Rietveld refinement study on variation of emission wavelength of $(Sr_{1-x},Ca_x)_2MgSi_2O_7:Eu^{2+}$ phosphor for white LED applications

Ki Hyuk Kwon, Won Bin Im, Ho Seong Jang, Hyoung Sun Yoo, and Duk Young Jeon*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

TEL:+82-42-350-3377, e-mail: dyj@kaist.ac.kr (corresponding author)

Keywords : LEDs, silicate phosphor, crystal field effect, rietveld refinement

Abstract

In this study, a blue-emitting $Sr_2MgSi_2O_7:Eu^{2+}$ (SMS) phosphor for white light-emitting diodes is reported. Through transition of 4f→5d in Eu^{2+}, SMS showed a strong blue emission under UV excitation. Additionally, the variation of emission wavelength of SMS is explained by crystal field effect and is supported by rietveld refinement.

1. Introduction

White light emitting diodes (white LEDs) have been used as illumination light source as well as components of display devices because of low power consumption and long life time [1]. Moreover, they have an environment benefit in that they do not use mercury in comparison to fluorescent lamps. Therefore, the white LEDs are expected to enable new concepts in lighting field. Commercial white LEDs are fabricated by combining blue LEDs with yellow-emitting phosphor. This type of white LEDs has some advantages such as simple structure and high brightness. However new type of white LEDs is needed because commercial white LEDs has poor color rendering and most of the phosphors have poor luminescent properties under 450nm excitation. Recently ultra violet LEDs (UV LEDs) combined with red, green and blue phosphor were developed[2]. This type of white LEDs has better color rendering compared with those of commercial white LEDs. So many researchers are researching good candidate phosphors for UV LEDs to develop white LEDs having good properties.

Silicates phosphors are good candidates for UV LEDs because of their high brightness, thermal and chemical stability[3]. In particular $Sr_2MgSi_2O_7$ (SMS) having tetragonal structure is founded to be a good candidate because of its rigid structure. This structure is helpful to be stable against heat occurred during operation of LEDs.

2. Experimental

Powder samples of $(Sr_{1-x},Ca_x)_2MgSi_2O_7:Eu^{2+}$ were prepared by a conventional solid-state reaction method. To synthesize the phosphor samples, $SrCO_3$(Aldrich, 99.9%), $CaCO_3$(Aldrich, 99.9%), MgO(Aldrich, 99.99%), SiO_2(Kojundo, 99.99%) and Eu_2O_3(Aldrich, 99.99%) were used as raw materials. The raw materials were mixed using an agate mortar for 1hour and subsequently heated in a temperature range of 1100°C to 1350°C in a reducing atmosphere of H_2 (5%) and N_2 (95%) for 5 hours.

In order to investigate its luminescent properties, photoluminescence (PL) and photoluminescence excitation (PLE) were characterized with DARSA PRO 5100 PL system (Professional Scientific Instrument Co., Korea) using a xenon lamp (500W) at room temperature. The crystal structures of the samples were investigated by X-ray diffraction (XRD) spectra obtained by a Rigaku diffractometer with Cu K_α radiation (λ=1.54 Å). The shape and size of prepared samples were observed by a Philips XL 30SFEG scanning electron microscope (SEM).

3. Results and discussion

Figure 1 shows the PLE and PL spectra of SMS phosphor under 400nm excitation. As shown in figure 1, SMS phosphor synthesized by solid state reaction has strong absorption band in UV region. So it is beneficial to apply it to the blue phosphor for UV LEDs. The maximum emission peak of SMS phosphor is 470nm. This broad blue emission is due to the transition from t_{2g} to $^8s_{7/2}$ of Eu^{2+} ion.

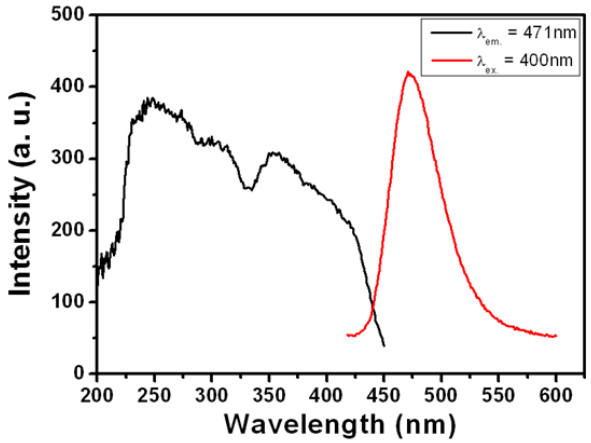
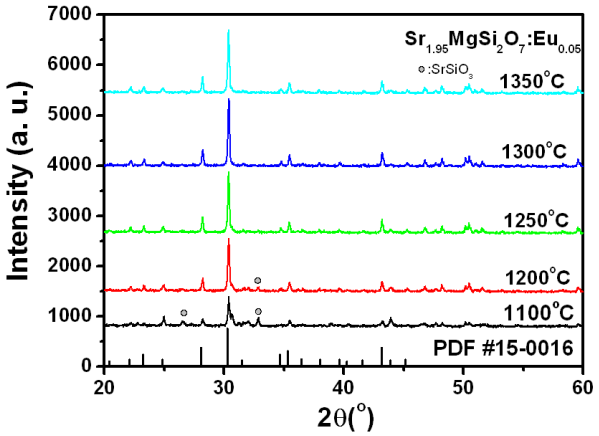


