

Sol-gel derived blue-emitting $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ oxide phosphor for ultraviolet emitting diodes

Seung Hwangbo^a, Young-Sun Jeon^b, Bo-An Kang^b, Yu-Sang Kim^c, Kyu-Seog Hwang^b and Jin-Tae Kim^{d,*}

^aDepartment of Electronic & Photonic Engineering, Honam University, 59-1 Seobong-dong, Gwangsan-gu, Gwangju 506-714, Korea

^bDepartment of Biomedical Engineering and Institute of Photoelectronic Technology, Nambu University, 864-1 wolgye-dong, Gwangsan-gu, Gwangju 506-824, Korea

^cKorea Institute of Science and Technology Information, 66 Hoegiro, Dongdaemun-gu, Seoul 130-741, Korea

^dDepartment of Photonic Engineering, College of Engineering, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501-759, Korea

Blue-emitting divalent europium-activated strontium magnesium orthosilicate ($\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$) oxide phosphor was synthesized through a low-temperature chemical solution process using tetraethyl orthosilicate and inorganic salts as starting materials. The transparent sol was preheated at 300 °C for 120 minutes and then the precursor was finally annealed at 900 °C for 240 minutes. Crystallinity, surface morphology and luminescent properties have been investigated. The phosphor emits blue luminescence with a peak wavelength at 457 nm under near-ultraviolet excitation at 365 nm.

Key words: $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$, phosphor, blue.

Introduction

White light-emitting diode (LEDs) offer benefits such as a high luminous efficiency, energy saving, maintenance and environmental protection and, therefore, they are tipped to be the next generation of solid-state lighting (SSL), in the replacement of conventional incandescent and fluorescent lamps. However, white LED with the blue GaN-pumped yellow $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG): Ce^{3+} phosphor has the following problems; the white emitting color changes with input power, a low color rendering index due to two color mixing and low reproducibility due to the strong dependence of white color quality on the amount of phosphor [1, 2]. To overcome these problems, near-UV (350–410 nm) LED plus red-green-blue (RGB) white LEDs have been suggested. This type of white LED has a high tolerance to color variation of a UV chip and an excellent color rendering index. However, the luminescent efficiency is low in this system due to the strong re-absorption of the blue light by the red or green phosphors [3]. The commercially available phosphors for near-UV InGaN-based LEDs are mainly red $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, green $\text{ZnS}:\text{Cu}^+$, Al^{3+} and blue $\text{BaMgAl}_{10}\text{O}_7:\text{Eu}^{2+}$, and these phosphors are unstable under UV irradiation [4]. Optical transitions of divalent europium ($4f-5d$) have been investigated in many phosphors. The spectra of Eu^{2+} -doped components are due to electric dipole transitions with parity allowed so that they occur with high transition

probabilities. The emission colors vary from ultraviolet to red depending on the host lattice. Covalence, the size of the cation, and the crystal-field strength influence the emission color of Eu^{2+} [5, 6]. Alkaline earth silicates are useful luminescent hosts with stable crystal structures and high physical and chemical stability and thus the fluorescence of Eu^{2+} -activated binary and ternary silicates has been studied [5–8]. Although the $\text{SrMgSi}_2\text{O}_8$ host material has excellent photoluminescence properties, less attention had been paid to it in the literature. Furthermore, as far as we know, there is a little information on the solution-based fabrication of $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor.

In this study, a blue-emitting $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor was prepared by a low-temperature chemical solution process. The excitation spectra, emission spectra and crystalline properties were investigated. The morphology of the phosphor was also characterized.

Experimental

The blue phosphor of $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ was prepared using strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], tetraethyl orthosilicate [TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$], and europium nitrate pentahydrate [$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$]. TEOS was dissolved in 20 ml ethanol. Inorganic salts with a stoichiometric molar ratio were dissolved with distilled water. The mixture was stirring vigorously for 5 h at 65 °C. Then, diluted HNO_3 solution was added dropwisely with vigorous stirring at 65 °C for 12 h. The homogeneous solution was preheated at 300 °C for 120 minutes, and then the precursor was finally annealed at 900 °C for 240 minutes in a 5% H_2 -95% N_2 atmosphere.

