponding to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ typical transitions of Eu^{3+} respectively, are relatively weak, which is advantageous to obtain the good CIE chromaticity coordinates. 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 $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ are close to the NTSC standard values. These results imply that the luminescent property of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ is fit for application in LED.

The effect of doped-Eu^{3+} concentration on the emission of SrB_2O_4:Eu^{3+} phosphor was also investigated. The emission

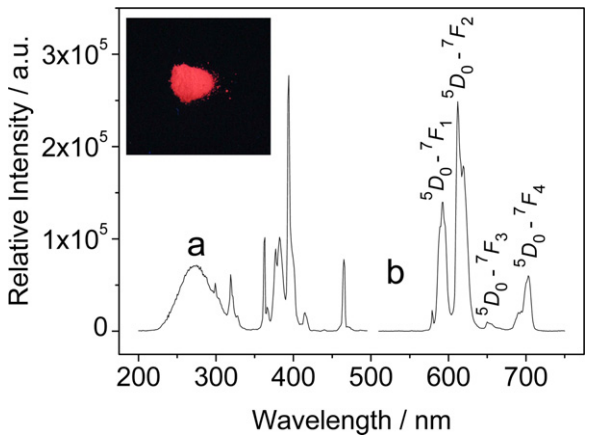

Fig. 3. Photoluminescence spectra of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$. (a) Excitation spectrum (λ_{em} = 611 nm) and (b) emission spectrum (λ_{ex} = 394 nm). Inset: the photograph of $Sr_{0.94}B_2O_4$:$Eu^{3+}_{0.06}$ under ultraviolet light irradiation.

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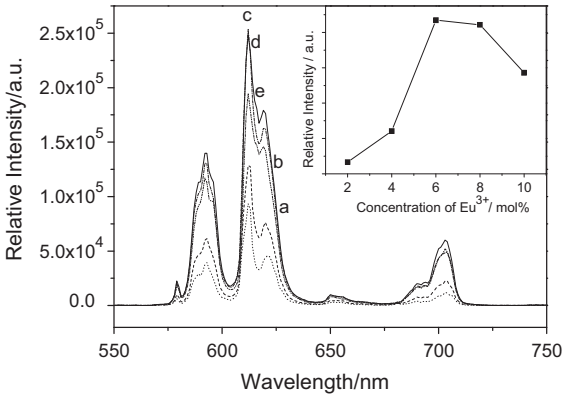

Fig. 4. Emission spectra of $Sr_{1-x}B_2O_4:Eu^{3+}{}_x$ with varying Eu^{3+} concentrations (a: $x = 0.02$, b: $x = 0.04$, c: $x = 0.06$, d: $x = 0.08$ and e: $x = 0.10$) ($\lambda_{ex} = 394$ nm). Inset: the dependence of PL intensity of $Sr_{1-x}B_2O_4:Eu^{3+}{}_x$ on Eu^{3+} concentration.

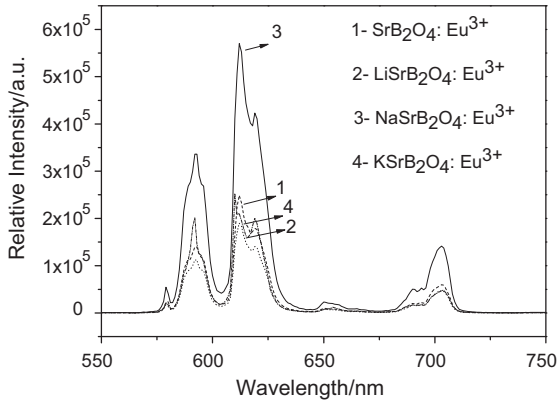

Fig. 6. Effect of different charge compensations on the emission intensity of $SrB_2O_4:Eu^{3+}$.

