

## Size-Dependent Luminescent Properties of Hollow and Dense $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ Blue Phosphor Particles Prepared by Spray Pyrolysis

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**Abstract**—Hollow and dense  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  (BAM) phosphor particles were synthesized by a spray pyrolysis process and their luminescent properties were investigated under vacuum ultraviolet (VUV) excitation as varying the average particle size. The dependence of the luminescent intensity on the particle size was greatly influenced by the morphology of BAM particles. For the BAM particles with a hollow structure, the luminescent intensity linearly increased with increasing the particle size. However, no significant change in the luminescent intensity was observed for dense particles as the particle size changed. Also, all dense BAM particles had higher photoluminescence intensity than that of the hollow ones regardless of the particle size. The luminescent intensity of BAM phosphor particles prepared by spray pyrolysis was found to have a linear relationship with the crystallite size. Therefore, it was concluded that suppressing the formation of a hollow structure and increasing the crystallite size are needed to obtain high luminous BAM phosphor particles with a spherical shape and fine size of less than 1  $\mu\text{m}$ . On the basis of penetration depth of VUV, a simple relation equation between the particle size and the luminescent intensity was derived and correlated with experimental results in order to interpret the luminescent behavior of BAM phosphor as the particle size changes.

Key words: Phosphor, Spray Pyrolysis, Optical Properties, Luminescence

### INTRODUCTION

Flat panel displays (FPDs) such as liquid crystal displays (LCD) and plasma display panels (PDP) have received much attention in the world display market because they are lightweight, not bulky, and do not take up much space in comparison to the conventional cathode ray tubes (CRT). In particular, PDPs are known to have the most potential because they can be made in large sizes. The most urgent tasks with which the PDP manufacturer is confronted are to not only improve the resolution and brightness but also lower the price of final goods so that the PDPs have the competitiveness in high definition television (HDTV) market. To meet these requisites, PDP makers are seeking new advanced materials and processes.

Phosphors are core materials directly affecting the brightness and lifetime of PDPs. In general, phosphors are placed in barrier ribs with a stripe structure [Kim et al., 2000]. In order to improve the resolution of PDPs, the barrier rib is getting smaller and more complicated as a closed cell type [Park et al., 2000]. Also, to make a good phosphor film in the narrowed barrier ribs, a new process like an ink-jet printing technique [Evans et al., 2001] is considered as a promising next generation process alternating with the conventional screen printing technique. Then, the phosphor particles with smaller size and spherical shape play an important role in obtaining high brightness because they can form better phosphor film within the

narrow barrier ribs compared with the irregular-shaped phosphor of large particle size. Therefore, many researchers have focused on the preparation of fine and spherical particles [Lee et al., 2003; Lenggoro et al., 2001; Kang and Park, 2000; Cho and Chang, 2003].

Now, commercially available phosphors have been prepared by a conventional solid-state reaction which produces large and irregular-shaped particles [Yu and Kim, 2003]. In recent years, spray pyrolysis has been known as a promising process for producing spherical particles, especially for multi-component oxides like phosphors for applications to PDP [Kang and Choi, 2002; Zhou et al., 2003; Kim et al., 2002; Kang et al., 2003; Jung and Park, 2003; Kim and Lee, 2000] and light-emitting diodes (LEDs) [Choi et al., 2003, 2004; Nahm et al., 2000]. In spray pyrolysis, however, hollow particles are frequently prepared. So, much effort has been expended to overcome the weakness of spray pyrolysis so that dense and spherical particles can be prepared. In our previous study on the application of spray pyrolysis to the preparation of phosphors such as Eu-doped  $\text{BaMgAl}_{10}\text{O}_{17}$ , Mn-doped  $\text{Zn}_2\text{SiO}_4$ , and Eu-doped  $\text{Y}_2\text{O}_3$ , particles, which are major blue, green, and red phosphors being used for PDPs, it was found that the particle morphology was successfully controlled by modifying the spray solution. For example, using colloidal particles which are well dispersed in the spray solution, was very helpful to improve the particle shape [Kang et al., 2000; Kang and Park, 2000]. Also, some organic additives such as citric acid and ethylene glycol were very effective in controlling the morphology of phosphor particles when prepared by spray pyrolysis [Roh et al., 2003]. Especially,  $\text{BaMgAl}_{10}\text{O}_{17}$  blue phosphor particles tend to crys-

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tallographically grow as a plate-like shape when prepared by the conventional solid-state reaction technique or spray pyrolysis using an aqueous nitrate solution. In order to avoid this morphological behavior of  $\text{BaMgAl}_{10}\text{O}_{17}$  particles, the modification of aqueous nitrate solution by adding some basic chemicals made it possible to prepare completely spherical particles using the spray pyrolysis process [Lee et al., 2003].

It is believed that spray pyrolysis is the most profitable process for preparing spherical phosphor particles of less than  $1\ \mu\text{m}$ , which are essentially needed for the next-generation HDTV which has a closed cell structure and narrow barrier ribs. In addition to reducing the particle size, the luminescent intensity of phosphor particles should be improved to guarantee the high brightness. So, to optimize the spray pyrolysis process and successfully apply it to the preparation of highly efficient phosphor particles, the behavior of the luminescent intensity of phosphor particles has to be studied more systematically and in-depth as the particle size varies. In this work, hollow and dense  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$  particles were prepared by the spray pyrolysis process and their luminescent characteristics under vacuum ultraviolet (VUV) excitation were investigated with changing the average particle size.

## EXPERIMENTAL

A spray pyrolysis system consisting of a droplet generator with 6 ultrasonic vibrators of 1.7 MHz, a quartz reactor, and a particle collector was used to prepare hollow and dense BAM particles. The length and inside diameter of the quartz reactor are 1,200 and 50 mm, respectively. The reactor temperature was fixed at  $900\ ^\circ\text{C}$  and the flow rate of air used as a carrier gas was 45 l/min.

