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Fine-sized $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor powders prepared by spray pyrolysis from the spray solution with BaF_2 flux

Sang Ho Lee, Hye Young Koo, Dae Soo Jung, Jang Heui Yi, Yun Chan Kang *

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

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Abstract

Fine-sized $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor powders with plate-like morphology were prepared by spray pyrolysis process. The effects of ratio of BaF_2 and $Ba(NO_3)_2$ used as the source materials of Ba component on the morphological and optical properties of the $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor powders were investigated. BaF_2 was used as the flux material as well as the source material of Ba component. The phosphor powders prepared from the spray solution with the same mole concentrations of BaF_2 and $Ba(NO_3)_2$ had fine size, plate-like morphology and narrow size distribution. The addition of BaF_2 as the source material of Ba component increased the photoluminescence intensities of the phosphor powders. The phosphor powders prepared from the spray solution with the ratios of BaF_2 and $Ba(NO_3)_2$ larger than 1 had the similar photoluminescence intensities to that of the commercial product.

Keywords: A. Powders-gas phase reaction; A. Powders-chemical preparation; C. Optical properties

1. Introduction

$BaMgAl_{10}O_{17}:Eu^{2+}$(BAM:Eu) phosphor, which has plate-like structure in conventional preparation methods, is an important blue-emitting phosphor for plasma display panels (PDPs) and fluorescent lamps [1–10]. The phosphor powders with fine size and regular morphology are required to obtain the good phosphor layer with low thickness for high definition PDPs. BAM:Eu phosphor powders with high photoluminescence intensities under ultraviolet and vacuum ultraviolet should be post-treated at high temperatures above 1500 °C under reducing atmosphere. Flux materials, such as AlF_3 and BaF_2, were applied in the solid-state reaction method to reduce the preparation temperature of the BAM:Eu phosphor powders.

Flux materials were also applied to the preparation of phosphor powders by spray pyrolysis. Flux materials dissolved to the spray solution were effective in improving the brightness of the phosphor powders by eliminating the surface defects of the powders [11–13]. In the previous paper, the AlF_3 flux material insoluble in distilled water was applied in the preparation of blue-emitting BAM:Eu phosphor powders by the spray pyrolysis [14]. The precursor powders prepared by spray pyrolysis from the spray solution without flux material were reacted with AlF_3 flux by solid-state reaction method. AlF_3 flux improved the morphological and optical properties of the BAM:Eu phosphor powders.

In this study, fine-sized BAM:Eu phosphor powders with plate-like morphology were prepared by spray pyrolysis process from the spray solution with flux material. The effects of ratio of BaF_2 and $Ba(NO_3)_2$ used as the source materials of Ba component on the morphological and optical properties of the BAM:Eu phosphor powders were investigated. BaF_2 was used as the flux material as well as the source material of Ba component.

2. Experiment

The BAM:Eu precursor powders were prepared by ultrasonic spray pyrolysis from the spray solutions with BaF_2 and $Ba(NO_3)_2$. The ultrasonic spray pyrolysis system has a droplet generator, a quartz reactor, and a powder collector. A 1.7 MHz ultrasonic spray generator with six resonators is used to generate large amount of droplets. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The flow

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* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

