Luminescent Properties of (Ba,Sr)$MgAl_{10}O_{17}$:Mn,Eu Green Phosphor Prepared by Spray Pyrolysis under VUV Excitation

Kyeong Youl Jung,*,† Hyun Woo Lee,†,|| Yun Chan Kang,‡ Seung Bin Park,§ and Young Suk Yang||

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong-gu, Daejeon 305-600, Republic of Korea, Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea, Department of Chemical Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea, and Department of Chemical Engineering, Woosuk University, 490 Hujung-ri, Samrae-up, Wanju-gun, Jeonbuk 565-701, Republic of Korea

Received January 13, 2005. Revised Manuscript Received March 15, 2005

$BaMgAl_{10}O_{17}$:Mn phosphor particles with a spherical shape and fine size of less than 1 μm were prepared by spray pyrolysis, and their luminescence properties under vacuum ultraviolet (VUV) excitation were investigated by changing the concentration of activators and the composition of host matrix. It was found that by substituting Sr for Ba sites in the conduction layers the excitation efficiency at wavelengths shorter than 160 nm is enhanced. As a result, the photoluminescence intensity of $BaMgAl_{10}O_{17}$:Mn phosphor increases under VUV excitation (147 nm) without any shift in the peak position of the emission spectrum. The photoluminescence intensity of (Ba,Sr)$MgAl_{10}O_{17}$:Mn phosphor was also additionally improved by codoping Eu^{2+} ions as a consequence of the energy transfer from Eu^{2+} in the conduction layer to Mn^{2+} in the spinel block. Finally, the highest photoluminescence intensity achieved when 40 at. % of Ba was replaced with Sr and 0.1 at. % Eu was codoped was about 20% higher than that of commercial $BaMgAl_{10}O_{17}$:Mn phosphor prepared by a conventional solid-state route.

Introduction

Phosphors are widely used in plasma display panels (PDPs), field emission displays (FEDs), and fluorescence lamps.[1−3] Among these, PDPs are recognized as the technology with the most potential for realization of a home theater or a large-screen wall-attached TV. The brightness and the lifetime of PDPs depend strongly on the quality of phosphors. Therefore, much attention has been paid to the development of good phosphor materials. For PDP applications, phosphors should efficiently absorb the vacuum ultraviolet (VUV) light coming from the resonance radiation line of Xe atoms (147 nm) and from the excited state of molecular Xe (172 nm). $BaMgAl_{10}O_{17}$ (BAM) has been used as an excellent host matrix for blue and green phosphor.[4−6] For example, Eu^{2+}-doped BAM phosphor is a representative blue phosphor for PDPs because it has a deep blue color, a short decay time, and a high VUV efficiency. Now, Zn_2SiO_4:Mn has been mostly used as a green phosphor in PDPs. Zn_2SiO_4:Mn phosphor, however, is known to have a long decay time and a high discharging voltage.[7] Thus, YBO_3:Tb and $BaAl_{12}O_{19}$:Mn or $BaMgAl_{10}O_{17}$:Mn phosphors are additionally necessary to optimize the luminance property of PDPs.[8,9]

The unit cell size of the PDPs is gradually becoming smaller for the fabrication of a high-defined TV. Phosphors with a spherical shape and a fine size less than 1 μm thus are required because the process for making a uniform phosphor layer in narrow barrier ribs strongly depends on these physical properties. In addition, the brightness of fine-sized phosphor particles should be much more improved to improve the small unit-cell efficiency. Accordingly, the preparation of spherical phosphor particles with a fine size and a high brightness has received much attention.[10−13] Thus far, commercialized PDP phosphors have been prepared using the solid-state reaction route which generally involves a repetitive heat treatment at high temperature and a post-milling process to obtain high crystalline powder. As a result, most commercial phosphor particles have an irregular shape and a large size of about 2−5 μm.

---

* To whom correspondence should be addressed. E-mail: kyjung@krict.re.kr. Tel: +82-42-860-7372. Fax: +82-42-861-4245.
† Korea Research Institute of Chemical Technology.
‡ Konkuk University.
§ Korea Advanced Institute of Science and Technology.
|| Woosuk University.

