Journal of the Korean Ceramic Society
Vol. 42, No. 3, pp. 145~149, 2005.

Green Light-Emitting Phosphor, $Ba_{2-x}CaMgSi_2O_8:Eu_x$

Jeong Seog Kim,† Ji Zhe Piao, Jin-Ho Choi, Chae Il Cheon, and Joo Suk Park*

Department of Digital Display, Hoseo University, Chungnam 336-795, Korea
**Functional Materials Research Center, KIER, DaeJeon 305-343, Korea*
(Received November 1, 2004; Accepted December 16, 2004)

ABSTRACT

Eu^{2+}-activated barium magnesium silicate phosphor, $(Ba,Ca)_3MgSi_2O_8:Eu_x$, has been known to emit blue-green light. In this study we report the manufacturing processes for producing either pure green or pure blue light-emitting phosphor from the same composition of $Ba_{2-x}CaMgSi_2O_8:Eu_x$ $(0 < x < 1)$ by controlling heat treatment conditions. Green light emitting phosphor of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ can be produced under the sample preparation condition of highly reducing atmosphere of 23% H_2/77% N_2, while blue or blue-green light emitting phosphor under reducing atmosphere of 5~20% H_2 / 95~80% N_2. The green light-emitting phosphors are prepared in two steps: firing at 800~1000°C for 2~5 h in air then at 1100~1350°C for 2~5 h under reducing atmosphere 23% H_2/77% N_2. The excitation spectrum of the green light-emitting phosphor shows a broadband of 300~410 nm. The emission spectrum has a maximum intensity at the wavelength of about 501 nm. The CIE value of green light emission is (0.162, 0.528). The pure blue light-emitting phosphors can be produced using the $Ba_{2-x}CaMgSi_2O_8:Eu_x$ by introducing additional firing step at 1150~1300°C in air before the final reducing treatment. The XRD analysis shows that the green light-emitting phosphor mainly consisted of $Ba_{1.31}Ca_{0.69}SiO_4$ (JCPDS # 36-1449) and other minor phases i.e., $MgSiO_3$ (JCPDS # 22-0714) and $Ca_2BaMgSi_2O_8$ (JCPDS # 31-0128). The blue light-emitting phosphor mainly consisted of $Ca_2BaMgSi_2O_8$ phase.

Key words : Eu^{2+}, Green, Blue, Light-emitting phosphor, Broadband excitation, Ultraviolet radiation

1. Introduction

High efficiency phosphors of UV (ultraviolet) excitation have been drawn interest for the purpose of producing white light lamp using UV-LED as a possible substitute for blue-LED:YAG. Alkaline earth silicate is one of useful host materials with stable crystal structure and high chemical stability. Therefore, numbers of studies have been made using alkaline earth silicate as host materials[1]: such as $A_3MgSi_2O_8$ (A = Ba, Sr, Ca), $A_2MgSi_2O_7$ (A = Ba, Sr, Ca), A_2SiO_4 (A = Ba, Sr, Ca), and $AMgSi_2O_6$ (A = Sr, Ca).[2,3] Barry *et al.*, studied the Eu^{2+} luminescence in the sub-solidus phase boundary by $Ba_3MgSi_2O_8$, $Sr_3MgSi_2O_8$, and $Ca_3MgSi_2O_8$.[4,5] The emission band becomes narrow and shifts toward short wavelength as the radius of the major alkaline earth ions (Ca, Sr, and Ba) increases. Normally, the phosphorescence of Eu^{2+} in the most of host materials is believed to be caused by the 4f → 5d transitions. Although the 4f electrons of Eu^{2+} are not sensitive to the changes of the crystals field strength due to the shielding effect of outer shell, the 5d electrons can be easily split by the crystal field change. The peak positions in the emission spectra depend strongly on the nature of the Eu^{2+} surroundings that can be changed by either atomic substitutions or crystal structures. Therefore, Eu^{2+} ions can emit different visible lights under the different crystal fields.[6]