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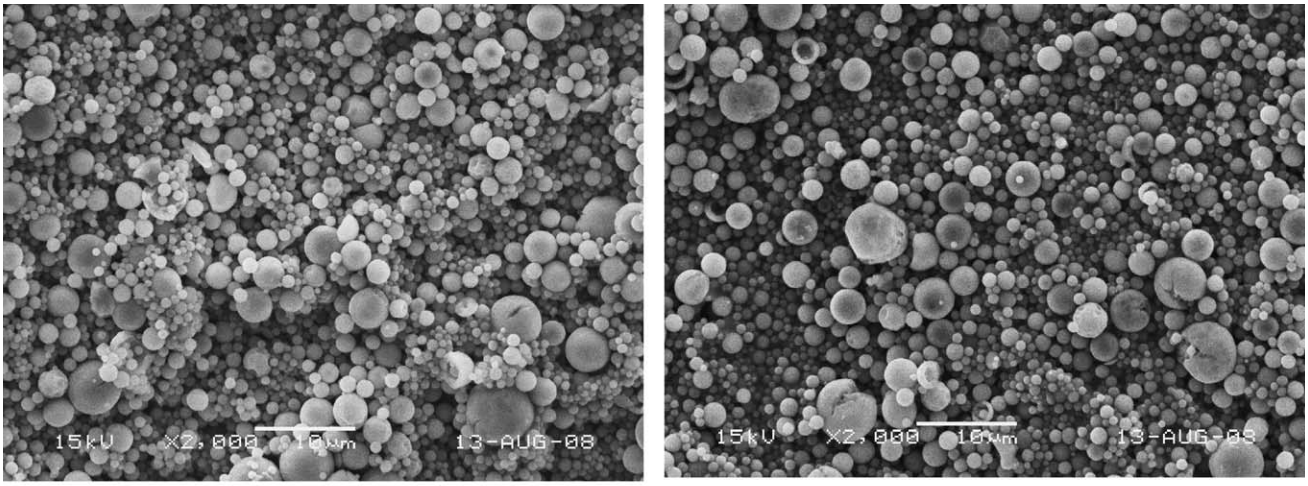
rate of the air used as the carrier gas was 30 L/min. The preparation temperature of the precursor powders was fixed at 900 °C. Al nitrate nonahydrate, Mg nitrate hexahydrate and Eu_2O_3 were used as the source materials of Al, Mg and Eu components, respectively. BaF_2 and $Ba(NO_3)_2$ were used as the source materials of Ba component. The ratios of BaF_2 and $Ba(NO_3)_2$ were changed from 0/1 to 1/0. The overall solution concentration of the metal precursors was 0.5 M. The doping concentration of Eu was fixed at 10 mol.% of the barium component. The precursor powders prepared by spray pyrolysis were post-treated at temperatures between 1200 and 1400 °C for 3 h using a 10% H_2/N_2-mixture gas.

The crystal structures of the powders were studied using X-ray diffraction (XRD, RIGAKU, DMAX-33) with Cu Kα radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The morphologies of the powders were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060). The compositions of the phosphor powders were analyzed by energy dispersive X-ray (EDX, OXFORD, INCA X-act). The optical properties of the powders were measured under 147 nm by vacuum ultraviolet (VUV) photoluminescence (PL) spectroscopy with a D_2 lamp.

