

## A blue-emitting phosphor of $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$ for white light UV light-emitting diodes

Nuan Xie<sup>a</sup>, Yanlin Huang<sup>a</sup> and Hyo Jin Seo<sup>b,\*</sup>

<sup>a</sup>College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

<sup>b</sup>Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

A novel blue-emitting phosphor of  $\text{Eu}^{2+}$ -doped  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  phosphate was prepared by a high-temperature solid-state reaction method. The phosphor was investigated by X-ray powder diffraction (XRD) measurements and confirmed to be the pure crystalline phase of  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ . The emission and excitation spectra of the phosphor were studied. The phosphor could be excited by UV light from 220 nm to 400 nm and emitted a blue luminescence peaked at 410 nm, which corresponds to the  $4f^65d^1 \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  ions. The dependence of luminescence intensities of  $\text{Eu}^{2+}$ -doped  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  on the heating temperature and doping concentrations were investigated. The phosphor had an excellent thermal stability to temperature quenching effects. The luminescence decay (lifetimes) of the phosphor is also discussed in order to further investigate its potential applications for white light-emitting diode phosphors pumped by a near-UV chip.

**Key words:** Solid-state lighting, Phosphors, Photoluminescence, Phosphate.

### Introduction

In recent years, white light-emitting diodes (W-LEDs) have gained much attention as devices for display and solid-state lighting [1, 2]. W-LEDs have many advantages, e.g., a single relatively small size, a low operating voltage, a naturally colored light, a low power consumption, a long life, a maintained high efficiency (power in versus light output), an acceptable dispersal of light, and a relatively low cost of manufacture compared to other light sources [3, 4].

Up to now, many materials have been studied in order to develop phosphor converted W-LEDs. Eu-activated phosphors, for example, aluminates, silicates, phosphates and derivatives, have been intensively studied for their luminescent properties [5–8]. As an activated ion,  $\text{Eu}^{2+}$  ion has the  $5d$  electron unshielded from the crystal field by the  $5s$  and  $5p$  electrons, and its spectral properties are strongly affected by the surrounding environment such as symmetry, covalence, coordination, bond length, site size and crystal-field strength, etc. The absorption and emission spectra of  $\text{Eu}^{2+}$  usually show a broad band due to transitions between the  $4f^7$  ground state and the crystal field components of the  $4f^65d^1$  excited state configuration [9]. Thus the  $\text{Eu}^{2+}$ -emission band may be changed from blue to red in the visible spectral region. The wavelengths of excitation and emission bands strongly depend on the host crystal. So the choice of host greatly affects the optical properties of  $\text{Eu}^{2+}$  ions. Phosphate compounds are the excellent

matrices to be developed for  $\text{Eu}^{2+}$ -activated phosphors. They have an excellent thermal stability and the tetrahedral rigid three dimensional matrix of the phosphate is thought to be ideal for charge stabilization [10–12].

In this paper, a new blue phosphor of  $\text{Eu}^{2+}$ -doped barium magnesium phosphate  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  was synthesized by a conventional high temperature solid-state reaction. The luminescent properties, concentration quenching, temperature dependence and decay time were investigated. The crucial properties for its potential application in W-LEDs, for example, thermal stability, are discussed.

### Experimental

Polycrystalline samples of  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.02, 0.04, 0.06, 0.08, 0.1$  and  $0.12$ ) were synthesized by a high temperature solid-state reaction. The starting material was a stoichiometric mixture of reagent grade  $\text{C}_4\text{Mg}_4\text{O}_2 \cdot \text{H}_2\text{MgO}_2 \cdot 5\text{H}_2\text{O}$  (magnesium carbonate basic pentahydrate),  $\text{BaCO}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and rare earth oxide  $\text{Eu}_2\text{O}_3$ . Firstly, the mixture was heated up to  $350^\circ\text{C}$  and kept at this temperature for 10 h. The powder obtained was thoroughly mixed in acetone and then heated up to  $750^\circ\text{C}$  and kept at this temperature for 5 h in air. After that, the sample was thoroughly mixed and heated in air at  $950^\circ\text{C}$  for 10 h under a carbon monoxide reductive atmosphere to reduce to  $\text{Eu}^{2+}$  activators.