Recently the phosphors, $X_{3-y}MgSi_2O_8:yEu^{2+}$ where X comprises at least one of Ba, Ca or Sr have been reported that they emit blue and green lights simultaneously in one sample.[7] The relative intensity between the green and blue light-emission peaks varied with composition. But the blue light was a major emission peak, while the green light was a minor emission peak. In our preliminary study we had found that, in the $X_{3-y}MgSi_2O_8:yEu^{2+}$ (X = Ba, Ca), the relative intensity of green to blue light strongly depends on the heat treatment conditions.[8]

In this study we report the PL (photoluminescence) characteristics of the $Ba_{2-x}CaMgSi_2O_8:Eu_x$ $(0 < x < 1)$ phosphor under varying heat treatment conditions, especially reducing atmosphere and firing temperatures. The dominating factor determining the relative intensity of green/blue light in this phosphor has been clarified. We could attain either pure green light or blue light emitting phosphor by controlling the heat treatment conditions from the same $Ba_2CaMgSi_2O_8:Eu^{2+}$ composition. For the understanding of these PL measurement results we investigated the relation between PL characteristic and crystal phases.

2. Experimental Procedure

The phosphor samples were synthesized by solid state reaction method.[9] The high purity $BaCO_3$, $CaCO_3$, MgO,

†Corresponding author : Jeong Seog Kim
E-mail : kimjungs@office.hoseo.ac.kr
Tel : +82-41-540-5921 Fax : +82-41-540-5345

SiO_2, and Eu_2O_3 powders were used as raw materials. According to the nominal composition of $Ba_{2-x}CaMgSi_2O_8$:Eu_x ($0 < x < 1$) the raw materials were weighed and mixed thoroughly with an appropriate amount of ethanol in an agate mortar and then dried at 80°C for 10 h. Fig. 1 shows the samples preparation routes. Three types of sample preparation routes have been adopted. The first type of route is a generally reported method in the literatures. The samples were calcined at 800~1000°C for 2~5 h in air and then reheated under reducing atmosphere of 5~20% H_2/95~80% N_2 gas mixture at 1100~1350°C for 2~5 h. Using the first type of route, blue-green light emitting phosphor was produced. In the second type of sample preparation route, the reducing atmosphere, i.e. the H_2/N_2 mixture ratio was increased to 23% H_2/77% N_2 with keeping the heat treatment conditions the same as the first route. Green light-emitting phosphor was produced under this condition. In the third type of sample preparation route, the samples were calcined at 900°C for 3 h and then fired at 1250°C for 3 h in air. Finally the reactants were fired at the reducing atmosphere of 5~20% H_2/95~80% N_2 gas mixture at 1100~1350°C for 2~5 h. Pure blue light-emitting phosphor could be produced from this route. The PL spectra of the sample were obtained using a Perkin Elmer LS55 fluorescent spectrophotometer. XRD diffraction study has been carried out for the phase analysis.[10-12]

3. Results and Discussion

The PL spectra of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ prepared by the first preparation route [Fig. 1(a)] are shown in Fig. 2. The samples show both blue and green light emission simultaneously. The sample preparation method of Fig. 1(a) is a very typical procedure that has been adopted in the most of the literatures. In the previous study by Park and Kim, the $X_{3-y}MgSi_2O_8:yEu^{2+}$ (X = Ba, Ca or Sr) phosphor also showed the blue and green lights simultaneously in one sample[7] in accordance to our study.

