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# Novel yellowish white-emitting $Eu^{2+}$ -activated phosphate phosphor based on $Rb_2Ba_3P_4O_{14}$

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 $Eu^{2+}$ -doped  $Rb_2Ba_3P_4O_{14}$  phosphors were synthesized in a single phase form by a conventional solid state reaction method and their optical properties were characterized. These phosphors showed broad optical absorption bands that can cover the UV and near-UV region, and exhibited a narrow deep-blue emission and broad reddish-yellow emission with peaks at 423 nm and 550 nm, respectively. The highest reddish-vellow emission intensity was obtained for  $Rb_2(Ba_{0.99}Eu_{0.01})_3P_4O_{14}$ .

Key words: White LED, Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub>, Reddish-yellow emission.

## Introduction

Phosphor converted white light emitting diodes (pc-WLEDs) are attracting significant attention as one of the most promising next generation light sources [1-3]. The pc-WLED have a number of advantages, such as a high luminescent efficiency, a long lifetime, compactness, and low energy consumption [4-6]. The luminescence efficiency, particularly color rendering index (CRI) of the pc-WLEDs is considerably affected by the emission color purity of the phosphor. Therefore, it is necessary to develop the novel phosphor with high emission intensity in longer wavelength side to enhance the CRI of the pc-WLEDs [7-13].

Among several phosphors,  $Eu^{2+}$ -activated phosphors have been usually used in the pc-WLEDs because these phosphors show the strong broad excitation and emission band due to the spin allowed energy transitions between the 4f ground state and 5d excited state of  $Eu^{2+}$ [14-16]. The peak intensity and position of the excitation and emission bands of  $Eu^{2+}$ -activated phosphors are strongly depend on the crystal structure, particularly the crystallographic environment of the dopant site for  $Eu^{2+}$ , of the host materials. To develop the novel phosphor exhibited longer wavelength emission with high emission intensity, therefore the selection of the host material is significantly important.

In this study, we focused on  $Rb_2Ba_3P_4O_{14}$ , which has orthorhombic structure with a space group of  $P2_12_12_1$ [17], as a host material for development of novel  $Eu^{2+}$ - activated phosphor for use in WLEDs. The crystal structure of  $Rb_2Ba_3P_4O_{14}$  is composed of a  $RbO_n$  (n = 10 and 11) polyhedra,  $BaO_n$  (n = 7 and 8) polyhedra, and P2O7 groups formed with two PO4 tetrahedra bridged with a oxygen ions on inversion centers, as shown in Fig. 1(a). In the crystal structure,  $Ba^{2+}$  ions occupy three different types of crystallographic sites with two  $BaO_7$  and a  $BaO_8$  and the average bond distances of Ba-O in each Ba<sup>2+</sup> site are 0.275, 0.276, and 0.280 nm for two  $BaO_7$  and  $BaO_8$  polyhedra, respectively (Fig. 1(b)). The average bond distance of Ba-O in Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> is shorter than that of a conventional  $Ba_2SiO_4$ :  $Eu^{2+}$  phosphor (0.2977 nm for  $BaO_{10}$  and 0.2875 nm for  $BaO_{9}$  [18, 19], which exhibit the green-emission under near-UV and blue light excitation. According to the crystal field theory, the small dopant site for Eu<sup>2+</sup> with short bond distance of



Fig. 1. Crystal structure of  $Rb_2Ba_3P_4O_{14}$  and coordination environment of  $Ba^{2+}$  sites.

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cation-anion and small coordination number will contribute to increase the crystal field strength around  $Eu^{2+}$  [20]. The strong crystal field strength usually results in the shift of the excitation and emission band to longer wavelength side.

In this study, therefore, novel  $\mathrm{Eu}^{2+}$ -activated  $\mathrm{Rb}_2\mathrm{Ba}_3\mathrm{P}_4\mathrm{O}_{14}$  phosphors were synthesized by a conventional solid state reaction method and their luminescence properties were characterized.