*Corresponding author:
Tel : +82-62-230-7019
Fax: +82-62-230-7437
E-mail: kimjt@mail.chosun.ac.kr

A sample doped with the optimum doping concentration of 1 mol% Eu^{2+} was tested.

X-ray diffraction (XRD) of the sample was examined on a D-Max-1200 (Rigaku, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The morphology of the sample was measured in a field emission - scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Photoluminescence at room temperature was measured using a fluorescent spectrophotometer (F-4500, Hitachi, Japan).

Results and Discussion

Measurement of XRD of powder sample was performed to verify the phase purity and to check the crystal structure. $\text{Sr}_3\text{MgSi}_2\text{O}_8$ belongs to the orthorhombic crystal system with cell parameters of $a = 5.4 \text{ \AA}$, $b = 9.6 \text{ \AA}$, $c = 7.2 \text{ \AA}$. Fig. 1 shows the XRD pattern of $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor after final annealing at 900°C . Nearly all the peaks can be indexed to the $\text{Sr}_3\text{MgSi}_2\text{O}_8$ phase according to JCPDS file 10-0075. The result indicates that the doping ion, Eu^{2+} had little influence on the crystal structure of the luminescent material, and did not form a new phase during the synthetic process. That is to say, single-phased $\text{Sr}_3\text{MgSi}_2\text{O}_8$ phosphor was obtained by this chemical solution

method at 900°C . The three sites available for incorporating Eu^{2+} in the $\text{Sr}_3\text{MgSi}_2\text{O}_8$ lattice are the Sr^{2+} sites or the Mg^{2+} sites, or the Si^{4+} sites. The ion radius of Mg^{2+} ($0.72 \text{ \AA}$) and Si^{4+} ($0.26 \text{ \AA}$) are too small, but for Sr^{2+} ($1.26 \text{ \AA}$) it is almost equal in size to Eu^{2+} ($1.12 \text{ \AA}$). Therefore, Eu^{2+} ions can only be incorporated into the Sr^{2+} sites. The result in Fig. 1 indicates that a well-crystalline phosphor may be obtained at 900°C in this study. Compared with a solid-state method, the temperature of the preparation is reduced by at least $200\text{--}300^\circ\text{C}$ [5, 6].

In the application of phosphors, the size distribution and shape of the particles are very important. Fig. 2 shows a FE-SEM micrograph of the $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ particles which were thermally treated at 900°C for 240 minutes under a H_2/N_2 atmosphere. The particles were agglomerated and have a pseudo-spherical shape. The phosphor particles grew to achieve diameters of $0.5\text{--}1 \text{ \mu m}$, which is suitable for fabrication of SSL devices. Also, the $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor particles exhibited regular morphological characteristics without any visible admixture of any impurity phases.

The excitation and emission spectra of $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ particles excited by 365 nm near-UV light excitation at room temperature are illustrated in Fig. 3(a) and (b),

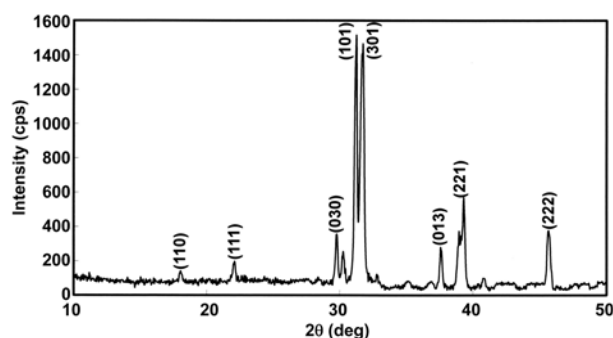


Fig. 1. XRD pattern of $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor after annealing at 900°C .