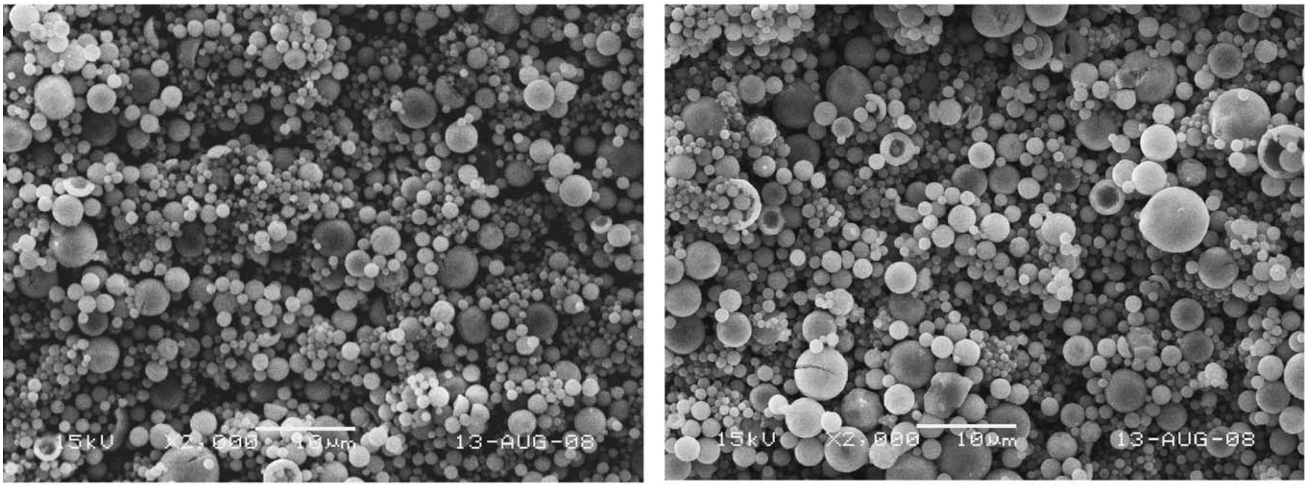
3. Results and discussion

The effect of BaF_2 flux on the optical properties of the BAM:Eu phosphor powders prepared by spray pyrolysis was investigated as the previous study. Small amount of BaF_2 added to the spray solution with stoichiometric composition of BAM:Eu phosphor did not improve the optical characteristics of the phosphor powders. Therefore, in this study, the amount of Ba component dissolved to the spray solution was maintained to the stoichiometric composition of BAM:Eu phosphor. Fig. 1 shows the SEM images of the precursor powders directly prepared by spray pyrolysis according to the ratio of BaF_2 and $Ba(NO_3)_2$. The precursor powders had spherical shape and micron size irrespective of the ratio of BaF_2 and $Ba(NO_3)_2$. Some of the precursor powders had hollow structures because of high drying rate of the droplets inside the hot wall reactor.



