

Morphological and optical characteristics of $\text{BaMg}_{0.9}\text{Al}_{10}\text{O}_{19}:\text{Mn}^{2+}$ phosphor powders prepared by flame spray pyrolysis

Jung Sang Cho, Dae Soo Jung, Sang Ho Lee and Yun Chan Kang*

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

Green-light emitting $\text{BaMg}_{0.9}\text{Al}_{10}\text{O}_{19}:\text{Mn}^{2+}$ phosphor powders, with fine sizes, spherical shapes, and filled morphologies, were prepared by flame spray pyrolysis. The precursor powders obtained by flame spray pyrolysis from the aluminum polycation solution at low flow rate of the carrier gas had a fine size, dense structure and narrow size distribution even at very fast drying and decomposition rates of droplets or powders. Therefore, the $\text{BAM}:\text{Mn}^{2+}$ phosphor powders obtained after post-treatment at a temperature of 1400°C had a spherical shape, fine size and filled morphology. The $\text{BAM}:\text{Mn}^{2+}$ phosphor powders obtained at a post-treatment temperature of 1400°C had a high photoluminescence intensity under a vacuum ultraviolet light of 147 nm because of high crystallinity and good morphology.

Key words: phosphor, flame spray pyrolysis, photoluminescence.

Introduction

$\text{BaMgAl}_{10}\text{O}_{19}:\text{Mn}^{2+}$ (BAM:Mn) phosphor, which has a plate-like structure made by conventional preparation methods, is considered as a green phosphor for plasma display panels (PDPs) due to its high VUV efficiency and excellent green color [1-3]. The unit cell size of the PDPs is gradually becoming smaller for the fabrication of high-definition TVs. Therefore, phosphor powders with a fine size and regular morphology are required to obtain a good phosphor layer with a low thickness [4-6]. New printing processes such as ink-jet also require phosphor powders with a fine size, narrow size distribution and regular morphology.

Flame spray pyrolysis, which is analogous to conventional spray pyrolysis except for its energy source for drying and decomposition of droplets, is considered as a potential process for the preparation of dense powders by melting the powders at a high temperature [7-11]. However, the control of morphology of the phosphor powders in flame spray pyrolysis is difficult because of the fast drying and decomposition rates of droplets or powders. In flame spray pyrolysis, blue-light emitting $\text{BaMgAl}_{10}\text{O}_{19}:\text{Eu}^{2+}$ (BAM:Eu) phosphor powders with a spherical shape and fine size have been prepared at various preparation conditions [12,13].

In this study, green-light emitting $\text{BAM}:\text{Mn}^{2+}$ phosphor powders with a spherical shape and fine size were prepared by flame spray pyrolysis. The effects of preparation conditions and types of spray solution on the

morphologies and photoluminescence characteristics of the $\text{BAM}:\text{Mn}$ phosphor powders were investigated.

Experimental procedure

$\text{BaMg}_{0.9}\text{Al}_{10}\text{O}_{19}:\text{Mn}_{0.1}^{2+}$ ($\text{BAM}:\text{Mn}^{2+}$) phosphor powders were prepared by a flame spray pyrolysis (FSP) process. The flame spray pyrolysis system as shown in Fig. 1 has a droplet generator, a flame nozzle, a quartz reactor, a powder collector, and a blower. A 1.7 MHz ultrasonic spray generator with six resonators is used to generate droplets, which are carried into the high-temperature diffusion flame by oxygen as the carrier gas. Propane, as the fuel, and oxygen, as the oxidizer, create the diffusion flame. The flame nozzle has five