Two different spray solutions were prepared in order to control the morphology of BAM particles. A nitrate aqueous solution denoted as 'NS' was obtained by only dissolving aluminum, barium, magnesium, and europium nitrate salts in purified water. Also, an aluminum polycation solution denoted as 'PS' was prepared by slowly adding  $\text{NH}_4\text{OH}$  to the nitrate aqueous solution (NS) in which the aluminum ions turn to polycations of  $(\text{Al}_x(\text{OH})_y(\text{H}_2\text{O}))^{3x-y}$ , where  $x$  and  $y$  depend on the concentration of aluminum nitrate and pH of the solution [Brinker and Scherer, 1990]. The total salt concentration was changed from 0.05 to 2 M. In the 'NS' solution, the maximum concentration obtainable for all components was limited to 0.7 M because the solubility of Ba nitrate precursor is very low as 3.9 at  $20\ ^\circ\text{C}$ . So, over 0.7 M, some of the Ba nitrate added was precipitated. As a result, an accurate BAM composition will not be achieved. In the 'PS' solution, the aluminum ions which are a majority component of BAM phosphor, exist as a 'polycation'. Then, the distance between the components such as Al, Ba, Mg, and Eu is elongated as shown in Fig. 1 schematically displaying the states of NS and PS solution. Accordingly, more Ba nitrate can be dissolved. So, the obtainable maximum concentration was increased up to 2 M.

The concentration of Eu activator was fixed at 10% in molar ratio with regard to barium element. All as-prepared particles were reduced at  $1,400\ ^\circ\text{C}$  for 2 hr flowing 5%  $\text{H}_2/\text{N}_2$  mixture gas for crystallization and activation of divalent europium. The crystal phase of prepared BAM particles was analyzed by an X-ray diffraction pattern (RIGAKU DMAX-33). The morphology of BAM particles before

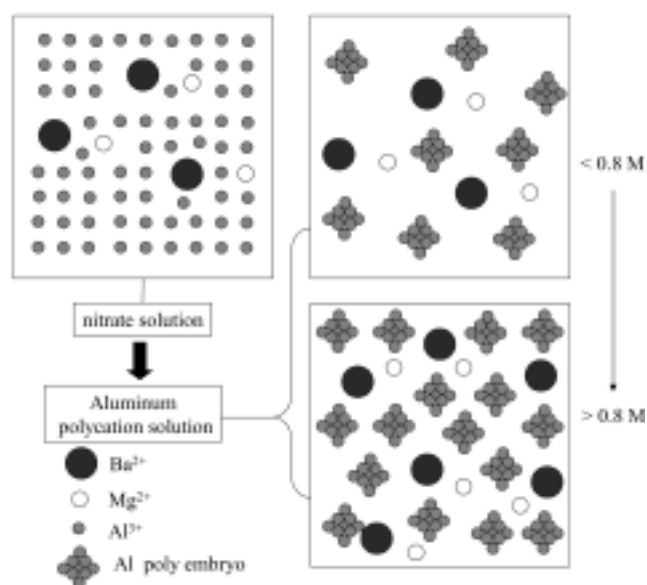


Fig. 1. Schematic diagram displaying the state of spray solutions.

and after the post heat treatment was observed by scanning electron microscopy (SEM, PHILIPS XL 30S FEG). In this work, the arithmetic mean size was calculated from individual particles observed in SEM photos and taken as the average particle size. The photoluminescence spectra of the BAM particles were measured under the illumination of vacuum ultraviolet (147 nm) emitting from Kr lamp.

## RESULTS AND DISCUSSION

When the phosphor powders are prepared by a spray pyrolysis process, the particle morphology strongly depends on the mechanism of particle formation, which is highly related to the drying condition and solution properties such as concentration, solubility of salts used, and concentration gradient in a droplet. In most cases, the spray pyrolysis process produces hollow-structured particles because the salt concentration at the surface of a droplet first reaches a critical supersaturation point due to the fast evaporation of water. As a result, a surface shell initially forms and gradually grows until all water is evaporated. On the contrary, dense morphology can be obtained when a volumetric precipitation or gelation takes place in a whole droplet during the evaporation step. Fig. 2 shows SEM photos of BAM particles prepared by the spray pyrolysis using the solution NS of which the total concentration was varied from 0.05 to 0.7 M. All as-prepared BAM particles had spherical shape. If the as-prepared particles have a dense structure, the spherical shape should be maintained even after the heat treatment at high temperature, which was  $1,400\ ^\circ\text{C}$  in this work. As shown in Fig. 2, however, the BAM particles prepared from the 'NS' solution lost their sphericity and agglomerates were produced by the heat treatment because they have a hollow structure. The agglomeration was getting severer and the particle shape turned to the plate-like shape as the particle size was reduced.