XRD data were collected on a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Bragg-Brentano geometry using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and analyzed using Jade-5.0 software. The excitation and emission spectra were recorded on a Perkin-Elmer LS-

\*Corresponding author:  
Tel : +82-51-629-5568  
Fax: +82-51-629-5549  
E-mail: hjseo@pknu.ac.kr

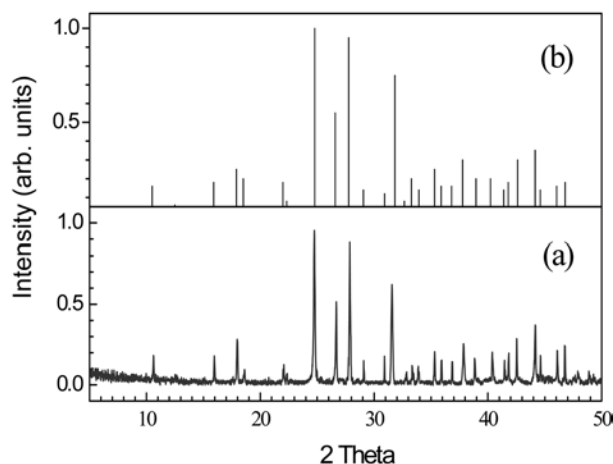
50B luminescence spectrometer with Monk-Gillieson type monochromators and a 20 kW xenon discharge lamp as excitation source. The luminescence decay was measured using the third harmonic (355 nm) of a pulsed Nd : YAG laser. To study the thermal quenching between 300 and 500 K the same spectrofluorimeter equipped with a homemade heating cell was used under the excitation of a 365 nm UV lamp.

## Results and Discussion

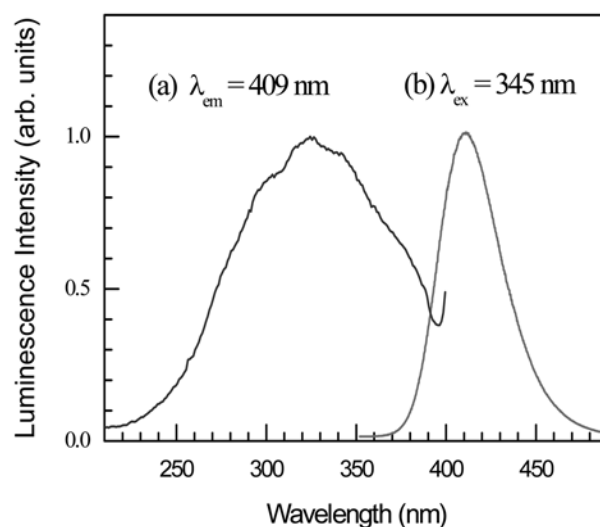
Fig. 1 shows the typical XRD pattern of  $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$  (a) and JCPDS card No.16-0640 (b). For all the samples, only the characteristic peaks corresponding to the  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  (JCPDS 16-0640,) were found, and no obvious impurities were detected. The sharp peaks in each XRD pattern indicate good crystallinity of the sample. The XRD data were fitted by the Jade 5.0 program. The result shows that  $\text{Eu}^{2+}$  ion doped  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  has an orthorhombic crystal structure. The refined unit cell lattice parameters are  $a = 7.0702 \text{ \AA}$ ,  $b = 12.23677 \text{ \AA}$ ,  $c = 5.70908 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $Z = 2$ , and  $497.97 \text{ \AA}^3$  is the volume. In  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ , the  $\text{Eu}^{2+}$  activator ions are substituted for  $\text{Ba}^{2+}$  sites based on their same valence state (+2) and close ionic radii ( $\text{Ba}^{2+} = 1.42 \text{ \AA}$ ,  $\text{Eu}^{2+} = 1.25 \text{ \AA}$ ) [13]. This has no obvious influence on the structure of the host.

Fig. 2 presents the excitation and emission spectra of  $\text{Ba}_{1.92}\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}_{0.08}$  at room temperature. The excitation spectrum monitored at 409 nm (Fig. 2(a)) consists of a broad absorption band extending from 250 to 420 nm centered at 280, 345 and 365 nm, which are ascribed to the 4f-5d transitions of  $\text{Eu}^{2+}$ . The broad excitation band implies that this phosphor can be well excited by NUV light matched with the UV-LED chips (360–400 nm) [14].

The emission spectrum (Fig. 2(b)) under the 345 nm excitation shows bright blue luminescence with a peak wavelength at 409 nm with a full width at half maximum (FWHM) of 73 nm. This blue emission band originates from the allowed  $4f5d^1 \rightarrow 4f^7$  electric dipole transition of  $\text{Eu}^{2+}$



**Fig. 1.** The XRD patterns of  $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$  phosphor (a), and JCPDS Card No.16-0640 (b).