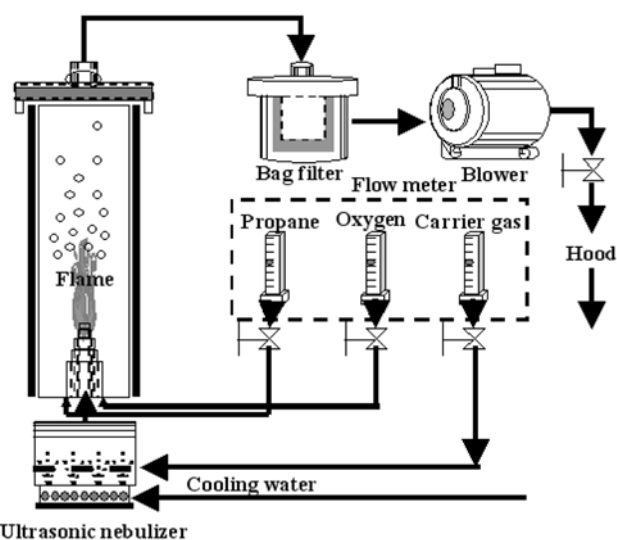


Fig. 1. A schematic diagram of the flame spray pyrolysis process.

*Corresponding author:
 Tel : +82-2-2049-6010
 Fax: +82-2-458-3504
 E-mail: yckang@konkuk.ac.kr

concentric pipes. The droplets generated from the precursor solution are supplied to the diffusion flame through the center pipe by different flow rates of the carrier gas. The temperatures of the diffusion flame and the residence time of the powders inside the diffusion flame are controlled by changing the amounts of the fuel, oxidizer, and carrier gases. The flow rate of the oxygen used as the carrier gas was changed from 10 to 40 l/minute. The flow rate of the propane used as the fuel gas and the flow rate of the oxygen used as the oxidizer gas was fixed at 4.2 and 35 l/minute respectively. The overall solution concentration of the metal precursors was 0.4 mol/l. The doping concentration of Mn was fixed at 10 mol% of the magnesium component. The precursor powders obtained by flame spray pyrolysis were post-treated at temperatures between 1100 and 1400°C for 3 h using a 5% H₂/N₂-mixture gas. The crystal structures of the powders were studied using X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies of the powders were investigated using scanning electron microscopy (SEM). The optical properties of the powders were measured at 147 nm by vacuum ultraviolet (VUV) photoluminescence (PL) spectroscopy with a D₂ lamp.

Results and Discussions

Figure 2 shows SEM micrographs of the precursor powders prepared by flame spray pyrolysis at different

flow rates of oxygen, which was used as the carrier gas. The flow rate of the carrier gas was changed from 10 to 40 l/minute. The morphologies of the precursor powders were affected by the flow rate of the carrier gas. The precursor powders obtained at a low flow rate of carrier gas had a spherical shape and regular morphology. On the other hand, the precursor powders prepared at high flow rates of the carrier gas had hollow structures, large sizes, and broad size distributions. The mean size of the precursor powders increased with an increase in the flow rate of the carrier gas. The change of the residence time of the powders inside the high temperature flame according to the flow rate of the carrier gas affected the morphologies of the precursor powders obtained by the flame spray pyrolysis.

Figure 3 shows SEM micrographs of the post-treated BAM:Mn²⁺ phosphor powders. The precursor powders obtained by flame spray pyrolysis at different flow rates of the carrier gas were post-treated at a temperature of 1400°C under a reducing atmosphere. The BAM:Mn²⁺ phosphor powders obtained from the precursor powders (Fig. 2a) with a fine size and spherical shape had a fine size and regular morphology after post-treatment. The spherical shape of the precursor powders was maintained after post-treatment at a high temperature. However, the BAM:Mn²⁺ phosphor powders had porous morphologies. On the other hand, the BAM:Mn²⁺ phosphor powders obtained from the precursor powders with hollow and fractured structures