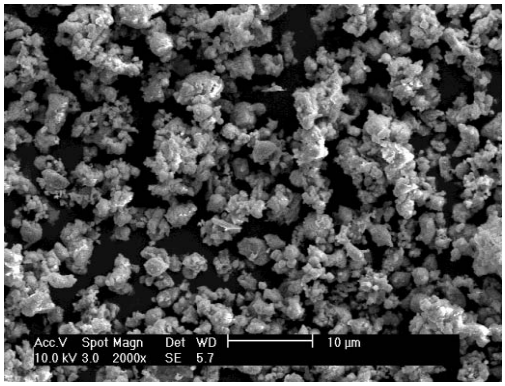
Fig. 1. PLE and PL spectra of SMS phosphor under 400nm excitation

Figure 2 shows the XRD patterns and SEM images of SMS phosphors synthesized under various reaction temperatures. In XRD results, secondary phases such as $SrSiO_3$ appeared below 1300°C. In SEM images, some agglomeration occurred above 1300°C. Consequently SMS phosphors are well synthesized at 1300°C as the optimum reaction temperature and it was confirmed by JCPDS cards.

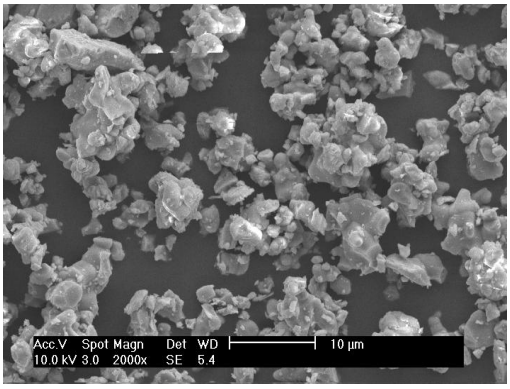
(a)



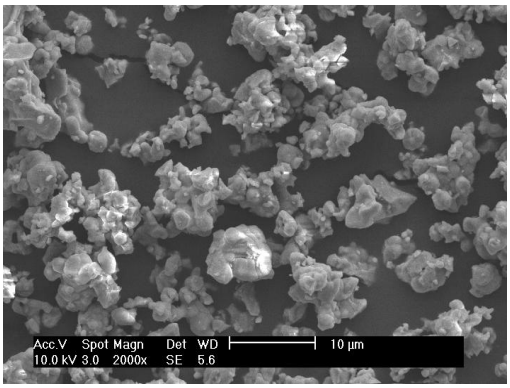
(b)



(c)



(d)



(e)

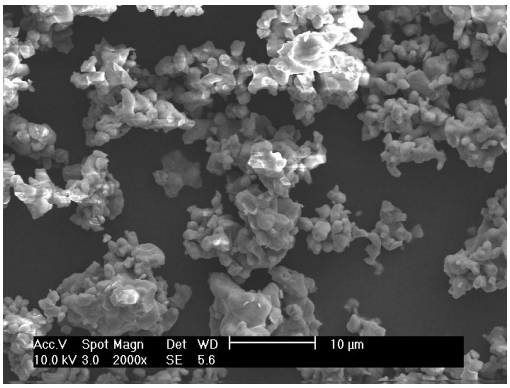


Fig.2. XRD patterns of (a)SMS phosphors synthesized with various reaction temperatures and (b)SEM images of synthesized at 1100°C, (c)1200°C, (d)1250°C and (e)1300°C, respectively

Figure 3 shows the PL spectra of SMS phosphor prepared with various activator concentrations. Eu^{2+} activated SMS phosphor samples were synthesized and Eu concentration has been optimized to obtain strong emission intensity. Blue emission is observed for all compositions of $Sr_{2-x}MgSi_2O_7:Eu_x$(x=0.001-0.09). The emission intensity increases up to x=0.07, beyond which concentration quenching occurs in the SMS host lattice.