(1) Ronda, C. R. *J. Alloys Comp.* **1995**, *225*, 534.
(2) Kim, C.-H.; Kwon, I.-E.; Park, C.-H.; Hwang, Y.-J.; Bae H.-S.; Yu, B.-Y.; Pyun, C.-Y.; Hong, G.-Y. *J. Alloys Comp*. **2000**, *311*, 33.
(3) Talin, A. A.; Dean, K. A.; Jaskie, J. E. *Solid-State Electron*. **2001**, *45*, 963.
(4) Kim, K.-B.; Kim, Y.-I.; Chun, H.-G.; Cho, T.-Y.; Jung, J.-S.; Kang, J.-G. *Chem. Mater.* **2002**, *14*, 5045.
(5) Zhang, J.; Zhang, Z.; Tang, Z.; Yao, Y.; Long, X. *Chem. Mater*. **2002**, *14*, 3005.
(6) Yang, P.; Yao, G.-Q.; Lin, J.-H. *Opt. Mater*. **2004**, *26*, 327.
(7) Lu, S. W.; Copeland, T.; Lee, B. I.; Tong, W.; Wagner, B. K.; Park, W.; Zhang, F. *J. Phys. Chem. Solids* **2001**, *62*, 777.
(8) Kwon, I.-E.; Yu, B.-Y.; Hea, H.; Hwang, Y.-J.; Kwon, T.-W.; Kim, C.-H.; Pyun, C.-H.; Kim, S.-J. *J. Lumin.* **2000**, 87−89, 1039.
(9) Lee, D. Y.; Kang, Y. C.; Park, H. D.; Ryu, S. K. *J. Alloys Compd.* **2003**, *353*, 252.
(10) Jung, K. Y.; Kang, Y. C. *Mater. Lett*. **2004**, *58*, 2165.
(11) Jung, K. Y.; Lee, D. Y.; Kang, Y. C.; Park, H. D. *J. Lumin*. **2003**, *105*, 127.
(12) Kang, Y. C.; Park, S. B.; Lenggoro, I. W.; Okuyama, K. *J. Phys. Chem. Solids* **1999**, *60*, 379.
(13) Lenggoro, I. W.; Xia, B.; Mizushima, H.; Okuyama, K.; Kijima, N. *Mater. Lett.* **2001**, *50*, 92.

10.1021/cm050074f CCC: $30.25

The spray pyrolysis is a gas-phase synthesis process and has been used to prepare spherical-shaped phosphor particles because the process has no repetitive heat treatment and easily produces phosphor particles with high phase purity.[10−14] In this work, (Ba,Sr)$MgAl_{10}O_{17}$:Mn,Eu phosphor particles with a fine size of less than 1 μm and spherical shape were synthesized by the spray pyrolysis. The photoluminescence characteristics of (Ba,Sr)$MgAl_{10}O_{17}$:Mn,Eu particles under VUV characteristics were systematically studied by changing the ratio of Ba to Sr and the concentration of Mn or Eu.

Experimental Section

(Ba,Sr)$MgAl_{10}O_{17}$:Mn^{2+},Eu^{2+} particles were prepared by an ultrasonic spray pyrolysis process. An ultrasonic aerosol generator with six vibrators (1.7 MHz) was used to atomize the precursor solution to form droplets that were carried by the air (45 L/min) in a hot furnace with a quartz tube (length, 1200 mm; inner diameter, 50 mm). The reactor temperature was maintained at 900 °C. The formed particles were collected by a Teflon bag filter.

A general nitrate spray solution was prepared by dissolving barium, magnesium, manganese, europium, and aluminum nitrate into purified water. The total salt concentration was maintained at 0.7 M, and the doping concentration (y) of Mn was varied from 0.01 to 0.4 mol. The ratio (x) of Sr to Ba in $(Ba_{1-x},Sr_x)_{1-z}Mg_{1-y}Al_{10}O_{17}$:$Mn_y$,$Eu_z$ phosphor particles was changed from 0 to 1.0 mol, and the concentration (z) of Eu^{2+} codopant was varied from 0 to 0.01 mol.

The morphology of (Ba,Sr)$MgAl_{10}O_{17}$:Mn^{2+},Eu^{2+} phosphor particles was controlled by changing the property of precursor solution. To do this, NH_4OH was slowly added into the nitrate solution prepared above. Then, the aluminum hydroxide molecules which are a majority element in the precursor solution are changed to polycations $(Al_x(OH)_y(H_2O)_z)^{3x-y}$, wherein the x and y values depend on the concentration of aluminum hydroxide and pH of solution (4.2−4.4 in this work).[15]

The as-prepared phosphor particles were post-treated at 1400 °C for 2 h under a reducing atmosphere (5% H_2/N_2 mixture gas) for crystallization and activation of divalent manganese and europium. The crystal phase of the prepared phosphors was analyzed by an X-ray diffraction pattern measured by diffractometry (RIGAKU DMAX-33). The morphology was observed by scanning electron microscopy (SEM, Philips XL 30S FEG). The photoluminescence spectra were measured under illumination of VUV light emitted from a deuterium lamp (147 nm). The excitation spectra were measured in the wavelength range from 125 to 350 nm using sodium salicylate powder as a reference.

Results and Discussion

The phase purity of phosphor greatly affects the luminous efficiency. Phosphor particles with higher phase purity have higher luminous efficiency. Figure 1 shows XRD patterns of commercial and prepared $BaMgAl_{10}O_{17}$:Mn particles with a change in the post-treatment temperature. When the post-treatment temperature was below 1000 °C, the prepared BAM:Mn particles had an amorphous phase. The crystallization begins at 1100 °C, and the crystallinity was gradually increased up to 1400 °C. The prepared and commercial BAM:Mn samples had a pure $BaMgAl_{10}O_{17}$ phase (JCPDS No. 26-0163) consisting of two spinel blocks ($MgAl_{10}O_{16}$) and one conduction layer (BaO). So, it was confirmed that the BAM:Mn particles prepared by the spray pyrolysis had pure BAM phase with no impurities.