In order to produce dense BAM particles, the spray solution, PS, was prepared by chemically modifying the NS solution with  $\text{NH}_4\text{OH}$ . As-prepared BAM particles from the 'PS' solution had a spherical

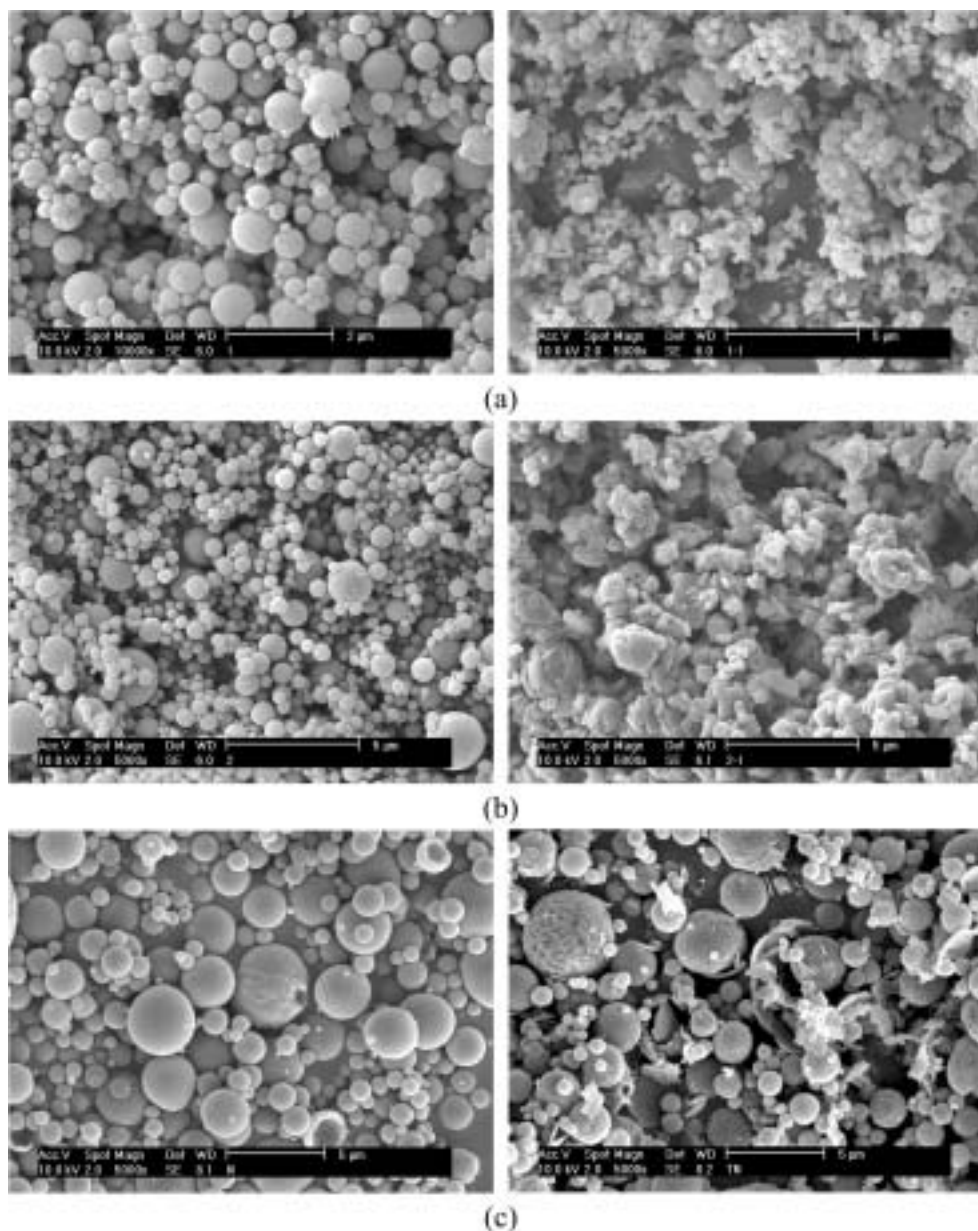


Fig. 2. BAM particles before (left) and after (right) the post heat treatment; (a) 0.05 M, (b) 0.1 M and (c) 0.7 M.

shape as shown in Fig. 3, which displays the SEM photos of BAM particles prepared at several concentrations. After the post treatment at 1,400 °C, high agglomeration between particles was observed at the low concentration of 0.05 M. When the concentration of the spray solution was greater than 0.1 M, however, there was no significant agglomeration. Also, the spherical shape was maintained even after the heat treatment. It is notable that the BAM particles have completely spherical shape when the concentration is higher than 1 M. This result supports that the as-prepared BAM particles using the 'PS' solution have a dense structure. So, we confirmed that the modification of aqueous nitrate solution (NS) by  $\text{NH}_4\text{OH}$  changed the pathway of the particle formation. That is, the evaporation of water induces an increase in the concentration of polycations, which are quickly and volumetrically gelated without any local precipitation of solutes. As a result, the dense particles could

be obtained from the 'PS' solution.

In spray pyrolysis, the particle size can be directly controlled by the concentration of the spray solution. Under the assumption that the prepared particle is dense, the average particle size of BAM phosphor produced by the spray pyrolysis can be calculated by the following relation equation [Nedeljkovic et al., 1997]:

$$d_p = d_0 \left[ \frac{CM_w}{\rho_p} \right]^{1/3} = AC^{1/3} \quad (1)$$

where,  $d_p$  is the final obtained particle size,  $M_w$  the molecular weight,  $C$  the concentration of BAM,  $\rho_p$  the density of BAM, and  $d_0$  drop-let size. For both hollow and dense BAM phosphor, the average particle sizes were calculated from the SEM photos of as-prepared particles and displayed in Fig. 4 as a function of the concentration of each solution. The estimated average particle size monotonically