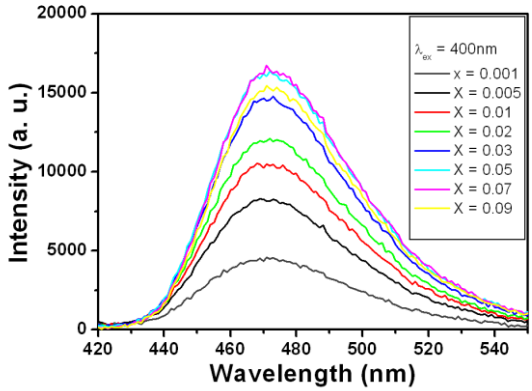
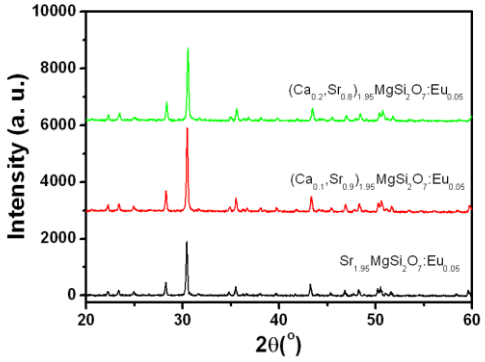


Fig. 3. PL spectra of SMS phosphor prepared with various activator concentrations

Figure 4 shows the XRD patterns and PL spectra of SMS phosphors substituted by Ca ion at the Sr sites. As shown in this figure, when the amount of Ca substitution increase, the XRD peak is moving to the right side. This phenomena indicates that lattice parameters of Ca substituted SMS phosphors are changed. Actually, when small ion substituted for a large site, the emission wavelength moves to shorter wavelength because lattice parameter is smaller than before[4]. For example, the lattice parameters of $Sr_{1.95}MgSi_2O_7:Eu_{0.05}$ phosphor are a=7.9873Å and c=5.1423Å, but the lattice parameters of $(Ca_{0.2},Sr_{0.8})_{1.95}MgSi_2O_7:Eu_{0.05}$ are a=7.9799Å and c=5.0956Å. This result is more accurately demonstrated by rietveld refinement.

(a)



(b)

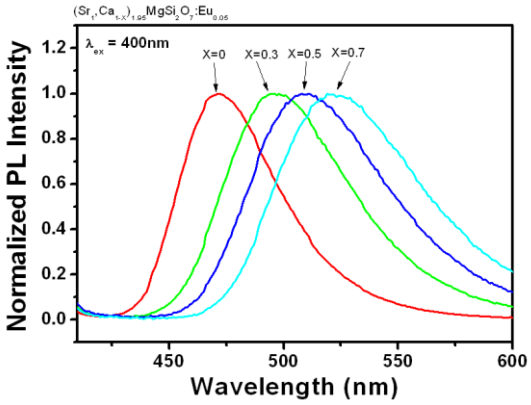


Fig. 4. (a)XRD patterns and (b)PL spectra of SMS phosphors substituted by Ca ion in the Sr sites

Table 1 shows the results of $Ca_2MgSi_2O_7$:Eu(CMS) and SMS phosphors via rietveld refinement. As shown in this result, when Eu substituted for a small site, the distance between a center ion and ligand ions is shorter than the opposite case. This result is well explained by crystal field effect. Crystal field splitting can be calculated by the following equation.

$$Dq = \frac{3Ze2r^4}{5R^4} \quad (1)$$

Where Dq is the crystal field splitting; Z is charge of the ligand, r is mean size of the d electron of a center ion, and R is the distance between a center ion and ligand ions, respectively. If the distance R is small, the emission wavelength is going to the longer wavelength because Dq value become large. This result is well matched with what is described in figure 4.

TABLE 1. results of $Ca_2MgSi_2O_7$:Eu(CMS) and SMS phosphors via rietveld refinement

	Distance(Å)		Distance(Å)
Ca-O	2.482(5)	Sr-O	2.597(9)
	2.465(5)		2.568(9)
	2.704(6)		2.764(7)
	2.705(3)		2.764(7)
	2.418(4)		2.532(6)
	2.703(4)		2.780(6)
	2.703(4)		2.780(6)
	2.418(4)		2.532(6)
Mean distance	2.575	Mean distance	2.665

4. Summary

$(Sr_{1-x},Ca_x)_2MgSi_2O_7:Eu^{2+}$ phosphor for LEDs was well synthesized and the luminescent properties of this phosphor were investigated. $Sr_2MgSi_2O_7:Eu^{2+}$ phosphor showed blue color under 400nm excitation. In addition, this phosphor has strong PL intensity in the UV region. When isovalent ion Ca substituted for the Sr site, the emission wavelength moved to the longer wavelength due to the crystal field effect. This phenomena was confirmed by the results of rietveld refinement.

5. References

1. S. Nakamura and G. Fasol, the Blue laser Diode, Springer, Berlin(1996).
2. Y. Uchda, et. al., Optical Engineering 44(12), 124003 (2005).
3. Fenglan Song, et. al., J. Alloys and Compound, in press (2007).
4. Y. Lin, et. al., Materials Chemistry and Physics 82 (2003).