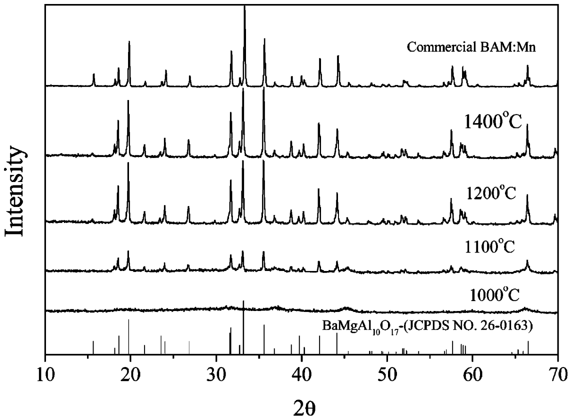

Figure 1. XRD patterns of prepared $BaMgAl_{10}O_{17}$:Mn particles and the commercial ones.

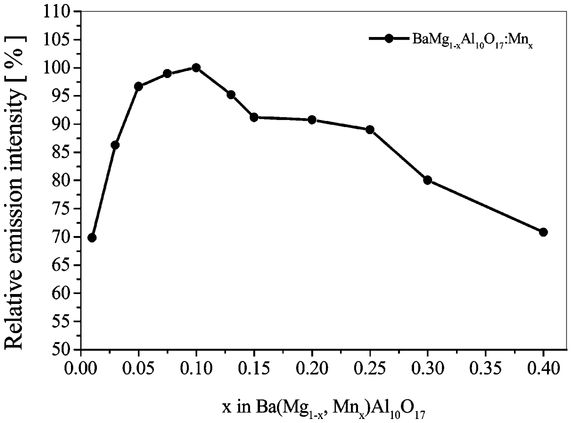

Figure 2. Relative emission intensity of $BaMgAl_{10}O_{17}$:Mn as a function of Mn concentration.

In Eu^{2+}-doped $BaMgAl_{10}O_{17}$ phosphor, Eu^{2+} ions are substituted for Ba^{2+} sites in the conduction layer. Mn ions, however, are incorporated into the spinel blocks ($MgAl_{10}O_{16}$) instead of the conduction layer (BaO) of BAM because the ionic radius (0.091 nm) of Mn^{2+} is close to that of Mg^{2+} (0.078 nm) rather than Ba^{2+} (0.143 nm).[18] In general, the photoluminescence is quenched by increasing the concentration of activators. So, it is necessary to experimentally find the critical concentration of Mn^{2+} in terms of optimizing the luminous efficiency of BAM:Mn under the VUV excitation. The emission intensity of BAM:Mn particles was monitored under VUV (147 nm) excitation with varying the Mn^{2+} concentration and shown in Figure 2. The concentration quenching was observed when the Mn content (x) was 0.1. At this critical Mn concentration (10 at. % of Mg), the photoluminescence spectra of prepared samples were compared with the commercial green phosphors in Figure 3. It is well known that the photoluminescence process of Mn-doped phosphors is characterized by the transition of $3d^5$

---

(14) Vanheusden, K.; Seager, C. H.; Warren, W. L.; Tallant, D. R.; Caruso, J.; Hampden-Smith, M. J.; Kodas, T. T. *J. Lumin.* **1997**, *75*, 11.

(15) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Express, 1990.

(16) Stevels, A. L. N.; Vink, A. T. *J. Lumin.* **1974**, *8*, 443.

(17) Robbins, D. J.; Mendez, E. E.; Giess, E. A.; Chang, I. F. *J. Electrochem. Soc.* **1984**, *131*, 141.

(18) Yang, P.; Yao, G.-Q.; Lin J.-H. *Opt. Mater.* **2004**, *26*, 327.

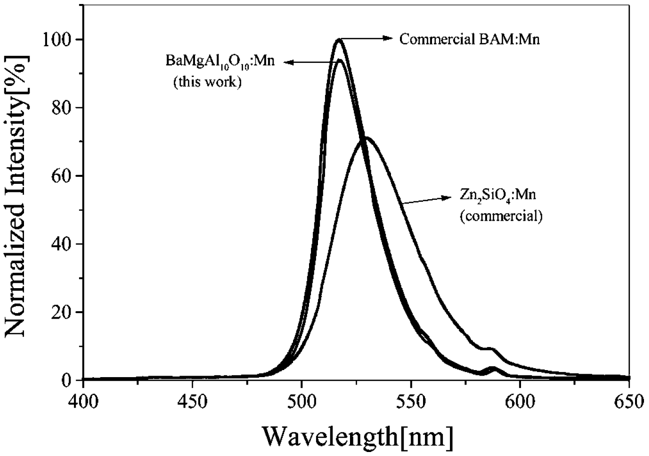

Figure 3. Emission spectra obtained by VUV (147 nm) excitation for the prepared BaMgAl$_{10}$O$_{17}$:Mn$_{0.1}$ particles and the commercial Zn$_2$SiO$_4$:Mn and BAM:Mn particles.

electrons in Mn ion as an activation center. The transition of $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ is responsible for the green emission of BaMgAl$_{10}$O$_{17}$:Mn and Zn$_2$SiO$_4$:Mn phosphors.[16−18] The emission intensity of the lab-made BaMgAl$_{10}$O$_{17}$:Mn phosphors is higher than that of the commercial Zn$_2$SiO$_4$:Mn phosphor (KASEI OPTONIX) but lower than that of the commercial BAM:Mn phosphor (SAMSEUNG SDI). To enhance the low luminescence intensity of prepared BAM:Mn particles compared with the commercial ones, in this work, it was tried to control the morphology and optimize the host composition.