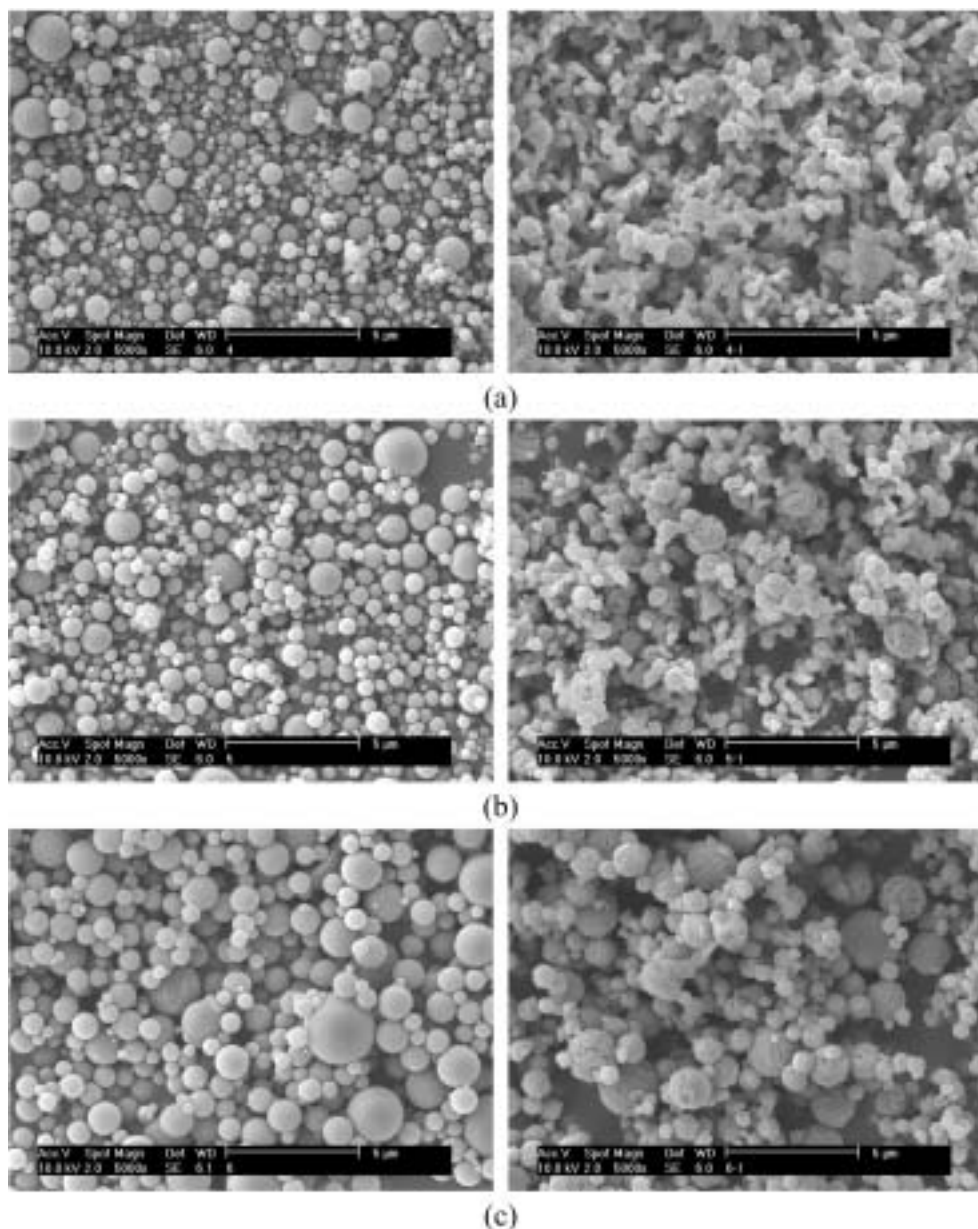


Fig. 3. SEM photos of BAM particles (left: as-prepared, right: heat treated at 1,400 °C) prepared from the polycation solution of (a) 0.05, (b) 0.1, (c) 0.7, (d) 1.0, and (e) 2.0 M.

increased with increasing the concentration. In this work, the average droplet size is fixed because only one type of ultrasonic vibrator with the frequency of 1.7 MHz was used. So, the coefficient  $A=d_0(M_w/\rho_p)^{1/3}$  should be constant and the particle size is supposed to have a linear relationship with  $C^{1/3}$  as long as the particle density is not varied. Fig. 4(b) shows the changes in the average particle size as a function of  $C^{1/3}$ . For the dense BAM particles, a linear relationship was well established between the average particle size and the concentration,  $C^{1/3}$ . In the case of hollow particles, however, the changes in the average particle size were not linear with respect to  $C^{1/3}$  due to the hollowness which makes the difference in the apparent bulk density ( $\rho_p$ ). Accordingly, the slope ( $A=d_0(M_w/\rho_p)^{1/3}$ ) was not constant. Also, the slope for hollow particles was steeper than that of dense particles, which indicates the shell density ( $\rho_p$ ) of

hollow particles is smaller than that of dense particles.

For hollow particles, the shell thickness was calculated by subtracting the radius of dense particle from that of hollow one and displayed in Fig. 5. It was found that the shell of the hollow particles was thickened with increasing the concentration. This result means that in a droplet the concentration gradient of salts induced by the evaporation of water becomes reduced as the concentration increases. So, more filled morphology could be achieved if the salt concentration is very close to the critical supersaturation point. Actually, the particles prepared from the NS solution of 0.7 M showed less agglomeration compared with the other concentration due to the thickened shell layer which has a resistance against the thermal deformation caused by the post treatment at a high temperature.