## **Experimental**

 $Rb_2CO_3$ ,  $BaCO_3$ ,  $NH_4H_2PO$  and  $Eu_2O_3$  were mixed in a stoichiometric ratio with acetone using a mortar. The homogeneous mixture was first calcined at 400 °C for 1 hr in air. After calcinations, the samples were reground again in a mortar and heated twice at 850 °C for 4 hrs in air and a flow of 95% N<sub>2</sub>-5% H<sub>2</sub> gas to reduce  $Eu^{3+}$  to  $Eu^{2+}$ .

The obtained samples were characterized by X-ray powder diffraction (XRD; Mac Science Ltd. MX-Labo). The emission and excitation spectra were measured at room temperature by using a spectrofluorometer (Jasco Corp. FP-6500/6600). The emission spectrum was obtained upon excitation at 365 nm, and the excitation spectrum was obtained by monitoring emission at 550 nm.

#### **Results and Discussion**

Fig. 2 shows the XRD patterns of the  $Rb_2(Ba_{1-x} Eu_x)_3P_4O_{14}$  (0.00  $\leq x \leq 0.03$ ) phosphors. The XRD simulation pattern of  $Rb_2Ba_3P_4O_{14}$  reported by S. Zhao *et al.* with single crystal analysis is also shown in Fig. 2 as a reference [17]. The XRD patterns of all samples were well indexed to that of a single-phase of the orthorhombic  $Rb_2Ba_3P_4O_{14}$  structure and diffraction peaks due to impurities corresponding to the starting materials were not observed in the patterns. A peak shift to higher diffraction angle is observed with the increasing in the  $Eu^{2+}$  content, because  $Ba^{2+}$  (ionic radius: 0.156 nm for 8-



Fig. 2. XRD patterns of the  $Rb_2(Ba_{1-x}Eu_x)_3P_4O_{14}$  (0.00  $\le x \le 0.03$ ).



Fig. 3. Excitation (left) and emission spectra (right) of the  $Rb_2$  (Ba\_{0.98}Eu\_{0.02})\_3P\_4O\_{14}.



Fig. 4. Temperature dependence of the relative emission intensities for the  $Rb_2(Ba_{0.98}Eu_{0.02})_3P_4O_{14}$  sample at 550 and 423 nm.

fold coordination [21]) in the host materials is partially substituted with the smaller  $Eu^{2+}$  (ionic radius: 0.139 nm for 8-fold coordination [21]).

The photoluminescence excitation and emission spectra of Rb<sub>2</sub>(Ba<sub>0.92</sub>Eu<sub>0.02</sub>)<sub>3</sub>P<sub>4</sub>O<sub>14</sub> phosphor are shown in Fig. 3. The excitation spectrum recorded for emission at 550 nm consisted of broad optical absorption bands from 250 to 400 nm, which correspond to the  $4f^7 \rightarrow 4f^65d^1$ allowed transition of Eu<sup>2+</sup> ions. The emission spectrum obtained for excitation at 365 nm shows a narrow deepblue emission with a peak at 423 nm and a broad reddish-yellow emission with a peak at 550 nm, which can be ascribed to the  $4f^{6}5d^{1} \rightarrow 4f^{7}$  allowed transition of Eu<sup>2+</sup> ions. Two different emission bands indicate the existence of different emission centers in accordance with the different types of crystallographic environment of  $Eu^{2+}$  in the host  $Rb_2Ba_3P_4O_{14}$  lattice [22]. As pointed out in the introduction, the Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> has three different Ba<sup>2+</sup> sites with different crystallographic environment with two  $BaO_7$  and  $BaO_8$  polyhedra. Besides  $Ba^{2+}$  sites, from an ionic radius point of view,  $Eu^{2+}$  (0.135 nm for 10-fold coordination) can be possible to dope into the Rb<sup>+</sup> (0.166 nm for 10-fold coordination ) sites in the



Fig. 5. A schematic illustration of configurational model.