The morphology of phosphor particles affects the luminous property.[19,20] It was reported that the phosphor particles with spherical shape and dense structure have better luminescence intensity than the hollow ones, especially when they were prepared by the spray pyrolysis.[19] In the spray pyrolysis using the nitrate aqueous solution, hollow-structured particles are usually formed because the precipitation of ingredients begins at the surface of droplets passing through the hot furnace. In the previous study on the BAM:Eu blue phosphor, we developed a new solution technique that successfully made it possible to prepare spherical-shaped and dense-structured BAM particles by the spray pyrolysis.[11,19] In this work, the same solution technique was applied to prepare BAM:Mn in order to improve the luminescence intensity under the VUV excitation. Figure 4 shows the SEM photos of prepared and commercial BAM:Mn particles. The lab-made samples were post-treated at 1400 °C for 3 h under the reduction atmosphere. In general, BAM phosphor has a plate-shaped morphology due to its crystallographic characteristic as shown in Figure 4. The BAM:Mn particles prepared by the spray pyrolysis with the polycation solution have a completely spherical shape, whereas the particles prepared with the nitrate solution have a hollow structure and some parts burst to fragments. Figure 5 shows the photoluminescence spectra of prepared BAM:Mn particles. The dense and spherical particles prepared from the polycation solution had about 8% improved photoluminescence compared with the hollow particles. From this result, we confirmed that to make phosphor particles to have a spherical shape and a dense structure rather than hollow and irregular-shape ones clearly improves the luminescence of phosphor particles. The relative intensity of the spherical BAM:Mn particles prepared, however, was still lower than that of the commercial ones. So, in this work, the host composition was changed and Eu^{2+} was codoped in order to further improve the luminescence intensity of BAM:Mn phosphor.

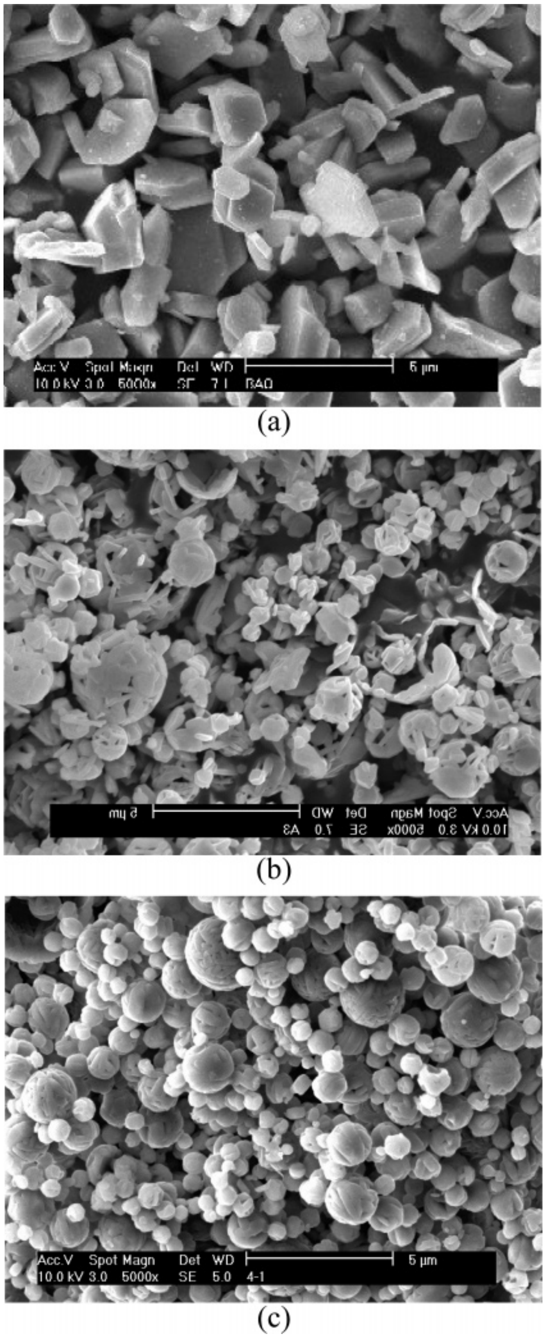

Figure 4. SEM photos of (a) commeercial BAM:Mn and the BAM:Mn particles preapred by the spray pyrolysis with (b) the nitrate solution and (c) the polycation solution.

Strontium magnesium hexaaluminate (SrMgAl$_{10}$O$_{17}$, SAM) has a β-alumina structure of space group $P6_3/mmc$ which is same to that of barium magnesium hexaaluminate (BAM).[21]

---

(19) Lee, D. Y.; Kang, Y. C.; Jung, K. Y. *Electrochem. Solid-State Lett.* **2003**, *6*, H27.

(20) Jung, K. Y.; Kim E. J.; Kang, Y. C. *J. Electochem. Soc.* **2004**, *151*, H69.

(21) Iyi, N.; Göbbels, M. *J. Solid State Chem.* **1996**, *122*, 46.