Fig. 6 shows the emission spectra of dense and hollow BAM par-

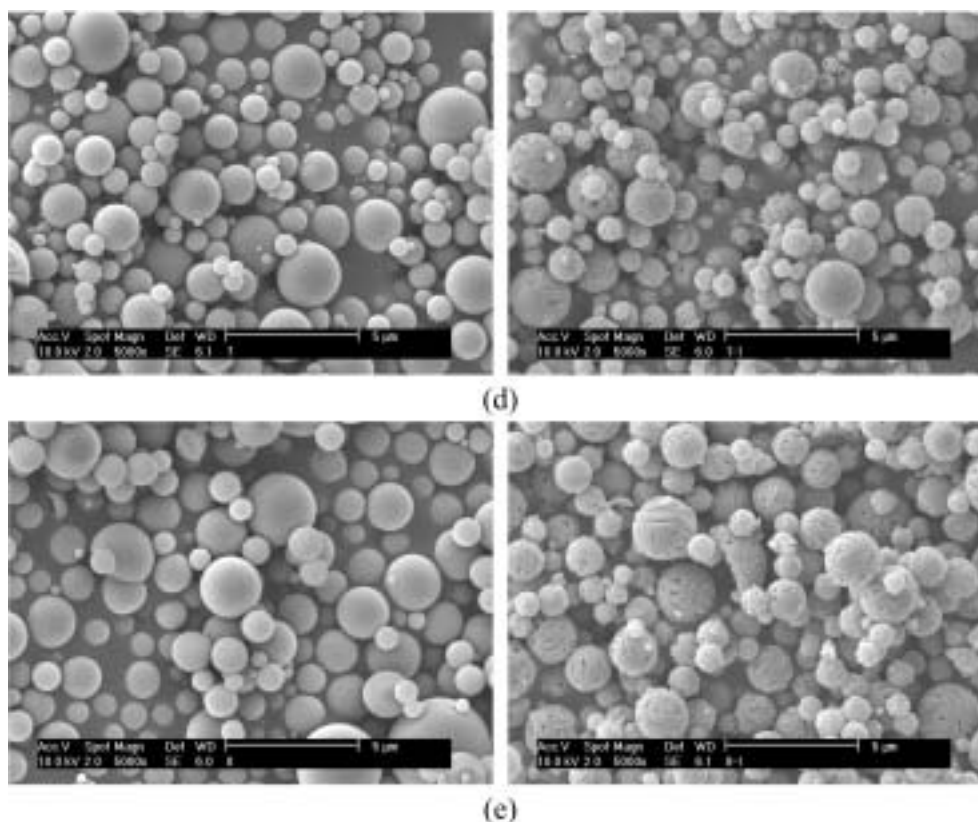


Fig. 3. Continued.

ticles prepared at the solution concentration of 0.7 M. A wide spectrum with a maximum peak at 450 nm is due to the 5d-4f transition of  $\text{Eu}^{2+}$ . The dense particles prepared from the 'PS' solution had higher intensity than that of the hollow. From this result, it was surmised that better distribution of  $\text{Eu}^{2+}$  activator in the BAM matrix is achieved in dense particles and less agglomeration or fragmentation in dense particles is helpful for the enhancement of the photoluminescence intensity. The relative emission intensity for all prepared BAM particles which were thermally treated at 1,400 °C for 3 hrs under a reducing atmosphere is shown in Fig. 7. For the hollow particles, the emission intensity monotonically increased with increasing average particle size. However, no significant change in the emission intensity was observed for the dense particles except for the smallest particle prepared at the lowest concentration (0.05 M). There are several changes caused by the reduction of the particle size:

1. The light absorption is reduced and the scattering increases.
2. The specific surface area increases. Accordingly, there are more surface defects and surface-bonded dangling bonds which easily induce the luminescence quenching.
3. The void space between the particles becomes smaller and the propagation of incident light into the phosphor layer is hindered. As a result, the thickness of the phosphor layer to which the incident light can reach is shortened. Then, the phosphor particles in the skin layer are supposed to absorb most of the incident light. In addition, the visible light emitted from the phosphors in the sublayer cannot escape out of the inner layer if the open spaces become much smaller

than the wavelength in the visible range.

Actually, the scattering coefficient is highly related to not only the particle size but also the size distribution. According to He et al. [2003], the scattering coefficient ( $k_s$ ) can be expressed as follows:

$$\ln k_s = \ln A - \ln D_p + 0.5 \ln^2 q \quad (2)$$

where  $A$  is a experimental constant,  $D_p$  the average particle size, and  $q$  the standard deviation of normal particle size distribution. The light scattering is getting larger as the particle size becomes smaller and the size distribution broadens. Accordingly, the light absorption of phosphor particles is reduced in proportion to the particle size, which may lead to decreasing the luminescence efficiency. Also, the phosphor particles with a clean surface and a spherical shape are supposed to have less light scattering than the irregular-shaped particles in which more surface defects or dangling bonds can exist. Therefore, it was speculated that the spherical BAM particles prepared from the 'PS' solution showed higher photoluminescence intensity than the hollow particles prepared from the 'NS' solution.

To better understand the reason why the luminescent intensity is decreased as the particle size becomes smaller as shown in Fig. 7, it was supposed that the phosphor particles are hexagonally stacked as a film type on a substrate as shown in Fig. 8. If the particle size is reduced in half, the number density of particles is increased twice. At a fixed space, the portion of the light passing through the void space constructed by three particles is getting smaller in proportion to  $D_p^2$  (radius). So, most of the incident light is absorbed by the par-