(a) $BaF_2/Ba(NO_3)_2$= 0.0/0.9

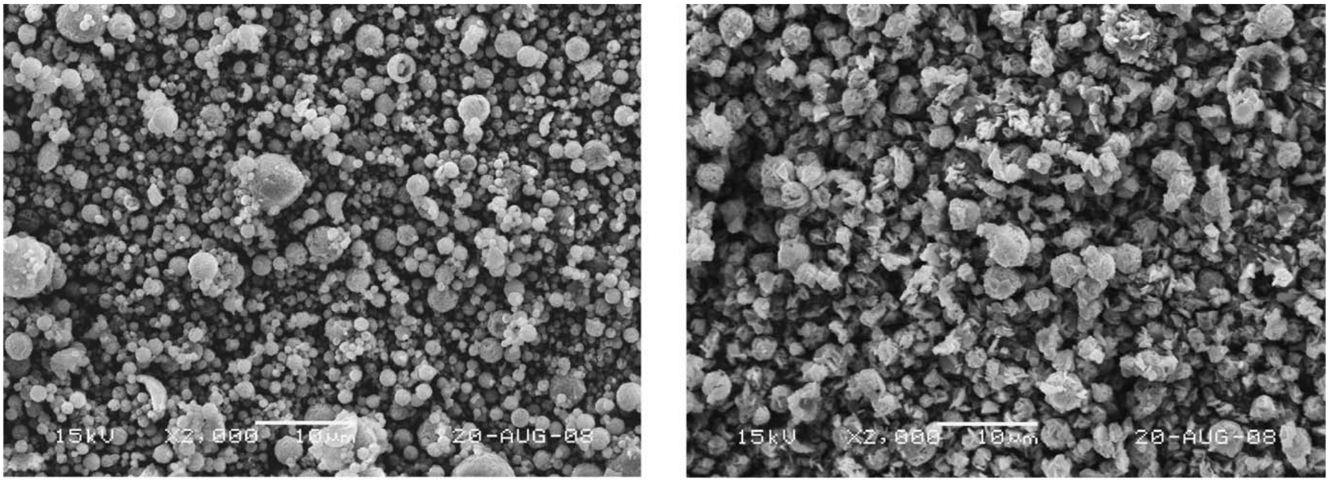
(c) $BaF_2/Ba(NO_3)_2$= 0.45/0.45



(b) $BaF_2/Ba(NO_3)_2$= 0.1/0.8

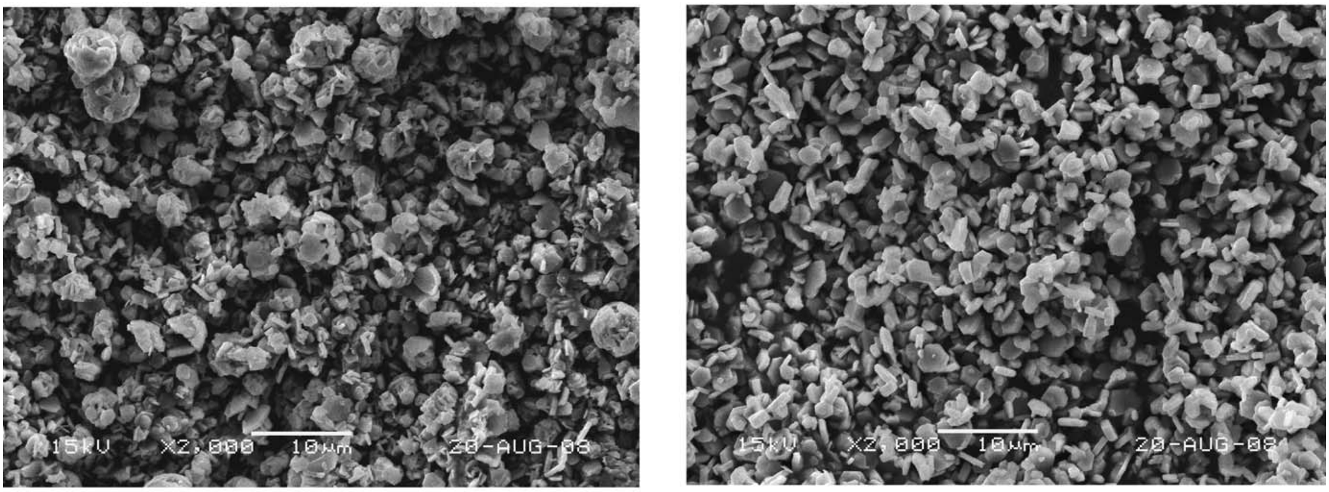
(d) $BaF_2/Ba(NO_3)_2$= 0.9/0.0

Fig. 1. SEM images of the as-prepared $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ powders.



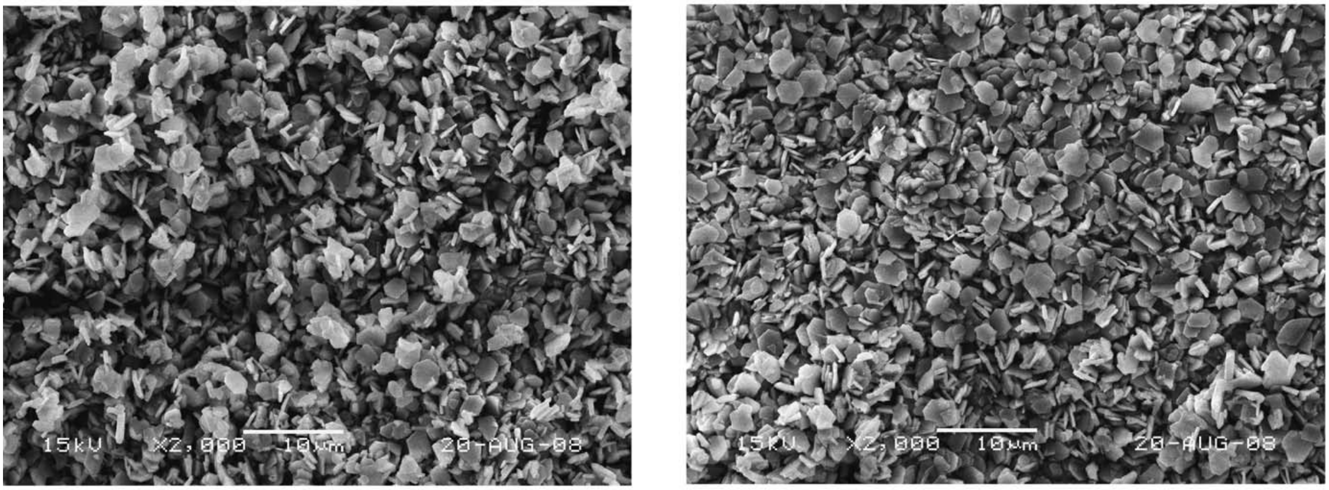
(a) $BaF_2/Ba(NO_3)_2$= 0.0/0.9

(b) $BaF_2/Ba(NO_3)_2$= 0.1/0.8



(c) $BaF_2/Ba(NO_3)_2$= 0.275/0.625

(d) $BaF_2/Ba(NO_3)_2$= 0.45/0.45



(e) $BaF_2/Ba(NO_3)_2$= 0.675/0.225

(f) $BaF_2/Ba(NO_3)_2$= 0.9/0.0

Fig. 2. SEM images of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders post-treated at a temperature of 1350 °C.