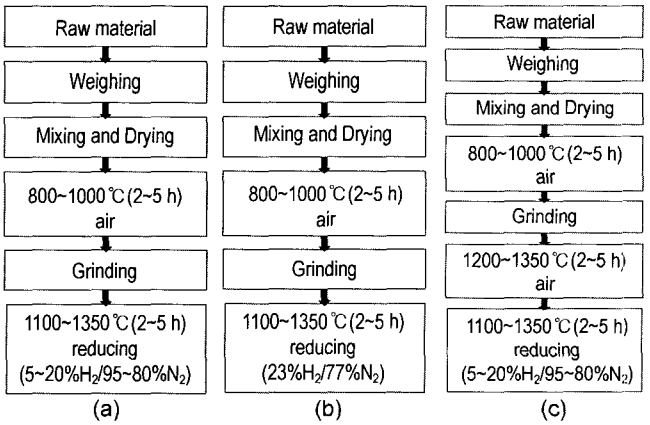

Fig. 1. Three types of sample preparation routes for (a) blue-green light emitting phosphor, (b) green light-emitting phosphor, and (c) blue light-emitting phosphor.

The PL spectra of the $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor prepared by the second route [Fig. 1(b)] are shown in Fig. 3. The H_2/N_2 mixture ratio in the reducing atmosphere has been increased to 23%/77% compared to the 5~20% H_2/95~80% N_2 in the first route. As can be seen in Fig. 3 compared with Fig. 2, the H_2/N_2 ratio in the reducing atmosphere is very important for producing pure green light-emitting phosphor. The temperature of reducing atmosphere could be also an important factor for refining PL characteristic of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor to pure green light emission. The main emission peak wavelength is about 501 nm. However, the emission intensities have been changed by heat treatment conditions, especially reducing atmosphere and calcination temperatures: the higher calcination temperature before reducing treatment, the higher

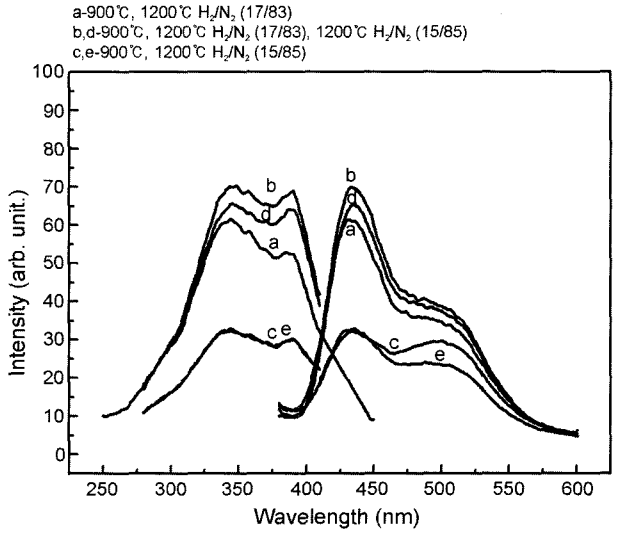

Fig. 2. PL spectra of blue-green light emitting phosphor, $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$.

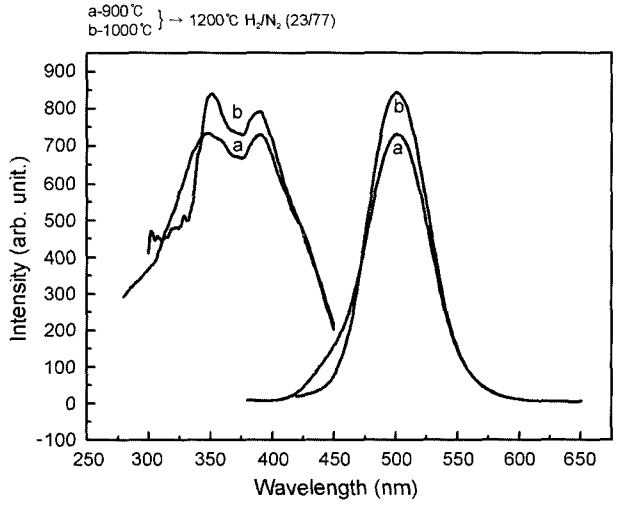

Fig. 3. PL spectra of green light emitting phosphors, $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ prepared under reducing atmosphere of 23% H_2/77% N_2.

emission intensity by final firing at the same reducing atmosphere.