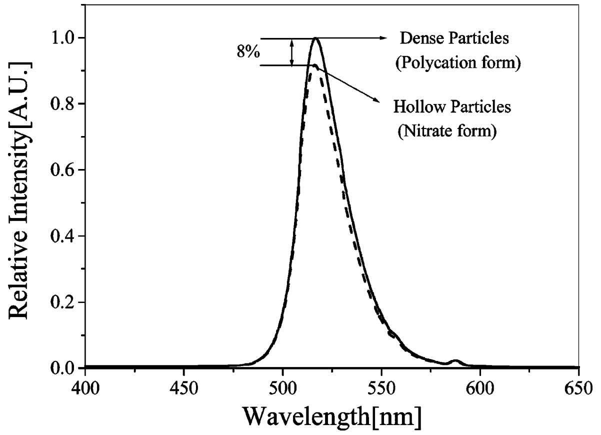

Figure 5. Relative emission intensity of $BaMgAl_{10}O_{17}$:Mn particles prepared by the spray pyrolysis with the nitrate solution and the polycation one. The excitation wavelength was 147 nm in both samples.

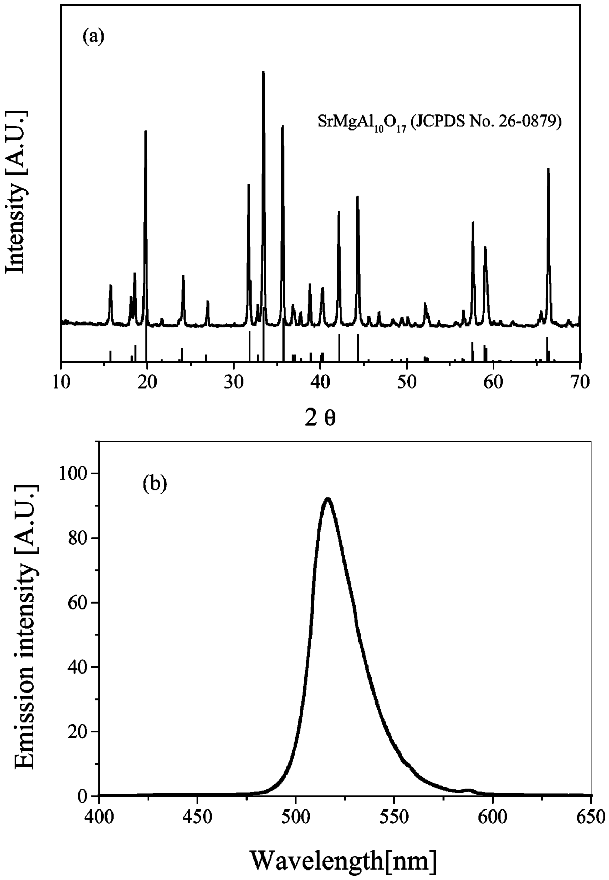

Figure 6. XRD pattern (a) and emission spectrum (b) of $SrMgAl_{10}O_{17}:Mn_{0.1}$ particles prepared by the spray pyrolysis. The excitation wavelength was 147 nm in both samples.

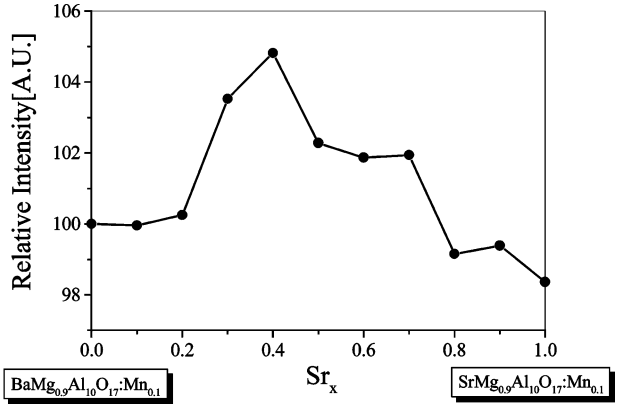

Figure 7. Relative emission intensity of $(Ba_{1-x},Sr_x)Mg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ particles prepared by the spray pyrolysis.

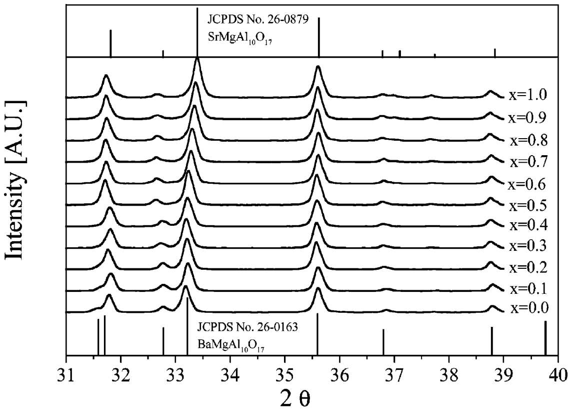

Figure 8. XRD patterns of $(Ba_{1-x},Sr_x)Mg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ particles prepared by the spray pyrolysis. All samples were post-treated at 1400 °C for 3 h under the reduction atmosphere (5% H_2/N_2).