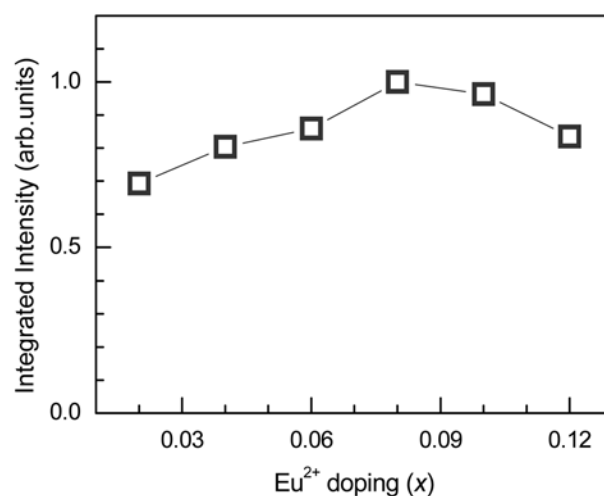


**Fig. 2.** (a) Excitation spectra of the 409 nm emission, and (b) emission spectra of  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.08$ ) under 365 nm excitation at room temperature.

at the  $\text{Ba}^{2+}$  site in the lattice. No emission for  $\text{Eu}^{3+}$  was detected in the spectrum, denoting that  $\text{Eu}^{3+}$  ions in the host were reduced to  $\text{Eu}^{2+}$  completely under the reducing atmosphere.

Fig. 3 shows the concentration dependence of the integrated emission intensity of  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.02, 0.04, 0.06, 0.08, 0.1$  and  $0.12$ ) obtained under the 365 nm-light excitation. The emission intensity increases with increasing  $\text{Eu}^{2+}$ -concentration up to  $x = 0.08$  and then it decreases due to the concentration quenching. The critical quenching concentration ( $\chi_c$ ) of  $\text{Eu}^{2+}$  in  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  is defined to be about 4 mol%. In addition, the band shape and position have no obvious dependence on  $\text{Eu}^{2+}$ -concentration.

It has been suggested that the critical transfer distance ( $R_c$ ) is approximately equal to twice the radius of a sphere



**Fig. 3.** Concentration dependence of the integrated emission intensity of  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.02, 0.04, 0.06, 0.08, 0.1$  and  $0.12$ ) under 365 nm excitation.

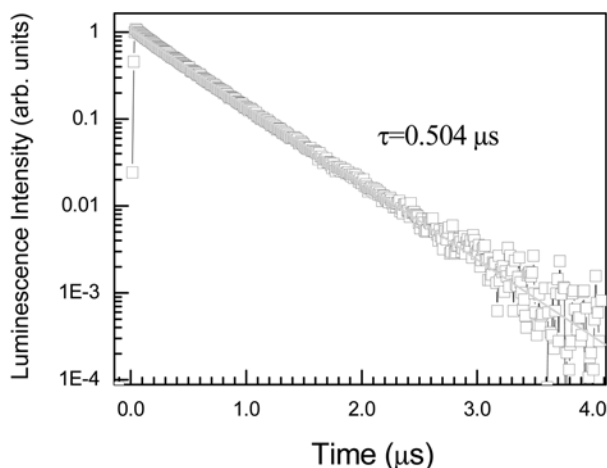
with the volume of the unit cell [15]. The critical distance ( $R_c$ ) between the  $\text{Eu}^{2+}$  ions for energy transfer was calculated using the following equation [16]:

$$R_c \approx 2 \left[ \frac{3V}{4\pi X_c N} \right]^{1/3} \quad (1)$$

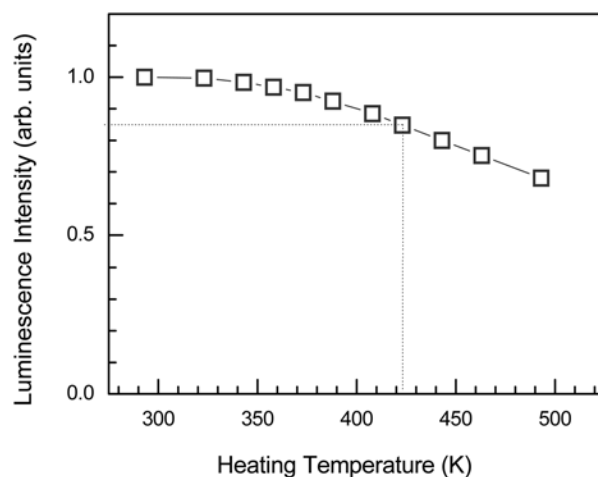
where  $V$  is the volume of the unit cell,  $X_c$  is the critical concentration of the activator ion,  $N$  is the number of formula units per unit cell. By taking the experimental and analytic values of  $V$ ,  $N$  and  $X_c$  ( $497.97 \text{ \AA}^3$ , 2, 0.04, respectively), the critical transfer distance  $\text{Eu}^{2+}$  in  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  host is calculated to be about  $23.5 \text{ \AA}$ . The large value of the critical distance between the  $\text{Eu}^{2+}$  ions has been observed in some mono-phosphate, e.g., the  $R_c$  value of  $\text{Eu}^{2+}$  is  $34 \text{ \AA}$  in a  $\text{KSrPO}_4$  host [10]. This larger value was suggested because of the stiffness of the host matrix due to the tetrahedral network of the phosphate and spectral overlap between the absorption and emission bands [17].