**Fig. 6.** Dependence of the emission intensity on  $Eu^{2+}$  concentration in the  $Rb_2(Ba_{1-x}Eu_x)_3P_4O_{14}$  samples (0.005  $\leq x \leq 0.03$ ).

host Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> lattice. The average bond distances of Ba-O in the  $Ba^{2+}$  sites are 0.275, 0.276, and 0.280 nm for two BaO7 and one BaO8 polyhedra, respectively. These results indicate that the crystal field strength of O<sup>2</sup> around Eu<sup>2+</sup> in the Ba<sup>2+</sup> sites is stronger than that of Rb<sup>+</sup> sites. The strong crystal field strength usually results in the emission band shift to longer wavelength side [19]. Therefore, it is possible to consider that the deep-blue and reddish-yellow emission of the  $Rb_2Ba_3P_4O_{14}$ :  $Eu^{2+}$  phosphor can be ascribed to  $Eu^{2+}$ doped into the RbO<sub>n</sub> (n = 10 and 11) and BaO<sub>n</sub> (n = 7 and 8), respectively. Furthermore, extremely broad reddishyellow emission band of the Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> : Eu<sup>2+</sup> phosphor is originate from  $4f^{6}5d^{1} \rightarrow 4f^{7}$  transition of Eu<sup>2+</sup> in different three Ba<sup>2+</sup> sites having different crystallographic environment.

The thermal quenching of the phosphor used in WLEDs is one of the most important technological problems because the temperature in the WLEDs reaches high temperature [23]. The temperature-dependent emission intensity of  $Rb_2Ba_3P_4O_{14}$ :  $Eu^{2+}$  phosphor is measured at

temperatures in the range of 25 to 150 °C, and the results are shown in Fig. 4. With increasing temperature, the emission intensity decreases. At 150 °C, the emission intensities at 550 and 423 nm are down to 14.4% and 78.4% of the initial value at 25 °C, respectively. The large difference of thermal quenching of the blue and reddishyellow emission can be explained using the configurational coordinate model [24]. Fig. 5 shows the configurational coordinate diagram. The thermal quenching of the phosphors is usually considered by thermally activated crossover from the 5d excited state to the 4f ground state [25]. The excited 5d electron is thermally activated through the phonon interaction and then thermally released through the crossing point between the 5d potential curve and the 4f ground potential curve [26]. In Fig. 5, A and B are the lowest position of the excited state of each dopant site, and the blue and reddishyellow emissions are due to the energy transfer of  $A \rightarrow F$  and  $B \rightarrow E$ , respectively. D and C are the crossing points of the ground state and excited state of the each dopant site. In other words, thermal quenching of each emission occurred through the electron transfer of  $A \rightarrow D \rightarrow F$  (blue emission) or  $B \rightarrow C \rightarrow E$  (reddish yellow emission), and the energy level of C is lower than that of D, which indicates that the energy for thermally activated of the reddish yellow emission is lower than that of the blue emission. Consequently, the reddish yellow emission showed the larger intensity reduction due to the thermal quenching than that of the blue emission. By the optimization of the Eu<sup>2+</sup> concentration in  $Rb_2(Ba_{1-x}Eu_x)_3P_4O_{14}$ , the highest reddish yellow emission intensity was obtained for Rb<sub>2</sub>(Ba<sub>0.99</sub> Eu<sub>0.01</sub>)<sub>3</sub>P<sub>4</sub>O<sub>14</sub> (Fig. 5).

# Conclusions

Novel Eu<sup>2+</sup>-activated Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> phosphors were synthesized by the conventional solid-state reaction method. The phosphors obtained in this study adopt a stable orthorhombic Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> structure in a single phase with high crystallinity.  $Rb_2Ba_3P_4O_{14}$ :  $Eu^{2+}$ phosphors exhibit the yellowish white emission under near-UV irradiation owing to the combination with deep-blue emission peaked at 423 nm and broad yellow emission peaked at 550 nm. This interesting emission is caused by the different environment Eu<sup>2+</sup> sites, such as Eu<sup>2+</sup> doped in Rb<sup>+</sup> or three different Ba<sup>2+</sup> sites. The  $Rb_2Ba_3P_4O_{14}$ :  $Eu^{2+}$  phosphors can be achieve tunable the emission color from bluish white to yellowish white by adjusting the  $Eu^{2+}$  concentration in  $Ra_2(Ba_{1-x}Eu_x)_3P_4O_{14}$ phosphors. The reddish yellow emission of Rb<sub>2</sub>Ba<sub>3</sub>P<sub>4</sub>O<sub>14</sub> :  $Eu^{2+}$  phosphors has strong emission intensity in the red light region, which indicates that this phosphor is expected to be a suitable candidate for pc-WLEDs.

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