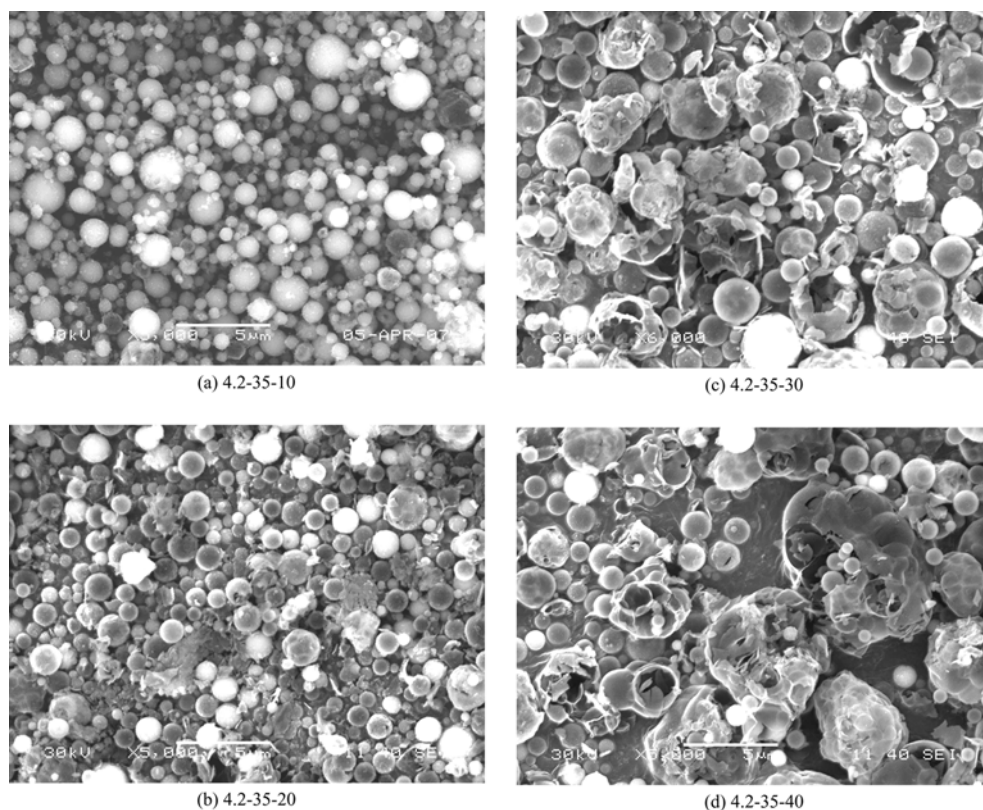


Fig. 2. SEM micrographs of the precursor powders prepared at different flow rates of the carrier gas. (fuel-oxidizer-carrier gas).