spectra of $SrB_2O_4:Eu^{3+}$ phosphors prepared at various concentrations of Eu^{3+} ($x = 0.02$–0.10) excited by 394 nm light and the dependence of photoluminescence (PL) intensity of $Sr_{1-x}B_2O_4:Eu^{3+}{}_x$ on doped-Eu^{3+} concentration are shown in Fig. 4. The PL intensity increases with Eu^{3+}-concentration increasing until a maximum intensity is reached, and then it decreases due to concentration quenching. The critical quenching concentration of Eu^{3+} (χ_c) is defined as the concentration at which the emission intensity begins to decrease and the critical distance is defined as the average distance between the nearest Eu^{3+} ions in which energy transfer occurs. From the inset of Fig. 4, we can see that χ_c of Eu^{3+} in $SrB_2O_4:Eu^{3+}$ phosphor is about 6 mol%.

3.4. Effect of charge compensation on $SrB_2O_4:Eu^{3+}$ luminescence intensity

In the $SrB_2O_4:Eu^{3+}$ crystallite, Eu^{3+} is expected to replace Sr^{2+}. It would be difficult to keep the charge balance in the crystallite sample, so univalent charge compensator was added. Fig. 5 shows the emission spectra of $Sr_{0.94}B_2O_4:Eu^{3+}{}_{0.06}$ and $Na_xSr_{1-2x}B_2O_4:Eu^{3+}{}_x$ with different Na_2CO_3 contents employed as compensator under 394 nm excitation. From the emission spectra, it can be seen that the emission intensity has been improved by adding Na^+ as charge compensator. Moreover, with Na^+ content increasing in the range of 3–9 mol%, the emitting intensity of samples increases greatly, and the emitting intensity is in the optimum state when Na^+ content is up to 9 mol%. Then the emitting intensity of the phosphor decreases when Na^+ content is beyond 9 mol%. It may be that some Na^+ works charge compensation in the phosphors, while superfluous Na_2CO_3 acts as flux agent to promote the formation of luminous material polycrystal and cripple the crystal structure. Also, the effect of Li^+ and K^+ contents on photoluminescence of $SrB_2O_4:Eu^{3+}$ phosphor was studied. The optimal content is 9 mol% for both Li^+ and K^+.

The different charge compensators influence the luminous characteristic of samples as shown in Fig. 6. It is found that the emitting intensity of the phosphors changes with different charge compensators. The emitting intensity of the phosphor increased observably by adding Na^+ as charge compensator, which is 2.3 times as strong as the ones without charge compensator. Contrarily, both Li^+ and K^+ anions decreased the luminescent intensity of $SrB_2O_4:Eu^{3+}$ slightly. These phenomena may be due to the fact that the ionic radius of Na^+ (102 pm) is similar to that of Sr^{2+} (113 pm) so that Na^+ can substitute Sr^{2+} easily without disturbing the crystal lattice, while the addition of Li^+ and K^+ results in the distortion of the crystal structure because of a big discrepancy between the ionic radius of Li^+ (59 nm), K^+ (138 nm) and Sr^{2+}, and then impacts on the luminous properties.

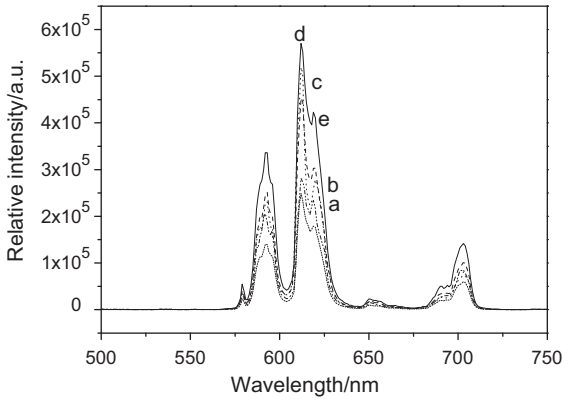

Fig. 5. Emission spectra of $Sr_{0.94}B_2O_4:Eu^{3+}{}_{0.06}$ (a) and $Na_xSr_{1-2x}B_2O_4:Eu^{3+}{}_x$ phosphor (b: $x = 0.03$, c: $x = 0.06$, d: $x = 0.09$ and e: $x = 0.12$).