The PL spectra for pure green light-emitting $Ba_{2-x}CaMgSi_2O_8:Eu_x$ phosphor with the variation of Eu content are presented in Fig. 4. The samples have been prepared through two steps: firing at 1000°C for 3 h in air and then firing at 1200°C for 3 h under reducing atmosphere (23% H_2/77% H_2). The excitation spectra show a broadband absorption from 300 nm to 410 nm. The emission intensity reaches to a maximum at x = 0.07 and then diminishes with further increasing Eu content. The main emission peak at 501 nm can be attributed to $^5D_2$-$^7F_2$ transition of Eu^{2+} ions and ascribed to an impurity trapped exciton emission. The emission spectrum of the Eu^{2+} ions depends on the host lattice, the size of cation and the strength of the crystal field and covalency and so on.[3]

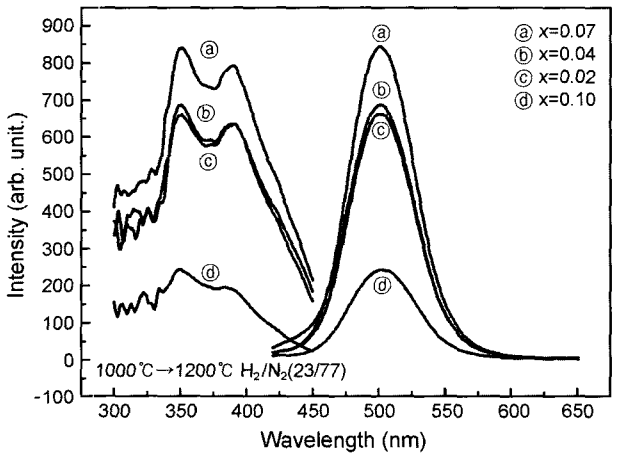

Fig. 4. PL spectra of green light emitting phosphors, $Ba_{2-x}CaMgSi_2O_8:Eu_x$ with the variation of Eu contents. Samples are prepared through two steps: firing at 1000°C for 3 h in air then at 1200°C for 3 h under reducing atmosphere of 23% H_2/77% N_2.

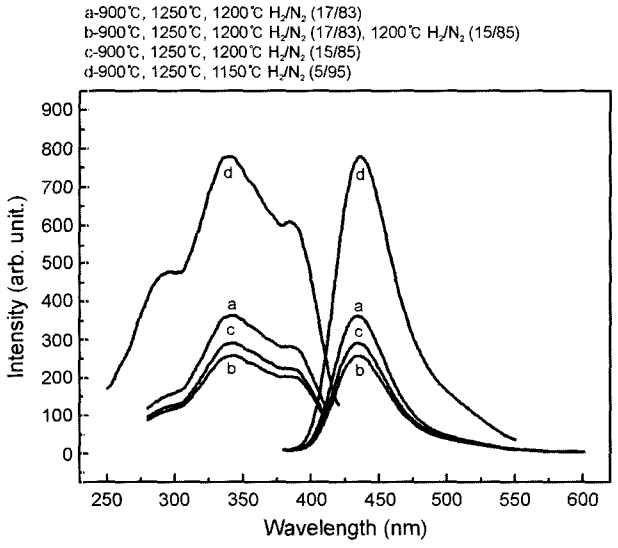

Fig. 5. PL spectra of blue light-emitting phosphors with the composition of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ prepared by varying the H_2/N_2 ratio (Reducing treatment was given twice for the sample b).