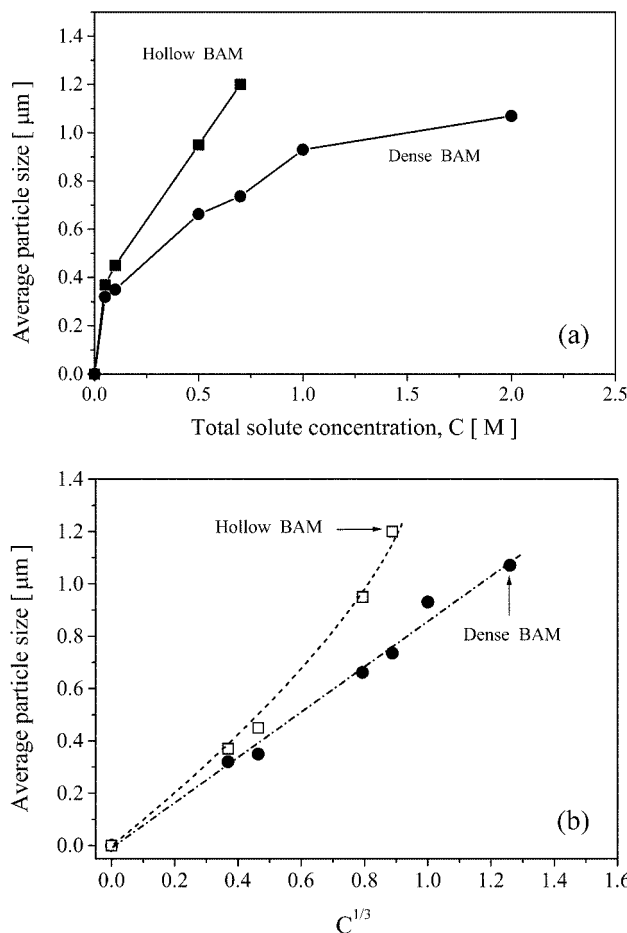


Fig. 4. Average particle size of BaMgAl<sub>10</sub>O<sub>17</sub> prepared by spray pyrolysis as a function of the solution concentration; C (a) and (b) C<sup>1/3</sup>.

ticles on the surface layer and some portions can propagate into the next inner phosphor layer. Thus, reducing the particle size seems to increase the reflection of the incident light and reduce the number of phosphor layers which can interact with the incident light. The effect of the particle size on the luminescent intensity can be expected by roughly calculating the change in the number density of Eu<sup>2+</sup> ions for the particles placed in the surface monolayer which is most intensively interacting with the incident light. For an ideal situation in which there is no concentration quenching, the emission intensity should be proportional to the number ( $N_a$ ) of Eu<sup>2+</sup> existing within the layer to which the VUV light reaches. This number  $N_a$  can be directly calculated by multiplying the initial Eu<sup>2+</sup> concentration ( $C_{a0}$ ) by the volume ( $V_{pat}$ ) where the incident light reaches.

$$N_a = V_{pat} \times C_{a0} = \frac{4\pi}{3} [D_p^3 - (D_p - l_p)^3] \times C_{a0} \quad (3)$$

In this work, the initial Eu<sup>2+</sup> concentration ( $C_{a0}$ ) was not changed. Accordingly, the number of Eu<sup>2+</sup> with varying the particle size is in proportion to the volume penetrated by the light. Consider two kinds of particles which have the radius of  $D_0$  and  $D_n$ , respectively, as shown in Fig. 7. If the penetration depth ( $l_p$ ) of VUV light is smaller than the radius of a given particle, the penetration volumes in the surface phosphor layer of a fixed space are calculated by the follows:

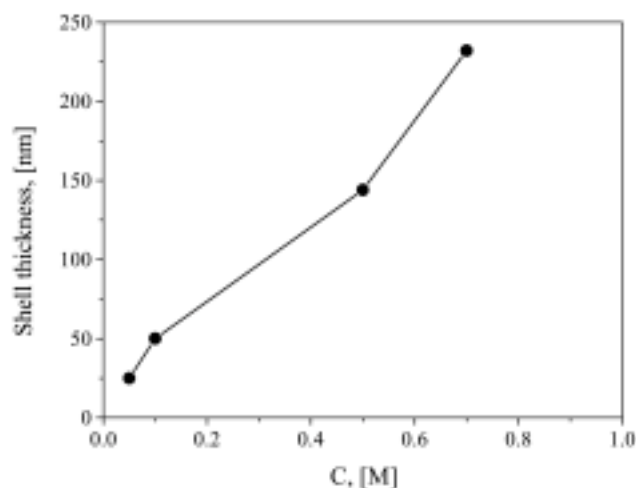


Fig. 5. Shell thickness of hollow BaMgAl<sub>10</sub>O<sub>17</sub> particles prepared from the aqueous nitrate solution as a function of the total concentration of spray solutions.

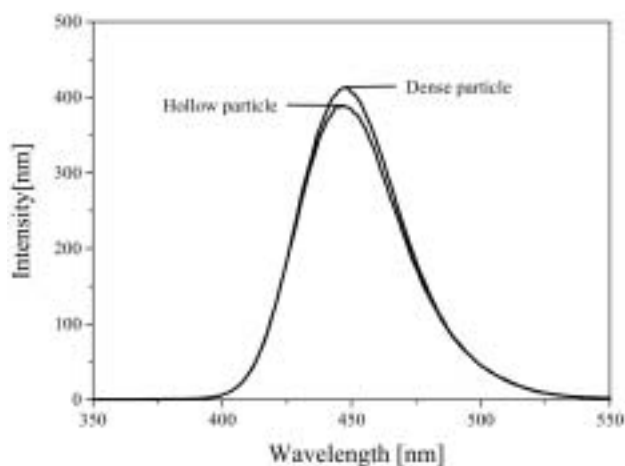


Fig. 6. Emission spectra of hollow and dense BAM particles under VUV excitation.

$$V_0 = \frac{4}{3}\pi \times [D_0^3 - (D_0 - l_p)^3] \quad (4)$$

$$V_n = \frac{4}{3}\pi \cdot n^k \times [D_n^3 - (D_n - l_p)^3] \quad (5)$$

$$D_0 = n \cdot D_n, (n \geq 1) \quad (6)$$

When  $l_p < D_0 \rightarrow k=2$ , that is, the number of particles increases 4 times as the particle size is reduced in half. Then, the volume ratio ( $\alpha$ ) between particles with the size of  $D_0$  and  $D_n$  is the following:

$$\alpha = \frac{V_n}{V_0} = \frac{n^2 \times [D_n^3 - (D_n - l_p)^3]}{(nD_n)^3 - (nD_n - l_p)^3} = \frac{1}{n} \cdot \frac{D_n^3 - (D_n - l_p)^3}{D_n^3 - \left[D_n - \frac{l_p}{n}\right]^3} \quad (7)$$