The precursor powders obtained by spray pyrolysis were post-treated at a temperature of 1350 °C, in which the BAM:Eu phosphor powders had the maximum photoluminescence intensity. Fig. 2 shows the SEM images of the post-treated BAM:Eu phosphor according to the ratio of BaF_2 and $Ba(NO_3)_2$. The BAM:Eu phosphor powders prepared from the spray solution with only $Ba(NO_3)_2$ as the Ba source had spherical shape and micron size. The spherical shape of the precursor powders was maintained after post-treatment. On the other hand, the increase in the ratio of BaF_2 and $Ba(NO_3)_2$ dissolved in the spray solution decreased the sphericity of the phosphor powders. The phosphor powders prepared from the spray solution with the same mole concentrations of BaF_2 and $Ba(NO_3)_2$ had plate-like morphology and narrow size distribution. The spherical shape of the precursor powders completely disappeared after post-treatment. BaF_2 used as the source material of Ba component acted as the flux material. The mean sizes and aspect ratios of the phosphor powders with plate-like morphologies increased with increasing the ratio of BaF_2 and $Ba(NO_3)_2$ dissolved in the spray solutions. However, the aspect ratio, which is the ratio of thickness and powder size, of the powders decreased with increasing the ratio of BaF_2 and $Ba(NO_3)_2$ dissolved in the spray solutions. The spherical shape phosphor powders prepared from the spray solution with only $Ba(NO_3)_2$ had broad size distribution due to the size distribution of droplets generated by ultrasonic spray generator. However, the plate-like shape phosphor powders prepared from the spray solution with the same mole concentrations of BaF_2 and $Ba(NO_3)_2$ had narrow size distribution even without milling and sorting processes. The size of the precursor powders obtained by spray pyrolysis did not affect the size of the BAM:Eu phosphor powders obtained after post-treatment at a temperature of 1350 °C. Therefore, spray generator with large production rate like two-fluid nozzle could be also applied to the preparation of the BAM:Eu phosphor powders with fine size, plate-like shape and narrow size distribution.

Fig. 3 shows the XRD patterns of the BAM:Eu phosphor powders post-treated at a temperature of 1350 °C. The prepared phosphor powders had pure hexagonal BAM phase irrespective of the ratio of BaF_2 and $Ba(NO_3)_2$ dissolved in the spray solution. The mean crystallite sizes of the BAM:Eu phosphor powders calculated from the Scherrer's equation were changed from 40 to 52 nm according to the ratio of BaF_2 and $Ba(NO_3)_2$.

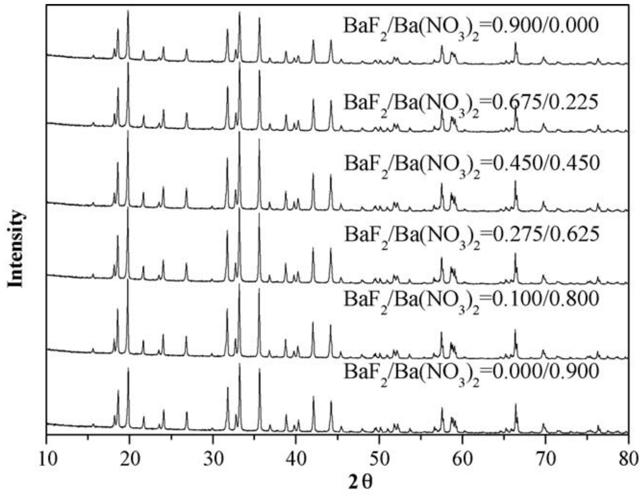
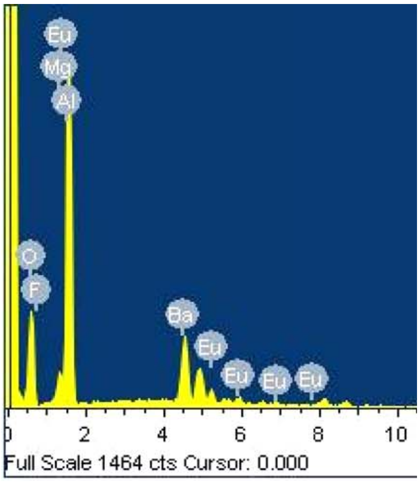
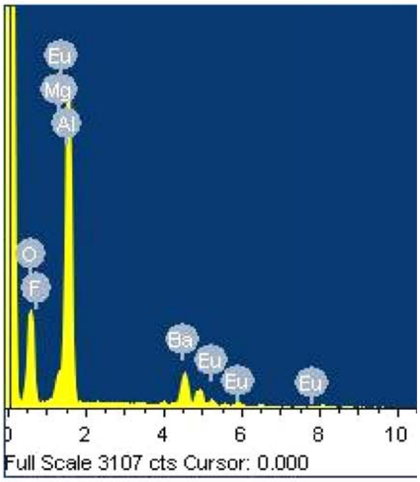