The PL spectra of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ prepared by the third type of sample preparation route [Fig. 1(c)] are shown in Fig. 5. The characteristic feature of this sample preparation route is the introduction of an additional firing step in air at 1200~1350°C before the final reducing heat treatment under gas mixture of 5~20% H_2/95~80% N_2 at 1100~1350°C. As can be seen in Fig. 5, the $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphors prepared by this procedure emit pure blue light. The excitation spectra show a broadband from 300 nm to 410 nm and the emission spectra also show a broadband from 400 nm to 600 nm. The main emission peak wavelength is about 443 nm. It can be ascribed to $4f^7$-$4f^65d$ interconfiguration transitions of Eu^{2+} ions. There are no other emission peaks. This indicates that Eu^{3+} has been completely reduced to Eu^{2+} in the host phase.[13-15] The relative emission intensities are varied with heat treatment conditions, especially reducing atmosphere and temperatures. The sample d prepared under the gas mixture of 5% H_2/95% N_2 shows the highest emission intensity. The above results indicate that the PL characteristics of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor can be refined from pure green light-emission to pure blue light-emission by controlling the heat treatment procedure and reducing atmosphere.

The CIE color coordinates in chromaticity diagram of the pure green and pure blue light-emitting phosphors of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ are shown in Fig. 6. The CIE coordinates of the green light-emitting phosphor (sample a in Fig. 3) is x = 0.162 and y = 0.528. The CIE coordinates of pure blue light (sample a in Fig. 4) is x = 0.200 and y = 0.275.

The XRD patterns of the four types of phosphors are shown in Fig. 7. Pattern A is for the $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ sample fired in air at 1250°C at the final preparation step, which does not emit any light. Pattern B is for the green light-emitting $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor prepared by

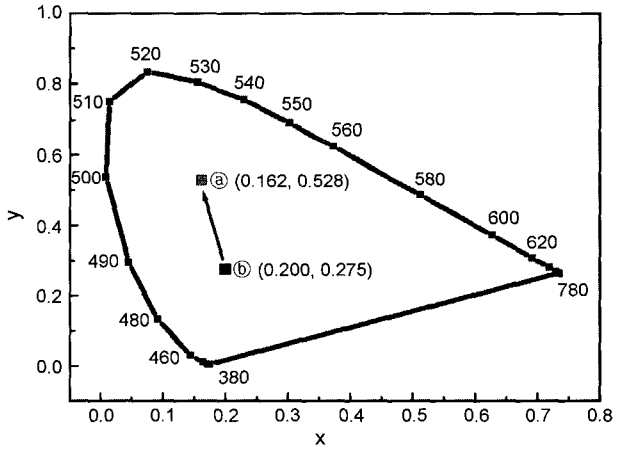

Fig. 6. CIE chromaticity diagram of the green (sample a in Fig. 3) and blue light-emitting phosphors (sample a in Fig. 4).

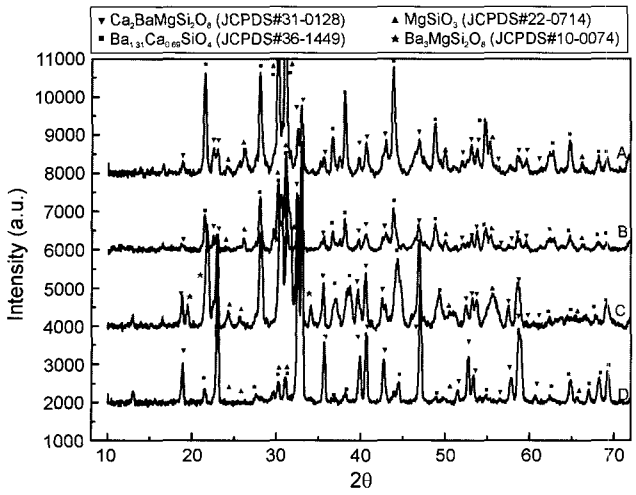

Fig. 7. The XRD patterns for four types of samples.
A : $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ (900°C, 1250°C in air)
B : $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ (900°C, 1200°C under 23% H_2/77% N_2)
C : $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ (900°C, 1250°C in air, 1150°C under 5% H_2/95% N_2)
D : $Ba_{0.94}Ca_2MgSi_2O_8:Eu_{0.06}$ (900°C, 1250°C in air, 1200°C under 5% H_2/95% N_2)