First, we prepared pure $SrMg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ particles and checked the crystal structure and the photoluminescence spectrum under VUV excitation. Figure 6 shows the XRD pattern and the photoluminescence spectrum of SAM:Mn particles prepared by the spray pyrolysis. It was clear that the prepared SAM:Mn particles have pure hexagonal β-alumina structure (JCPDS No. 26-0879) and emit a good green light under VUV excitation. One interesting fact was that there was no change in the peak position of the emission spectrum. In general, the transition of $3d^5$ electrons in the manganese is strongly affected by the crystal field of the host matrix. In both BAM:Mn and SAM:Mn phosphor, Mn was incorporated into Mg sites of the spinel blocks. Thus, it seems that the surroundings of Mn^{2+} are not affected by the change of the conduction layers from BaO to SrO. Figure 7 shows the relative emission intensity of the prepared $(Ba_{1-x},Sr_x)Mg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ phosphor particles as a function of the Sr content (x). The pure $SrMgAl_{10}O_{17}$:Mn particles showed lower photoluminescence intensity than the pure $BaMgAl_{10}O_{17}$:Mn particles. A synergy effect in the photoluminescence intensity was observed by substituting Sr for Ba in the conduction layers. The highest photoluminescence intensity was obtained when 40% of Ba was replaced with Sr. The improvement, however, was less than 5%. Figure 8 shows the XRD patterns of $(Ba_{1-x},Sr_x)MgAl_{10}O_{17}$:Mn phosphor particles prepared by the spray pyrolysis and reduced at 1400 °C for 3 h. The SAM and BAM particles have the same crystal structure but different main peak positions as shown in Figure 8. The BAM crystal structure was maintained as a dominant phase as long as the content of Sr was less than 50 at. % with respect to Ba. As the content of Sr was over 50%, the main peak ($2\theta = 33.2$) shifted to the right, which means that the SAM structure progressively becomes a dominant phase. So, with keeping the BAM structure as the dominant phase, the substitution of strontium for the Ba sites in the conduction layers is helpful to improve the photoluminescence.

Figure 9 shows the excitation spectra of prepared $BaMgAl_{10}O_{17}$:Mn and $(Ba_{0.6},Sr_{0.4})MgAl_{10}O_{17}$:Mn particles. The band gap[22] of BAM host is about 6.5 eV. Then, host-

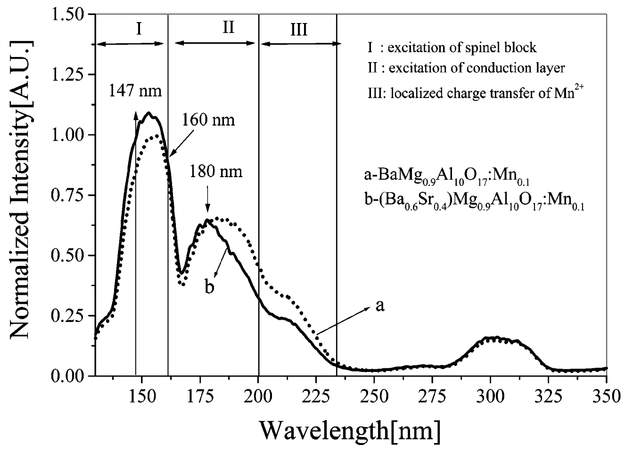

Figure 9. Excitation spectra at $\lambda_{em} = 517$ nm of $BaMg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ and $(Ba_{0.6},Sr_{0.4})Mg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ particles prepared by the spray pyrolysis.

lattice absorption occurs at a wavelength shorter than 190 nm. According to the previous report[23,24] for Eu^{2+}-doped BAM or SAM phosphor, excitation at a wavelength shorter than 160 nm occurs in the spinel blocks. So, we thought that the first (I) and second (II) regions in Figure 9 are due to the excitation in the spinel blocks and the conduction layer of Mn-doped BAM and $(Ba,Sr)MgAl_{10}O_{17}$ phosphor, respectively. Jüstel et al. reported that the excitation spectrum of BAM:Mn is very similar to that of undoped BAM since Mn^{2+} has only forbidden transitions resulting in low absorption coefficients.[25] They showed that doping Mn^{2+} produces the new shoulder band from 200 to 230 nm, which is absolutely caused by the replacement of Mg^{2+} by Mn^{2+}. So, the third region (III), which is not observed in undoped BAM phosphor,[26] is due to the localized charge-transfer transition in $Mn^{2+}-O^{2-}$ bonds. It was clear that the Sr substitution improved the excitation efficiency of the spinel blocks, simultaneously reducing the efficiency for the charge-transfer transition and the excitation in the conduction layer. Howe and Diaz reported that undoped BAM has an efficient host lattice emission at 265 nm.[27] That is responsible for a significant fraction of the energy transfer to the conduction layer and exciton recombination at Ba−O groups.[27] The authors proposed that excitation near the band edge of BAM host takes place in Ba 5d levels, which is region II in Figure 9. In a different way in BAM:Eu blue phosphor, the lattice emission cannot be reused by the Mn^{2+} activators because the direct excitation of manganese which is Mn^{2+}'s $3d^5$ splitting scheme[28,29] occurs at wavelengths from 400 to 500 nm. Therefore, BAM:Mn has no excitation peak around 260 nm. To obtain high intense green emission for BAM:Mn phosphor, the energy transfer to the conduction layer should be inhibited as possible and large numbers of excitons produced by the host lattice absorption should be involved in the energy transfer to the activator center (Mn^{2+}) in the spinel blocks. On the base of the result shown in Figure 9, we surmised that the Sr substitution into Ba sites reduces not only the excitation near the band edge at wavelengths from 180 to 200 nm but also the charge transfer of excitons to the conduction layer. Consequently, the photoluminescence intensity of $(Ba_{0.6},Sr_{0.4})Mg_{0.9}Al_{10}O_{17}:Mn_{0.1}$ phosphor particles was improved in comparison with $BAM:Mn_{0.1}$ particles under VUV (147 nm) excitation.