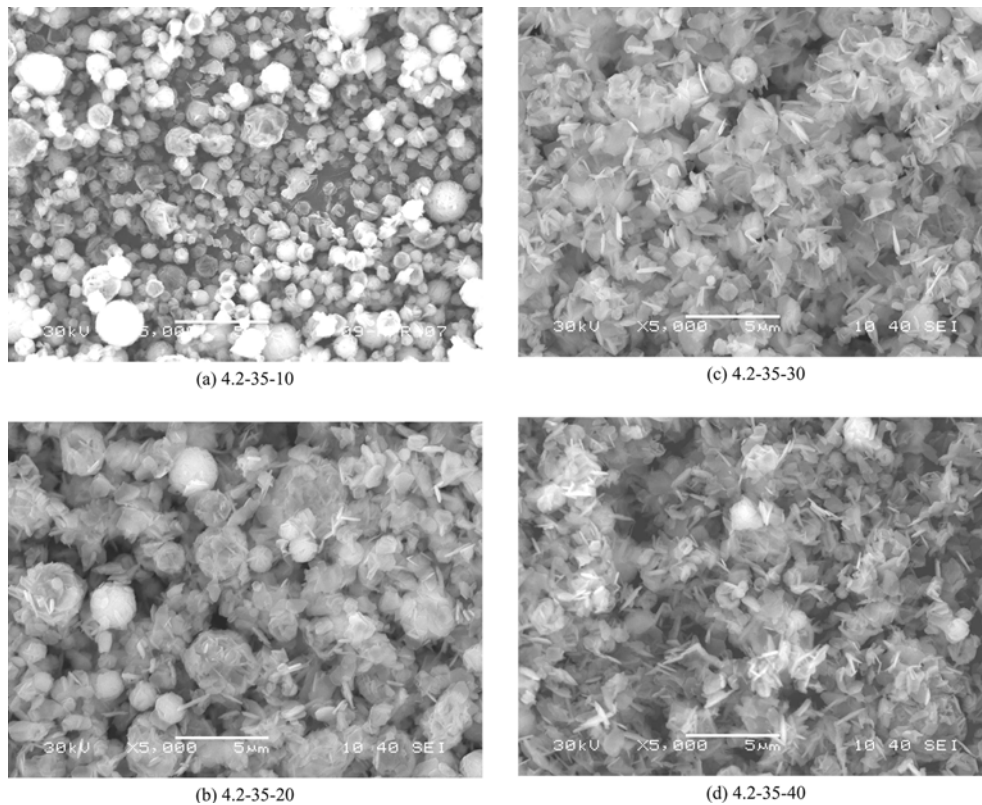


Fig. 3. SEM micrographs of the post-treated BAM:Mn phosphor powders at different flow rates of carrier gas. (fuel-oxidizer-carrier gas)

had large sizes and irregular morphologies. The spherical morphologies of the precursor powders disappeared after post-treatment at a high temperature. The post-treated BAM:Mn²⁺ phosphor powders had plate-like morphologies.

To avoid the formation of porous and hollow morphology, an aluminum polycation solution was obtained by modifying the aqueous nitrate solution with an ammonium solution. More details on how to prepare the aluminum polycation solution are given in the references [14,15]. Barium, magnesium, and manganese nitrate were dissolved in the aluminum polycation solution to obtain the spray solution. Figure 4 shows SEM micrographs of the precursor and post-treated BAM:Mn²⁺ phosphor powders. The precursor powders obtained by flame spray pyrolysis from the aluminum polycation solution were post-treated at a temperature of 1400°C under a reducing atmosphere. The precursor powders obtained by flame spray pyrolysis had a fine size, dense structure and narrow size distribution even with very fast drying and decomposition rates of droplets or powders. The BAM:Mn²⁺ phosphor powders obtained after post-treatment at a high temperature had a spherical shape, fine size and filled morphology.

Figure 5 shows the XRD spectra of the precursor powders prepared by flame spray pyrolysis at different flow rates of the carrier gas. All of the diffraction peaks are not assigned to the BAM phase. The short residence times of the powders inside the high-temperature diffusion

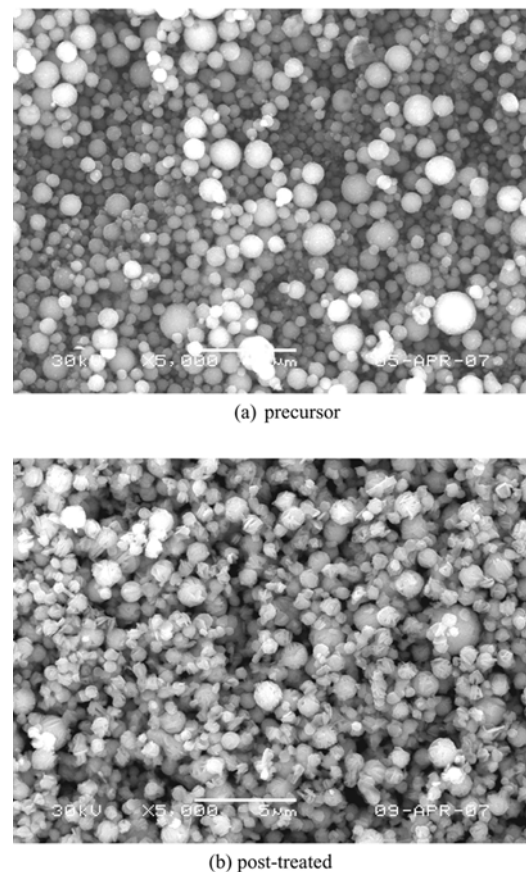


Fig. 4. SEM micrographs of the precursor and post-treated powders obtained from the aluminum polycation solution.