the route b in Fig. 1. Pattern C is for the blue light-emitting $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor prepared by the route c of Fig. 1. Pattern D is for the blue light-emitting $Ba_{0.94}Ca_2MgSi_2O_8:Eu_{0.06}$ phosphor prepared by the route c in Fig. 1. The results of XRD pattern analysis are summarized in Table 1. The pattern A can be indexed consisting of the three phases: $Ba_{1.31}Ca_{0.69}SiO_4$ (JCPDS # 36-1449), $MgSiO_3$ (JCPDS # 22-0714), and $Ca_2BaMgSi_2O_8$ (JCPDS # 31-0128) (in the order of relative peak intensity). The pattern B appears to be the same as that of the pattern A. The pattern C consists of four phases: $Ca_2BaMgSi_2O_8$, $Ba_{1.31}Ca_{0.69}SiO_4$, $Ba_3MgSi_2O_8$ (JCPDS # 10-0074) and $MgSiO_3$. The pattern D consists of the three phases: $Ca_2BaMgSi_2O_8$, $Ba_{1.31}Ca_{0.69}SiO_4$, and $MgSiO_3$.

The relation between the PL characteristics and the crystal phases consisting the phosphors can be deduced based on the XRD analysis results. The blue light-emitting phosphors (sample C and D) are mainly consisted of $Ca_2BaMgSi_2O_8$. On the while, the pure green light emitting phosphor (sample B) is mainly consisted of $Ba_{1.31}Ca_{0.69}SiO_4$. The variation of PL characteristics with H_2/N_2 ratio and sample preparation routes can be ascribed to the change of crystal phases produced in the phosphors.

4. Conclusion

The PL characteristics of $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ phosphor can be refined from blue-green light emission to either pure green light-emission or pure blue light-emission by controlling the heat treatment procedures and H_2/N_2 ratio in the reducing atmosphere. The pure green light-emitting $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ can be prepared under the highly reducing atmosphere of 23% H_2/77% N_2 mixture. The green light-emitting phosphor can be prepared in two steps : firing at 800~1000°C for 2~5 h in air then at 1100~1350°C for 2~5 h under reducing atmosphere of 23% H_2/77% N_2. The excitation spectrum of the green light-emitting phosphor shows a broadband (300~410 nm). The emission spectrum shows maximum intensity at the wavelength of about 501 nm. The blue light-emitting phosphor, $Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ can be obtained when an additional firing step in air at the temperature range of 1200~1350°C is introduced before the final reducing treatment. The variation of the PL characteristic by the sample manufacturing route can be ascribed to the variation of crystal phases consisting the phosphors. The blue light-emitting phosphors are mainly consisted of $Ca_2BaMgSi_2O_8$ (JCPDS # 31-0128) phase, while the green light emitting phosphor is mainly consisted of $Ba_{1.31}Ca_{0.69}SiO_4$ (JCPDS # 36-1449).

Acknowledgement

This study was financially supported by Hoseo SERC (RRC supported by KOSEF).