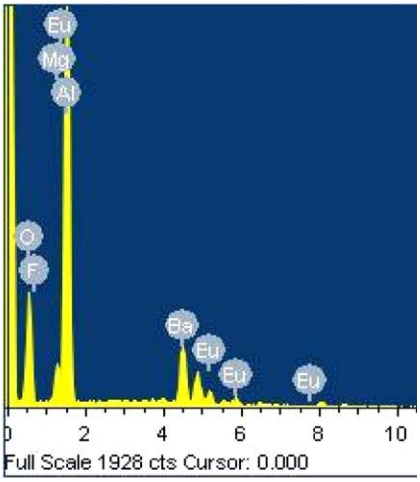
Fig. 3. XRD patterns of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders post-treated at a temperature of 1350 °C.



(a) $BaF_2/Ba(NO_3)_2$= 0.0/0.9



(b) $BaF_2/Ba(NO_3)_2$= 0.45/0.45



(c) $BaF_2/Ba(NO_3)_2$= 0.9/0.0

Fig. 4. EDX spectra of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders post-treated at a temperature of 1350 °C.

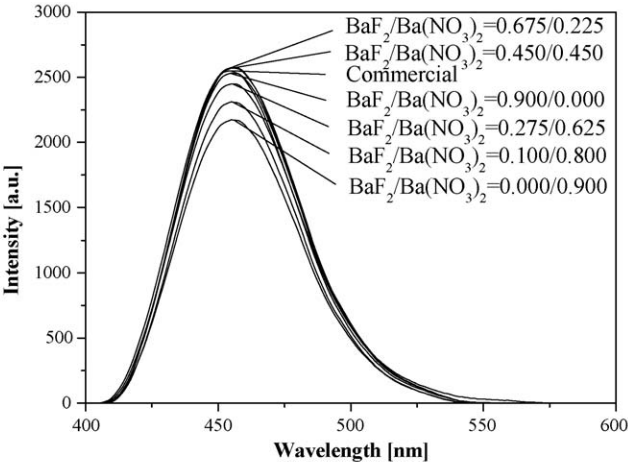


Fig. 5. Photoluminescence spectra of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders post-treated at a temperature of 1350 °C.

The EDX spectra of the BAM:Eu phosphor powders prepared from the spray solutions with different ratios of BaF_2 and $Ba(NO_3)_2$ were shown in Fig. 4. The compositions of the BAM:Eu phosphor powders were measured by EDX spectra. The composition ratios of Ba, Mg, Al, and Eu components dissolved in the spray solution were well maintained in the BAM:Eu phosphor powders. The peaks of fluorine composing the BaF_2 were not detected in the EDX spectra.

The photoluminescence spectra of the prepared and the commercial BAM:Eu phosphor powders under vacuum ultraviolet were shown in Fig. 5. The commercial BAM:Eu phosphor powders were prepared by solid-state reaction method using flux material. Both the prepared and the commercial BAM:Eu phosphors exhibit the maximum of the emission at 453 nm. However, the ratio of BaF_2 and $Ba(NO_3)_2$ dissolved in the spray solution affected the photoluminescence intensities of the phosphor powders. The addition of BaF_2 as the source material of Ba component increased the photoluminescence intensities of the phosphor powders. The photoluminescence intensity of the phosphor powders prepared from the spray solution with only $Ba(NO_3)_2$ was 85% of that of the commercial phosphor powders. The phosphor powders with the maximum photoluminescence intensity was obtained from the spray solution with the same mole concentration of BaF_2 and $Ba(NO_3)_2$. The phosphor powders prepared from the spray solution with the ratios of BaF_2 and $Ba(NO_3)_2$ larger than 1 had the similar photoluminescence intensities to that of the commercial product. The chromaticities of the prepared and the commercial BAM:Eu phosphor powders were shown in Table 1. The value of CIE *y* of the prepared phosphor powders post-treated at a temperature of 1350 °C was similar to that of the commercial product.

Table 1
Chromaticity of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders.