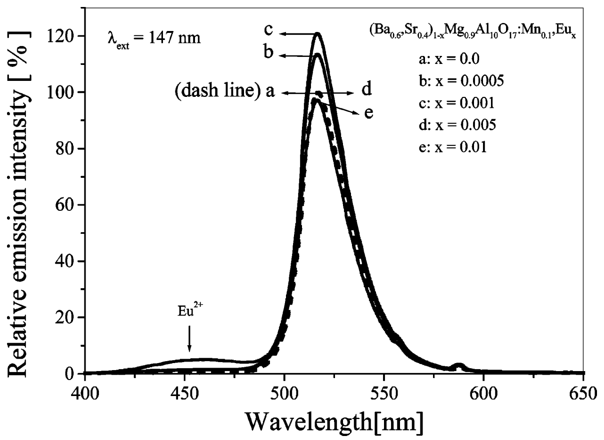

Figure 10. Emission spectra of $(Ba_{0.6},Sr_{0.4})_{1-y}Mg_{0.9}Al_{10}O_{17}:Mn_{0.1},Eu_y$ particles under VUV (147 nm) excitation.

In Eu^{2+}-doped BAM, the activator Eu^{2+} is substituted for Ba^{2+} in the conduction layer. As mentioned before, the excitation of BAM at wavelengths shorter than 160 nm occurs in the spinel blocks. Then, the excitons are transferred to the Eu^{2+} color center. As a result, BAM:Eu shows a strong blue emission with a peak at 450 nm as a consequence of $4f^6d^1 \rightarrow 4f^7$ electron transition in Eu^{2+}.[30] It was also reported that the host emission of BAM at about 265 nm overlaps very well with the direct excitation mode of Eu^{2+}, which makes it possible to the radiative energy transfer between excitons and Eu^{2+} activators in the conduction layers. Sohn et al.[29] reported that the adsorption bands of Mn^{2+} at wavelengths from 400 to 500 nm overlap very well with the emission peak for the $4f^6d^1 \rightarrow 4f^7$ transition of Eu^{2+} in the $BaAl_{12}O_{19}$ matrix. Therefore, some portions of radiationless energy transfer should occur between Eu^{2+} and Mn^{2+} ions. At the same point of view, Yang et al. reported the efficient energy transfer from Eu^{2+} to Mn^{2+} in the BAM matrix when it was excited by UV light.[6] In this work, Eu^{2+} ions were introduced as a coactivator in the conduction layer of $(Ba,Sr)MgAl_{10}O_{17}:Mn$ phosphor particles with the intention of inducing the energy transfer to Mn^{2+} ions in the spinel blocks. Figure 10 shows the emission spectra of $(Ba_{0.6},Sr_{0.4})_{1-x}Mg_{0.9}Al_{10}O_{17}:Mn_{0.1},Eu_x$ phosphor particles prepared by spray pyrolysis. Apparently, codoping a small amount of Eu^{2+} significantly improves the photoluminescence intensity of $(Ba,Sr)MgAl_{10}O_{17}:Mn$ phosphor as a consequence of the radiationless energy transfer from Eu^{2+}

---

(22) Pike, V.; Patraw, S.; Diaz, A. L.; Beboer, B. G. *J. Solid State Chem.* **2003**, *173*, 359.

(23) Jüstel, T.; Bechtel, H.; Mayr, W.; Wiechert, D. U. *J. Lumin.* **2003**, *104*, 137.

(24) Lushchik, A.; Kirm, M.; Kotlov, A.; Liblik, P.; Lushchik, Ch.; Maaroos, A.; Nagirnyi, V.; Savikhina, T.; Zimmerer, G. *J. Lumin.* **2003**, 102−103, 38.

(25) Jüstel, T.; Lade, H.; Mayr, W.; Meijerink, A.; Wiechert, D. U. *J. Lumin.* **2003**, *101*, 195.

(26) Dawson, B.; Ferguson, M.; Marking, G.; Diaz, A. L. *Chem. Mater.* **2004**, *16*, 5311.

(27) Howe, B.; Diaz, A. L. *J. Lumin.* **2004**, *109*, 51.

(28) Palumbo, D. T.; Brown Jr., J. J. *J. Electrochem. Soc.* **1970**, *117*, 1184.

(29) Shon, K.-S.; Park, E. S.; Kim, C. H.; Park, H. D. *J. Electrochem. Soc.* **2000**, *147*, 4368.