3.5. Comparison of photoluminescence between $NaSrB_2O_4:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$

The photoluminescence spectra of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ and $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ are shown in Fig. 7. Since the purpose of present investigation is on the near NUV LED phosphor, only the spectroscopic properties in the range of 350–500 nm are exhibited in Fig. 7. In curve (a), the band from 350 to 390 nm is the

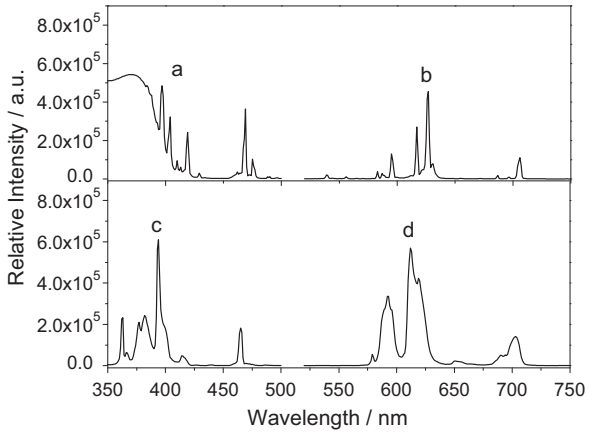

Fig. 7. Photoluminescence spectra of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ (a: excitation spectrum, $\lambda_{em} = 626$ nm and b: emission spectrum, $\lambda_{ex} = 395$ nm) and $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ (c: excitation spectrum, $\lambda_{em} = 611$ nm and d: emission spectrum, $\lambda_{ex} = 394$ nm).

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$Eu^{3+} \leftarrow S^{2-}$ charge transfer (CT) in Y_2O_2S and the lines in 390–500 nm range are intra-configurational 4*f*–4*f* transitions of Eu^{3+} in the host lattices. The emission spectra of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ (λ_{ex} = 395 nm) and $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ (λ_{ex} = 394 nm) are shown in curves (b) and (d), respectively. In curve (b), the main emission peaks at 626 and 616 nm of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ are ascribed to Eu^{3+} transition from $^5D_0$ to $^7F_2$ and its strongest peak is at 626 nm, other transitions from the ^5D_J (J = 0, 1, 2, 3) excited levels to ^7F_J (J = 0, 1, 2, 3, 4, 5, 6) ground states are very weak. Comparing curve (b) with curve (d), the following results can be found. First, the integral emission intensity of $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ under 394 nm irradiation is about 3.7 times higher than that of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ excited at 395 nm. Second, the CIE chromaticity coordinates are calculated to be x = 0.64, y = 0.35 for $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ and x = 0.63, y = 0.35 for $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$. Compared with the NTSC standard CIE chromaticity coordinate values for red (x = 0.67, y = 0.33), it was found that the CIE chromaticity coordinates of $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ were closer to the NTSC standard values than those of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$. These results imply that the luminescent properties of $Na_{0.09}Sr_{0.82}B_2O_4:Eu^{3+}{}_{0.09}$ may be better than those of $Y_{1.95}O_2S:Eu^{3+}{}_{0.05}$ when they are applied in LED.

4. Conclusion

A new red-emitting phosphor of $SrB_2O_4:Eu^{3+}$ was prepared by conventional solid-state reaction at 750 °C and its photoluminescence properties were investigated. The phosphor $SrB_2O_4:Eu^{3+}$ exhibits efficient red-emitting at 394 nm excitation. The critical quenching concentration of Eu^{3+} in $SrB_2O_4:Eu^{3+}$ phosphor is about 6 mol%. The charge compensations of Na^+ increased the luminescent intensity of $SrB_2O_4:Eu^{3+}$ obviously, while Li^+ and K^+ anions decreased the luminescent intensity of $SrB_2O_4:Eu^{3+}$ slightly. Na^+ is the optimal charge compensator for $SrB_2O_4:Eu^{3+}$. Compared with $Y_2O_2S:Eu^{3+}$, $NaSrB_2O_4:Eu^{3+}$ shows more excellent photoluminescence properties.

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