Temp. (°C)	$BaF_2/Ba(NO_3)_2$	CIE *x*	CIE *y*
–	Commercial	0.1421	0.0622
1200	0.450/0.450	0.1411	0.0998
1300	0.450/0.450	0.1425	0.0711
1350	0.450/0.450	0.1406	0.0619
1400	0.450/0.450	0.1412	0.0692

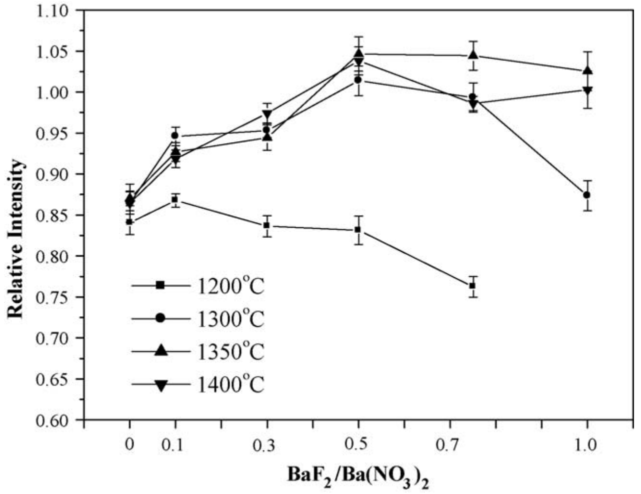
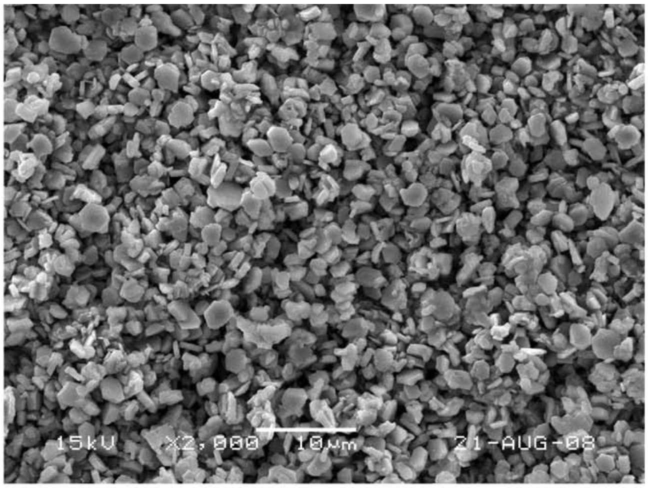


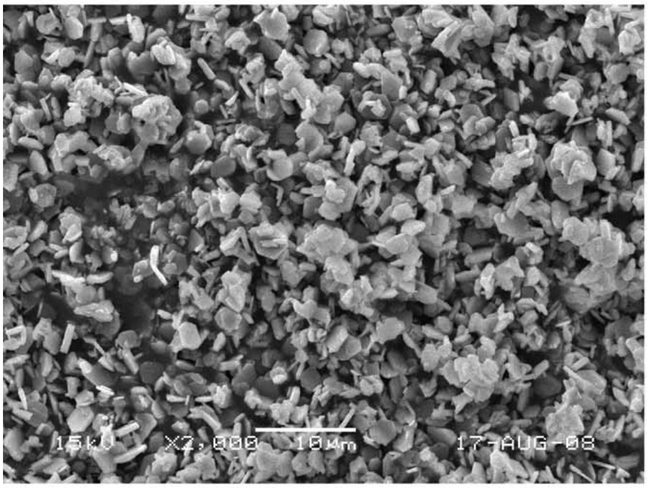
Fig. 6. The photoluminescence intensities of the $Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$ phosphor powders post-treated at different temperatures.

Fig. 6 shows the relative photoluminescence intensities of the phosphor powders post-treated at various temperatures. The photoluminescence intensities of the phosphor powders post-treated at temperatures of 1350 and 1400 °C were monotonically increased with the ratio of BaF_2 and $Ba(NO_3)_2$. However, the phosphor powders prepared from the spray solution with only BaF_2 as the source material of Ba component had low photoluminescence intensity at a low post-treatment temperature of 1300 °C. The phosphor powders prepared from the spray solutions with high ratios of BaF_2 and $Ba(NO_3)_2$ had also low photoluminescence intensities at a post-treatment temperature of 1200 °C.