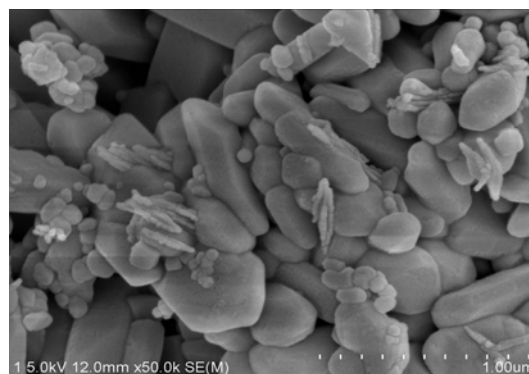


Fig. 2. FE-SEM micrograph of $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor after annealing at 900°C .

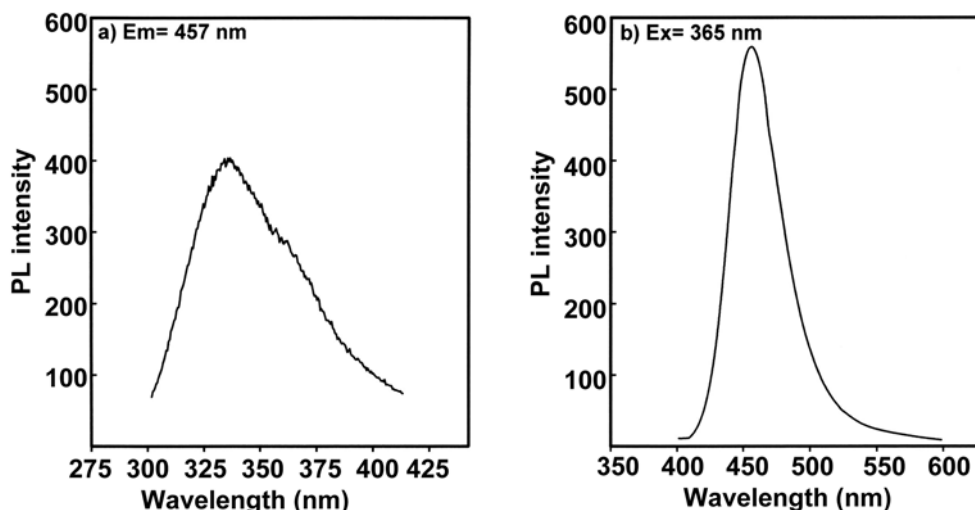


Fig. 3. Excitation and emission spectra of $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ blue phosphor after annealing at 900°C .

respectively. As shown in Fig. 3(a), a broad excitation band appears in the wavelength range of 300–400 nm, which means that this phosphor can be excited well by UV and near UV. Since the host $\text{Sr}_3\text{MgSi}_2\text{O}_8$ shows hardly any absorption between 300–400 nm, the excitation band must originate from the transitions of Eu^{2+} from the $4f^7$ ground state to the $4f^65d^1$ excited state. The $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor shows a broad emission with a maximum at about 457 nm, which can be viewed as the typical emission of Eu^{2+} ascribed to the $4f5d$ transitions. No emission peaks of the Eu^{3+} were observed in this study, indicating that Eu^{3+} ions in the matrix crystal have been reduced to Eu^{2+} completely.

Merwinite [$\text{X}_3\text{MgSi}_2\text{O}_8$ ($\text{X} = \text{Ba}, \text{Sr}, \text{Ca}$)] has a space group $\text{P}_{21/a}$ and has three different X sites in a unit cell: one 12-coordinated X(I) site, two 10-coordinated X(II, III) sites [7]. The bond length (R) of X–O affects the crystal-field strength (D_q) significantly, i.e., D_q is proportional to $1/R^5$ [5]. The weak crystal-field is exerted on the X(I) site with the longest bond length. The Eu^{2+} ions substituted in the X(I) site show a blue emission due to weak crystal field. By contrast a strong crystal-field is exerted on the X(II) and X(III) sites due to the short bond length, resulting in green emission [5].