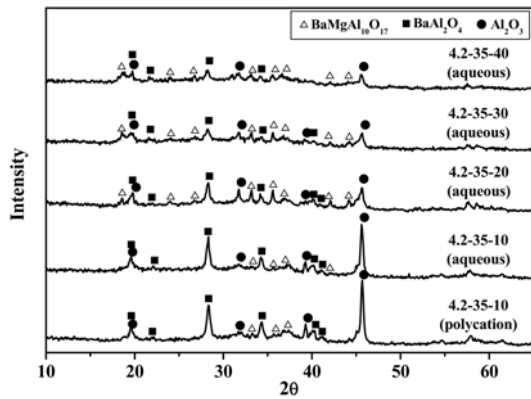


Fig. 5. XRD spectra of the precursor powders obtained by flame spray pyrolysis.

flame did not form the crystal structure of the BAM phase. From the XRD analysis, peaks from BaAl_2O_4 and Al_2O_3 have been observed. The peak intensities of BaAl_2O_4 and Al_2O_3 phases increased with a decrease in the flow rate of the carrier gases. The crystal structures of the post-treated powders at different temperatures are shown in Fig. 6. The precursor powders obtained from the aluminum polycation solution were post-treated at temperatures between 1100 and 1400°C for 3 h under a reducing atmosphere. When the post-treatment temperature was below 1200°C, the BaAl_2O_4 and Al_2O_3 were the main phases in the powders. However, the powders post-treated at temperatures above 1300°C had pure crystal structures of the BAM phase. The phosphor powders obtained from the aqueous spray solution also had pure BAM phase at a post-treatment temperature of 1400°C.

Photoluminescence characteristics of the $\text{BAM}:\text{Mn}^{2+}$ phosphor powders prepared by flame spray pyrolysis at different flow rates of the carrier gas under vacuum ultraviolet (VUV, 147 nm) are shown in Fig. 7. The precursor powders obtained from the aqueous and aluminum polycation solutions were post-treated at a temperature of 1400°C. A single green band with a peak of the wide spectrum was observed at 517 nm which corresponds to the ${}^6\text{A}_1\text{-}{}^4\text{E}$, ${}^4\text{A}_1\text{(}{}^4\text{G)}$ transition of

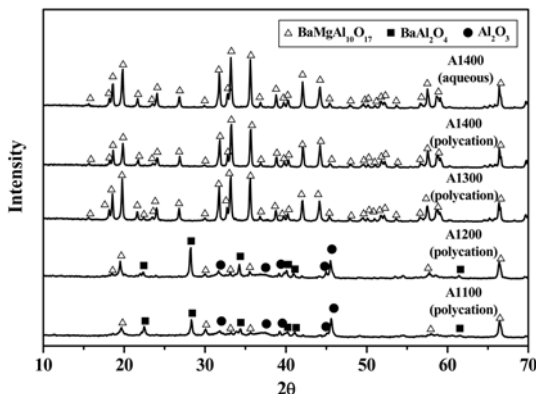


Fig. 6. XRD spectra of the post-treated powders at different temperatures.

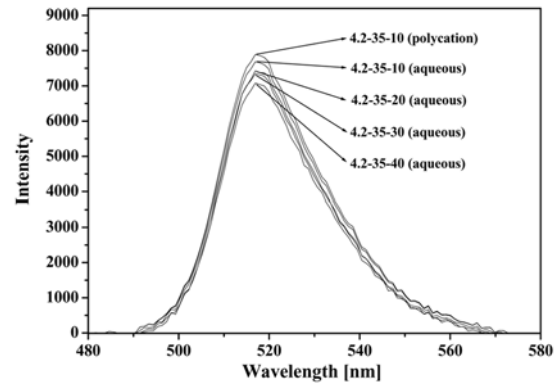


Fig. 7. Photoluminescence spectra of the $\text{BAM}:\text{Mn}$ phosphor powders prepared by flame spray pyrolysis.

Mn^{2+} ions [16]. The photoluminescence intensities of the phosphor powders slightly increased with a decrease in the flow rate of the carrier gas. The good morphology of the powders prepared by flame spray pyrolysis at a low flow rate of the carrier gas improved the photoluminescence intensity of the phosphor powders. The $\text{BAM}:\text{Mn}^{2+}$ phosphor powders obtained from the aluminum polycation solution had similar photoluminescence intensity to that of the phosphor powders obtained from the aqueous spray solution.