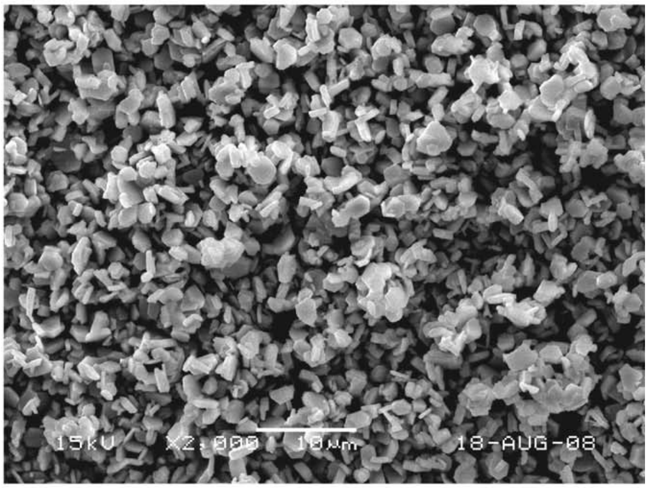
Fig. 7 shows the SEM images of the BAM:Eu phosphor powders post-treated at various temperatures. The precursor powders obtained from the spray solution with the same mole concentrations of BaF_2 and $Ba(NO_3)_2$ were post-treated at temperatures between 1200 and 1400 °C. The spherical shape of the precursor powders disappeared after post-treatment at temperatures between 1200 and 1400 °C. BaF_2 was acted as a flux material during the post-treatment process of the phosphor powders. Therefore, plate-like shape phosphor powders with regular morphology were prepared even at a low post-treatment temperature of 1200 °C. The phosphor powders had similar mean sizes and morphologies irrespective of the post-treatment temperatures. Fig. 8 shows the XRD patterns of the phosphor powders post-treated at various temperatures. The phosphor powders had pure hexagonal BAM phase irrespective of the post-treatment temperatures. The mean crystallite sizes of the BAM:Eu phosphor powders calculated from the Scherrer's equation were changed from 44 to 52 nm when the post-treatment temperatures were changed from 1200 to 1400 °C. Therefore, the phosphor powders post-treated at temperatures between 1200 and 1400 °C had similar morphologies and crystal structures. However, the photoluminescence intensities of the phosphor powders were strongly affected by



(a) 1200°C



(b) 1300°C



(c) 1400°C

Fig. 7. SEM images of the $Ba_{0.9}MgAl_{10}O_{17}$:$Eu_{0.1}$ phosphor powders post-treated at different temperatures.

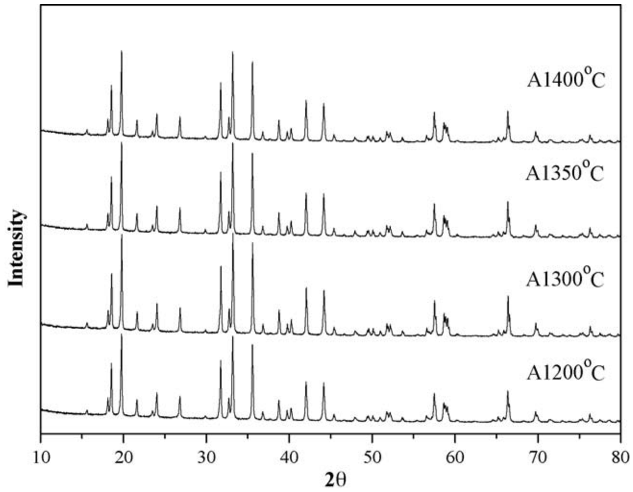


Fig. 8. XRD patterns of the $Ba_{0.9}MgAl_{10}O_{17}$:$Eu_{0.1}$ phosphor powders post-treated at different temperatures.

the post-treatment temperatures as shown in Fig. 6. The phosphor powders post-treated at low post-treatment temperatures of 1200 and 1300 °C had also large CIE *y* values. Doping of Eu component to the matrix of BAM host was not completely occurred at low post-treatment temperatures.

4. Conclusions

The BAM:Eu phosphor powders were prepared by spray pyrolysis process from the spray solutions with the various ratios of BaF_2 and $Ba(NO_3)_2$. BAM:Eu phosphor powders prepared from the spray solutions with appropriate BaF_2 contents had regular morphologies, fine sizes and narrow size distributions. Addition of BaF_2 improved the photoluminescence intensities of the BAM:Eu phosphor powders. The phosphor powders with the maximum photoluminescence intensity was obtained from the spray solution with the same mole concentration of BaF_2 and $Ba(NO_3)_2$. BaF_2 acted as the flux material as well as the source material of Ba component.

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