Eq. (7) gives information about the change of the relative emission intensity as the particle size changes because of  $\alpha = I_n/I_0$ . If the penetration depth is greater than the particle size, the calculation of  $V_n$  is not limited to the surface monolayer. A large portion of the incident light penetrates the surface layer and interacts with the particles



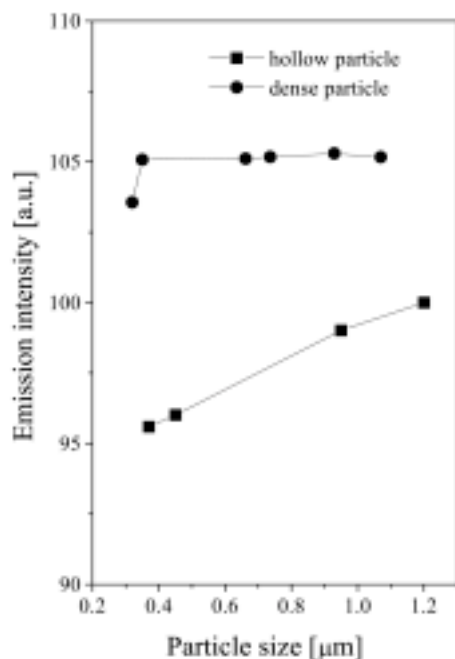


Fig. 7. Emission intensities of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$  particles as a function of the average particle size.

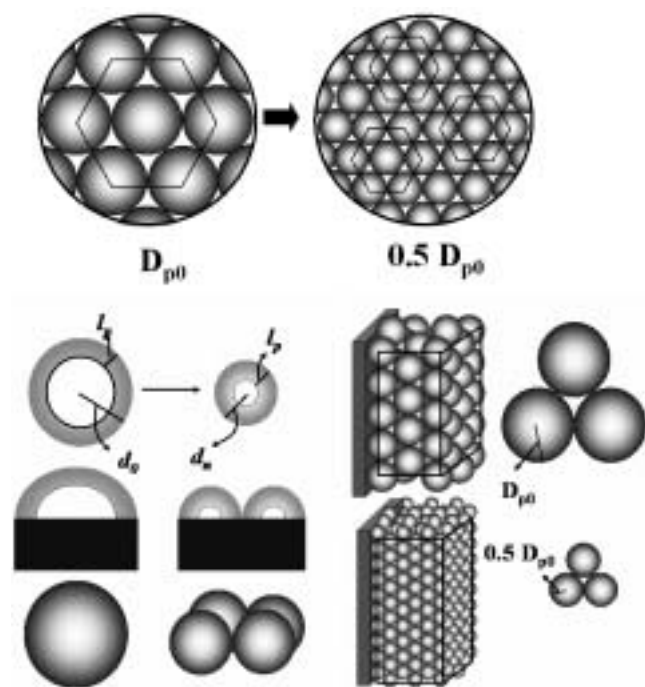


Fig. 8. Schematic diagram for a simulated phosphor layer for BAM particles with different particle size.

placed in the sublayer. Then, the light always can be absorbed by a whole phosphor layer with a penetration thickness of  $t$  regardless of the particle size. In this case, the space formed between neighboring particles becomes an important factor. That is, the light in a visible range might not escape from the inner layer if the void space between particles is much smaller than the wavelength. In this work, this situation was excluded because actually for all phosphor parti-

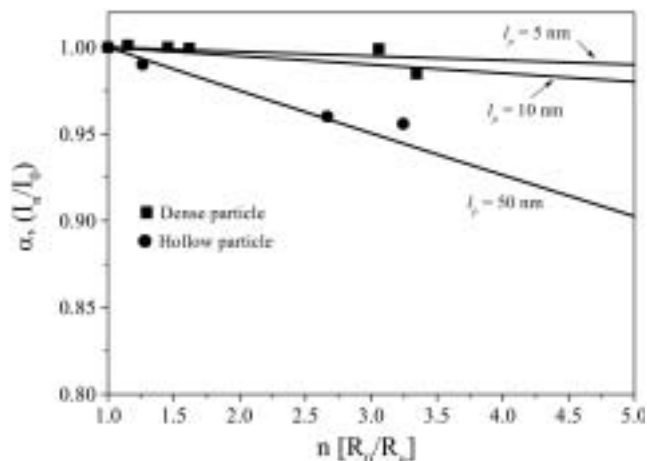


Fig. 9. Volume ratio ( $\alpha$ ) calculated from Eq. (6) and relative emission intensity ( $I/I_0$ ) as a function of particle size ( $n$ ); wherein,  $I_0$  is the emission intensity of BAM particles prepared at the highest concentration of 'NS' and 'PS' solution and  $I_n$  is the emission intensity at each concentration. Increasing the number  $n$  means a reduction of particle size.

cles the penetration depth of VUV light is not more than several dozens nanometer.