REFERENCES

1. Y. H. Lin, Z. L. Tang, Z. T. Zhang, and C. W. Nan, "Luminescence of Eu^{2+} and Dy^{3+} Activated $R_3MgSi_2O_8$-Based (R=Ca,Sr,Ba) Phosphors," *J. Alloy. Comp.*, **348** 76-9 (2003).
2. A. M. Srivastava, "White Light Emitting Phosphor Blends for LED Divices," U.S. Patent 6621211 (2003).
3. S. H. M. Poort and G. Blasse, "The Influence of the Host Lattice on the Luminescence of Divalent Europium," *J. Lumin.*, **247** 72-4 (1997).
4. Y. H. Lin, Z. L. Tang, Z. T. Zhang, X. X. Wang, J. Y. Zhang, and Z. S. Zheng, "Luminescent Properties of a New Long Afterglow Eu^{2+} and Dy^{3+} Activated $Ca_3MgSi_2O_8$ Phosphor," *J. Eur. Ceram. Soc.*, **21** 683-85 (2001).
5. S. H. M. Poort, H. M. Rejinhoudt, H. O. T van der Kuip, and G. Blasse, "Luminescence of Eu^{2+} in Silicate Host Lattices

Table 1. Summary of XRD Phase Analysis Results of Fig. 7 (Strong, Medium, and Weak Represent the Relative Peak Intensity of Each Phase in the XRD Patterns)

Sample \ Phase	$Ba_{1.31}Ca_{0.69}SiO_4$	$Ca_2BaMgSi_2O_8$	$MgSiO_3$	$Ba_3MgSi_2O_8$
$Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ green emission (B)	strong	weak	medium	–
$Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ no emission (A)	strong	weak	medium	–
$Ba_{1.9}CaMgSi_2O_8:Eu_{0.1}$ blue emission (C)	medium	strong	very weak	weak
$Ba_{0.94}Ca_2MgSi_2O_8:Eu_{0.06}$ blue emission (D)	very weak	strong	weak	–

with Alkaline Earth Ions in a Row," *J. Alloy. Comp.*, **241** 75-81 (1996).
6. Y. H. Lin, C. W. Nan, X. S. Zhou, J. B. Wu, H. F. Wang, D. P. Chen, and S. M. Xu, "Preparation and Characterization of Long Afterglow $M_2MgSi_2O_7$-Based (M:Ca,Sr,Ba) Photoluminescent Phosphors," *Mater. Chem. Phys.*, **82** 860-63 (2003).
7. H. L. Park and J. S. Kim, "White-Light-Emitting Device Fabricated with a Mixture Phosphors," Korea Patent 10-0425749 (2004).
8. A. M. Srivastava, "Phosphor for Down Converting Ultraviolet Light of LEDs to Blue-Green Light," U.S. Patent 6555958 (2003).
9. K. J. Choi, J. K. Park, K. N. Kim, C. H. Kim, and H. K. Kim, "Luminescence Characteristics of $Sr_3MgSi_2O_8$:Eu Blue Phosphor for Light Emitting Diodes," *J. Kor. Ceram. Soc.*, **41** [2] 573-77 (2004).
10. S. H. M. Poort, W. Janssen, and G. Blasse, "Optical Properties of Eu^{2+}-Activated Orthosilicates and Orthophosphates," *J. Alloy. Comp.*, **260** 93-7 (1997).
11. S. Ekambaram and K. C. Patil, "Synthesis and Properties of Eu^{2+} Activated Blue Phosphors," *J. Alloy. Comp.*, **248** 7-12 (1997).
12. L. H. Huang, X. Zhang, and X. R. Liu, "Studies on Luminescence Properties and Crystallographic Sites of Ce^{3+} in $Ca_3MgSi_2O_8$," *J. Alloy. Comp.*, **305** 14-6 (2000).
13. L. Jiang, C. K. Chang, D. L. Mao, and C. L. Feng, "Concentration Quenching of Eu^{2+} in $Ca_2MgSi_2O_7$:Eu^{2+} Phosphor," *Mater. Sci. Eng.*, **B103** 271-75 (2003).
14. K. N. Kim, H. K. Jung, H. D. Park, and D. J. Kim, "High Luminance of New Green Emitting Phosphor Mg_2SnO_4: Mn," *J. Lumin.*, **99** 169-73 (2002).
15. G. Blasse and B. C. Grabmaier, "Luminescent Materials," **Ch2** and **Ch3**, *Spinger-Verlag*, Berlin (1994).