The photoluminescence characteristics of the $\text{BAM}:\text{Mn}^{2+}$ phosphor powders obtained from the aluminum polycation solution at different post-treatment temperatures are shown in Fig. 8. The phosphor powders had low photoluminescence intensities at low post-treatment temperatures below 1200°C. In the XRD spectra of the powders as shown in Fig. 6, phase pure $\text{BAM}:\text{Mn}^{2+}$ phosphor powders were prepared at a post-treatment temperature of 1300°C. Therefore, the photoluminescence intensity of the phosphor powders abruptly increased at a post-treatment temperature of 1300°C. $\text{BAM}:\text{Mn}^{2+}$ phosphor powders with a high photoluminescence intensity were prepared at a post-treatment temperature of 1400°C because of high crystallinity and good morphology. Figure 9 shows SEM micrographs of the powders post-treated at different temperatures. The

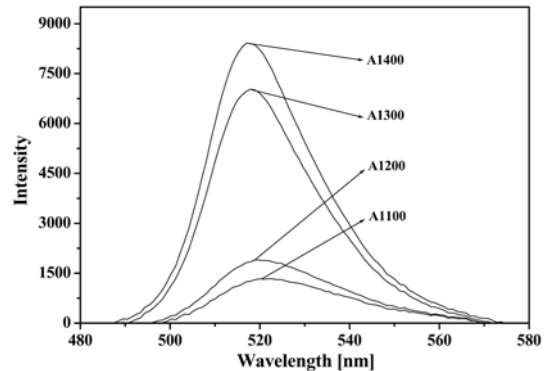


Fig. 8. Photoluminescence spectra of the phosphor powders post-treated at different temperatures.

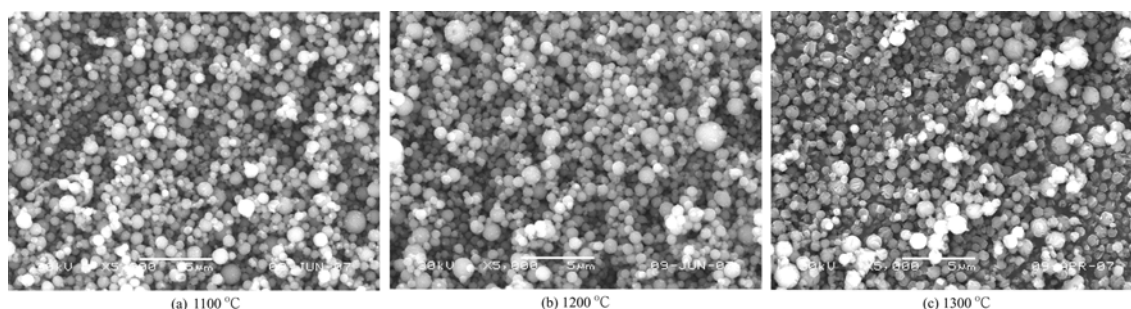


Fig. 9. SEM micrographs of the phosphor powders post-treated at different temperatures.

powders post-treated at low temperatures below 1200°C had smooth surfaces. However, the powders post-treated at temperatures of 1300 and 1400°C had plate-like crystal structures, which is a characteristic of the BAM phase.

Conclusions

$\text{BaMg}_{0.9}\text{Al}_{10}\text{O}_{19}:\text{Mn}^{2+}$ phosphor powders were prepared by flame spray pyrolysis (FSP) from aqueous and aluminum polycation solutions at various flow rates of the carrier gas. The morphologies of the precursor powders were affected by the flow rates of the carrier gas because of the change of the residence time of the powders inside the high temperature diffusion flame. The precursor powders obtained at a low flow rate of the carrier gas had a spherical shape and regular morphology. To avoid the formation of a porous and hollow morphology, an aluminum polycation solution was obtained by modifying the nitrate aqueous solution with ammonium solution. The BAM: Mn^{2+} phosphor powders obtained from the precursor powders with a fine size and spherical shape had a fine size and a regular morphology after post-treatment. The BAM: Mn^{2+} phosphor powders prepared by flame spray pyrolysis obtained from the aluminum polycation solution had good photoluminescence intensities under vacuum ultra-violet of 147 nm.

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