(30) Dorenbos, P. *J. Lumin.* **2003**, 104, 239.

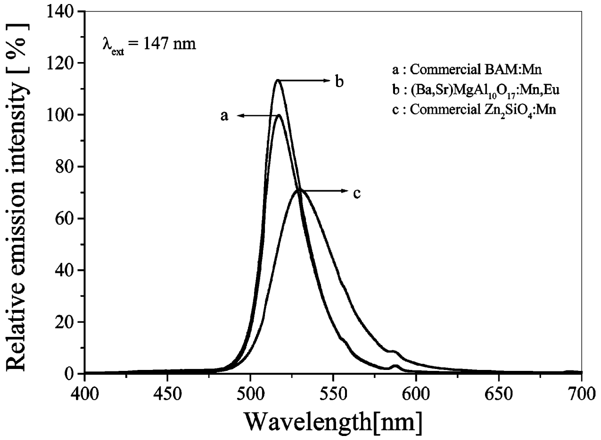

Figure 11. Relative emission spectra of the optimized $(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu sample, commercial BAM:Mn, and Zn_2SiO_4:Mn particles under VUV (147 nm) excitation.

Table 1. Relative Emission Intensity, Brightness, and CIE Chromaticity Coordinates of Green Phosphors

	λmax (nm)	peak intensity (%)	brightness (%)	CIE (x, y)
Zn_2SiO_4:Mn (commercial)	530	100	100	(0.255, 0.680)
BAM:Mn (commercial)	517	141	104	(0.157, 0.736)
$BaMgAl_{10}O_{17}$:Mn (this work)	517	132	95	(0.159, 0.735)
$(Ba,Sr)MgAl_{10}O_{17}$:Mn (this work)	517	137	90	(0.159, 0.735)
$(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu (this work)	517	160	106	(0.156, 0.717)

ion in the conduction layers to Mn^{2+} in the spinel blocks. No emission peak due to $4f^6d^1 \rightarrow 4f^7$ transition of Eu^{2+} was observed as long as the concentration of Eu^{2+} was less than 0.5 at. %. With increasing Eu^{2+} concentration, the photoluminescence intensity increased and reached a maximum at 0.1 at. %. The blue emission due to Eu^{2+}'s $4fd^5$ transition degrades the color purity of $(Ba,Sr)MgAl_{10}O_{17}$:Mn green phosphor. Thus, it is necessary to improve the photoluminescence intensity of $(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu phosphor without any blue emission. In accordance with this point of view, the desirable codoping level of Eu^{2+} was less than 0.5 at. %.

The highest photoluminescence intensity of $(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu phosphor was compared with that of the commercial BAM:Mn in Figure 11. The phosphor particles optimized in terms of Mn concentration, host composition, and codopant concentration showed higher photoluminescence intensity than that of commercial BAM:Mn phosphor as well as commercial Zn_2SiO_4. The emission peak position, the emission intensity, and the CIE chromaticity coordinate of commercial and lab-made samples were summarized in Table 1 to evaluate the phosphor performance. The brightness was calculated by integrating the spectrum of each sample within wavelengths from 425 to 625 nm. For Mn-activated commercial BAM or lab-made phosphor particles, there was no difference in the peak position because such Sr^{2+} substitution and Eu^{2+} codoping was restricted within the conduction layer and there is no change in the environment of Mn^{2+} color center ion in the spinel blocks. The $BaMgAl_{10}O_{17}$:Mn phosphor particles prepared by spray pyrolysis have smaller brightness than the commercial Zn_2SiO_4:Mn even though their relative emission intensity was greater. The optimized $(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu phosphor particles, however, showed better brightness compared with the commercial Zn_2SiO_4:Mn and BAM:Mn green phosphor without any significant change of CIE coordinates.

Conclusions

$(Ba,Sr)MgAl_{10}O_{17}$:Mn,Eu phosphor particles with high brightness, spherical shape, and fine size were prepared by the spray pyrolysis. Substituting Sr for Mg sites on the spinel blocks of $BaMgAl_{10}O_{17}$:Mn enhances the photoluminescence intensity under VUV excitation without any change in the peak position of the emission spectrum. The highest emission intensity of $(Ba,Sr)MgAl_{10}O_{17}$:Mn phosphor was obtained when 40 at. % of Mg was replaced with Sr. It was clear that codoping a small amount of Eu^{2+} significantly improved the photoluminescence intensity of $(Ba,Sr)MgAl_{10}O_{17}$:Mn phosphor as a consequence of the radiationless energy transfer from Eu^{2+} ion in the conduction layers to Mn^{2+} in the spinel blocks. No emission peak due to $4f^6d^1 \rightarrow 4f^7$ transition of Eu^{2+} was observed as long as the concentration of Eu^{2+} was less than 0.5 at. %. Finally, the optimized phosphor composition was $(Ba_{0.6},Sr_{0.4})_{0.999}Mg_{0.1}Al_{10}O_{17}$:$Mn_{0.1}$,$Eu_{0.001}$, at which the phosphor particles prepared had about 20% higher photoluminescence intensity than the commercial BAM:Mn phosphor prepared by a conventional solid-state route.

Acknowledgment. This work was supported by the Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology of Korea.

CM050074F