Non-radiative energy transfer often occurs by an exchange interaction, a radiation re-absorption, or a multipole-multipole interaction. The exchange interaction is generally responsible for the energy transfer of forbidden transitions and the typical critical distance is about  $5 \text{ \AA}$  [15]. The mechanism of radiation re-absorption comes into effect only when there is a broad overlap of the emission spectrum of the sensitizer and the excitation spectrum of the activator [18]. In  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  host,  $\text{Eu}^{2+}$  ion shows the allowed  $4f \rightarrow 5d$  transition and there is no overlap between the excitation and emission spectra.

Therefore the exchange and re-absorption interaction cannot be ascribed to the energy transfer of  $\text{Eu}^{2+}$  ions in the  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  host. The energy transfer process should be controlled by the electric multipole-multipole interaction according to Dexter's theory [15]. As shown in Fig. 4 the decay curve of  $\text{Eu}^{2+}$  luminescence is a single exponential with an average decay time of  $0.504 \mu\text{s}$  which is reasonable for isolated  $\text{Eu}^{2+}$  ions in the host lattice. When energy



**Fig. 4.** Decay curve of the  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.08$ ) phosphor. The curve was fitted by a single exponential decay.



**Fig. 5.** Temperature dependence of the integrated emission intensity normalized to the 293 K value of  $\text{Ba}_{2-x}\text{MgP}_4\text{O}_{13} : \text{Eu}_x$  ( $x = 0.08$ ) at different temperatures from 298 to 493 K.

transfer occurs from  $\text{Eu}^{2+}$  ions to defect centers (killer centers) the decay time becomes shorter and the decay curve is nonexponential due to the energy transfer.

In general, the temperature dependence of phosphors used in phosphor conversion W-LEDs is important because it has a great influence on the light output and color rendering index. The phosphors for LEDs must maintain high emission efficiency at high temperature ( $150^\circ\text{C}$ ) for a long term in order to achieve a long lifetime of the LEDs [19]. Thus, a high thermal stability for the phosphors is required. The temperature dependence of luminescence of  $\text{Ba}_{1.92}\text{MgP}_4\text{O}_{13} : \text{Eu}_{0.08}$  phosphor was investigated in the temperature range of 293–493 K.

Fig. 5 represents the temperature dependence of integrated emission intensity normalized to the value at 293 K under the excitation at 365 nm. With an increase in the temperature up to 423 and 493 K, the normalized emission intensity of  $\text{Ba}_{1.92}\text{MgP}_4\text{O}_{13} : \text{Eu}_{0.08}$  decreases from 85 to 68% of the initial value at 293 K, respectively. Wu et al. reported that with increasing temperature from 270 to 450 K the normalized emission intensity of  $\text{Sr}_{0.97}\text{Mg}_2(\text{PO}_4)_2 : \text{Eu}^{2+}_{0.03}$  is decreased to 63% of the initial value at 270 K, whereas 52% for commercially available  $\text{YAG} : \text{Ce}^{3+}$  phosphor [20]. Tang et al. reported that the thermal stability of  $\text{KSr}_{0.995}\text{PO}_4 : \text{Eu}_{0.005}$  is higher than that of commercially available  $\text{YAG} : \text{Ce}$  phosphor [10]. The relative luminescence intensity of  $\text{KSr}_{0.995}\text{PO}_4 : \text{Eu}_{0.005}$  decreases 10% of its initial value at  $150^\circ\text{C}$ . Recently, Li et al. reported that the decrease in emission intensity at  $150^\circ\text{C}$  is 12% for  $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$  [19]. The result in  $\text{Ba}_{1.92}\text{MgP}_4\text{O}_{13} : \text{Eu}_{0.08}$  indicates that the  $\text{Eu}^{2+}$ -doped  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  phosphor is thermally stable for application in W-LEDs.

## Conclusion

$\text{Eu}^{2+}$ -doped  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  phosphors were synthesized by a conventional high-temperature solid-state method

and their luminescence properties were investigated. The synthesized powder has the single-phase crystal structure  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ . The  $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$  phosphor showed the strongest emission intensity when the concentration of  $\text{Eu}^{2+}$  was 0.04 mol%. For a higher doping level above 0.04 mol%, the dipole-dipole interaction might be the major mechanism for concentration quenching. The phosphors are suitable to be excited by an N-UV-emitting LED chip due to their broad excitation band from 250 to 400 nm and an intense emission in blue region. The temperature dependence of phosphors shows the  $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$  have an excellent thermal stability against the temperature quenching effect. The results indicate that  $\text{Ba}_2\text{MgP}_4\text{O}_{13} : \text{Eu}^{2+}$  phosphor could be further investigated for its potential application as a blue component for NUV-based white LEDs.

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