When the divalent Eu ions ($r_{\text{Eu}^{2+}} = 1.12 \text{ \AA}$) substitute for the large divalent alkaline earth ions, the shifting and broadening in the emission spectra of Eu^{2+} is most pronounced in Ba^{2+} sites, less pronounced in Sr^{2+} sites and least pronounced in Ca^{2+} sites. As previously reported [9, 10], different host structures and crystallographic distortions will influence the crystal field environment of rare earth ions in the host structure. When the rare earth ions substitute the corresponding cations of the hosts, the emission peaks will vary greatly. For example, for a $\text{X}_3\text{MgSi}_2\text{O}_8$ ($\text{X} = \text{Ba}, \text{Sr}, \text{Ca}$) phosphor prepared by a conventional solid-state reaction, the main emission peaks are 439.1, 458.2 and 471.3 nm, respectively [6]. In the $\text{X}_3\text{MgSi}_2\text{O}_8$ ($\text{X} = \text{Ba}, \text{Sr}, \text{Ca}$) hosts, the radius of alkaline earth ions decreases from barium to calcium. In the present study, the main emission wavelength of $\text{X}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor is above that of a $\text{Ca}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor in a previous study [6].

A sol-gel derived Eu^{2+} -activated $\text{Sr}_3\text{MgSi}_2\text{O}_8$ phosphor showing a homogeneous surface and particle shape, which are favorable as regards the luminescent properties because of lesser contamination or fewer dead layers on the phosphor surface, are exceptionally attractive as a near-UV convertible phosphor. Moreover, compared with the solid-state reaction, the temperature of preparation is reduced at least about 200–300 °C.

Conclusions

Using a sol-gel method, a Eu^{2+} -activated single-phase $\text{Sr}_3\text{MgSi}_2\text{O}_8$ blue phosphor was prepared. Well-crystalline particles with a regular shape could be obtained at 900 °C. The excitation spectra show a broad absorption band within the 300–400 nm UV range and this is due to transition from the $4f^7$ ground state of Eu^{2+} to the $4f^65d^1$ excited state. Under 365 nm radiation, the $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ phosphor shows intense and broad blue emission at 457 nm. The $\text{Sr}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ prepared by a sol-gel method can be applied as a blue phosphor for a white LED.

References

1. G. Xia, S. Zhou, J. Zhang and J. Xu, *J. Cryst. Growth* 279 (2005) 357–362.
2. D. Jia, Y. Wang, X. Guo, K. Li, Y. K. Zou and W. Jia, *J. Electrochem. Soc.* 154[1] (2007) J1–J4.
3. C.K. Kang and T.M. Chen, *Appl. Phys. Lett.* 90 (2007) 161901–161903.
4. S. Neeraj, N. Kijima and A. K. Cheetham, *Chem. Phys. Lett.* 387 (2004) 2–6.
5. J.S. Kim, A.K. Kwon, Y.H. Park, J.C. Choi, H.L. Park and G. C. Kim, *J. Luminescence* 122–123 (2007) 583–586.
6. Y. Lin, Z. Tang, Z. Zhang and C.W. Nan, *J. Alloys and Compounds* 348 (2003) 76–79.
7. J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, S.I. Mho and G.C. Kim, *Appl. Phys. Lett.* 84[15] (2004) 2931–2993.
8. W. Pan and G. Ning, *Sensors and Actuators A* 139 (2007) 318–322.
9. Y. Lin, Z. Zhang, Z. Tang, J. Zhang, Z. Zheng and X. Lu, *Mater. Chem. Phys.* 70[2] (2001) 156–159.
10. W.J. Park, M.K. Jung, S.M. Kang, T. Masaki and D.H. Yoon, *J. Chem. & Phys. Solids* 69 (2008) 1505–1508.