Fig. 9 shows the value of  $\alpha$  calculated by Eq. (7) at several penetration depths ( $l_p$ ). Also, the experimental values are displayed together in Fig. 9. The photoluminescence intensity tends to decrease as the particle size is getting smaller. The slope of  $\alpha$  becomes steeper with increasing the penetration depth, which means that the phosphor materials with larger penetration depth are more sensitive to the change of particle size. The changes of  $\alpha$  can be in agreement with that of experimental results by adjusting the penetration depth as shown in Fig. 9. For the hollow and dense particles, the adjusted penetration depth was within 50 nm. The hollow particles had larger penetration depth than the dense particles. From the above discussion, it was deduced that the penetration depth of VUV light is very small at nanometer scale, and the lesser sensitivity of the dense particles compared with the hollow particles to the change of particle size as shown in Fig. 7 is due to the shorter penetration depth.

Given that the photoluminescence is the result of the transition of photoelectrons from the excited state to the ground state of activators, the luminescence efficiency is highly related to the destiny of photo-excited electrons. The bulk or surface defects can consume the photo-excited electrons resulting in quenching of the fluorescence. Higher crystallinity means higher ordered structure and less bulk defect which acts as a quenching site consuming excited photoelectrons without the radiation. In general, the phosphor particles are treated thermally at high temperature to obtain high crystalline after being prepared. So, there are many reports that the photoluminescence intensity is gradually increased with increasing the treatment temperature as long as the bulk crystal structure is not destroyed. From this point of view, the crystallite size was considered as the critical variable affecting the photoluminescence intensity of BAM particles prepared by spray pyrolysis, because it is acceptable that larger crystallite size means more ordered structure and fewer bulk defects as long as the domain growth is induced by a thermal treatment. So, from the X-ray diffraction (XRD) analysis

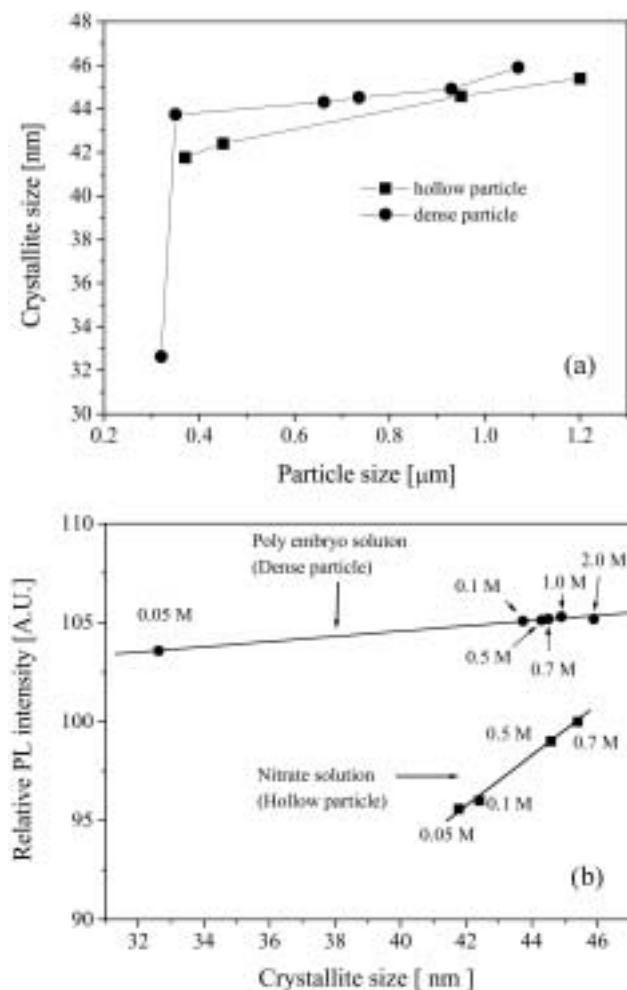


Fig. 10. Changes in the crystallite size as a function of average particle size (a) and the relative photoluminescence intensity of BAM particles as a crystallite size (b).

for the prepared particles the crystallite size was calculated by the Scherrer equation and displayed in Fig. 10(a) as a function of particle size. All dense particles had larger crystallite size than that of the hollow ones except for the smallest particles prepared at a solution concentration of 0.05 M. This result supports that the dense particles have higher crystallinity than that of the hollow particles. Also, it is no doubt that the spherical particles have cleaner surface compared to the hollow one. A more notable result was found in the linear relationship between the crystallite size and the photoluminescence intensity of each hollow and dense particle as shown in Fig. 10(b). Therefore, it was concluded that increasing the crystallite size is one way to suppress the decrease of photoluminescence intensity by the reduction of particle size. At a similar crystallite size, the dense BAM particles with spherical shape had higher photoluminescence intensity than that of hollow particles even though the average size of dense BAM particles was smaller than the hollow ones. This result says that the particle morphology becomes much more important factor in improving the photoluminescence intensity. So, we concluded that enlarging the crystallite size as well as making the particle dense and spherical is very important to improve the luminescent intensity of BAM particles with a fine size

of less than 1 μm.

## CONCLUSIONS

Spray pyrolysis was applied to prepare hollow and dense BaMg Al<sub>10</sub>O<sub>17</sub>: Eu<sup>2+</sup> (BAM) phosphor particles and their luminescent properties were investigated under vacuum ultraviolet (VUV) excitation with varying the average particle size. The luminescent intensity was generally reduced with decreasing the particle size as long as the penetration depth of VUV was small enough compared to the particle size and greatly affected by the morphology of BAM particles. As the particle size was reduced, the photoluminescence intensity of hollow particles was gradually decreased, whereas the dense particles had no significant change. It was found that the crystallite size of BAM particles plays an important role in determining their luminescent intensities as varying the particle size. That is, the larger crystallite size led to the higher photoluminescence intensity. Therefore, it was concluded that suppressing the formation of a hollow structure and simultaneously increasing the crystallinity is essentially needed to obtain high luminous BAM phosphor particles with a spherical shape and fine size of less than 1 μm when they are prepared by the spray pyrolysis process.

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