

## Photoluminescence and morphology of flux grown BAM phosphor using a novel synthesis method

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Small Eu<sup>2+</sup> doped barium magnesium aluminate (BAM : Eu) phosphor particles with a narrow size distribution were prepared using a flux-assisted liquid phase precursor (LPP) method. XRD showed that the crystallinity of BAM particles increased significantly with an increase in the boric acid concentration, as a flux, and the firing temperature. According to FESEM, the phosphor particles produced without the flux and fired at 1450 °C had a rod type morphology, 60-100 nm in diameter and 500-700 nm in length. The morphology of the phosphor particles transformed from a rod to a hexagonal type with a concomitant increase in the particle size (from ~1 to 2 μm) when 1, 2 and 5 wt% of boric acid was added. The photoluminescence intensity of phosphor particles was also influenced by the addition of the flux due to the enhanced particle size, crystallinity and activator ion distribution.

**Key words:** Liquid phase precursor method, boric acid, phosphor, rod shaped morphology.

### Introduction

Blue emitting Eu<sup>2+</sup> doped barium magnesium aluminate is an important metal oxide phosphor for lighting and display applications on account of its high emission efficiency and color purity. The size and morphology of phosphor particles are essential parameters for the development of new luminescent devices. For display applications, a high resolution can be obtained by integrating millions of pixels into a small area, and the pixel efficiency can be enhanced by preventing the scattering of vacuum ultraviolet light and enlarging the discharge space. Therefore, each pixel should be densely packed with phosphor particles in a thin layer without porosity. This can be achieved using very small phosphor particles with a narrow size distribution [1-5].

Until now, a conventional solid-state route has been used for the synthesis of multi-component metal oxide particles. Although highly crystalline and pure particles are produced by conventional solid state routes, the final product particles sizes are large (~3 or 5 μm) and they are not uniform due to the requirement of a high synthesis temperature [6]. In this case, a fluxing material plays an important role to obtain smaller particles with better crystallinity by decreasing the synthesis temperature [7]. It was reported that, not only the particle size and crystallinity but also the morphology can be controlled in the presence of flux [8, 9]. Here, a liquid phase precursor (LPP) method

was used for the synthesis of a BAM phosphor. According to this method, it is expected that smaller particles with better crystallinity can be obtained since a solution of raw materials is used as the starting material in contrast to micrometer size solid powders in the conventional solid state route and porous structured cellulose fibers prevent aggregation [10-12].

In this study, our aim is to obtain smaller particles with better crystallinity at a low temperature by using a LPP method and control the morphology with boric acid flux. Here, we report that rod and hexagonal shaped phosphor particles with a narrow size distribution were prepared by changing the firing temperature and flux concentration and also the effect of the boric acid flux on the optical properties.

### Experimental Procedure

Cellulose pulp was used as a template for the formation of the BAM particle seeds. A solution of each metal salt was prepared with deionized water and consisted of a 10 wt% barium chloride (BaCl<sub>2</sub>·6H<sub>2</sub>O, ≥ 99%), 20 wt% magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ≥ 99%), 20 wt% aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ≥ 99%) and 20 wt% europium chloride (EuCl<sub>3</sub>·6H<sub>2</sub>O, ≥ 99%). Aqueous solutions of metal salts were mixed corresponding to the mol ratio of Ba<sub>0.88</sub>Mg<sub>0.93</sub>Al<sub>10</sub>O<sub>16.96</sub> : Eu<sub>0.1</sub> and 100 g of cellulose pulp was impregnated into 100 ml of the resulting mixed solution. This specimen did not contain a flux material. For the preparation of flux-containing specimens, 10 wt% boric acid (H<sub>3</sub>BO<sub>3</sub>, < 99%) was dissolved in 100 ml of deionized water, and 1, 2, and 5 wt% of this solution was added to the mixed solution of metal salts. All specimens

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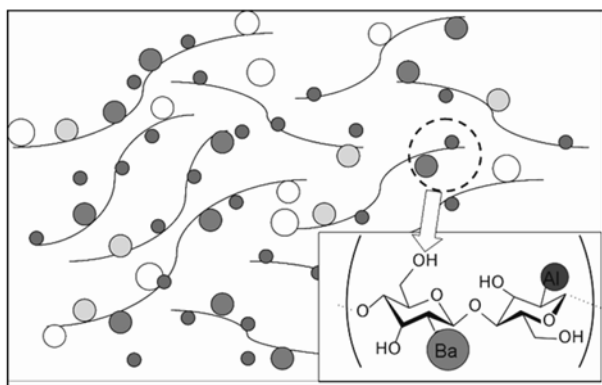
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were dried at 80 °C in an oven. The impregnated pulp was calcined at 800 °C to evaporate the remaining organic products during cellulose decomposition. The calcination conditions were as follows: heating from room temperature to 800 °C at a heating rate of 573 K/h<sup>-1</sup>, the temperature maintained at 800 °C for 1 h and cooling to room temperature. After this, the calcined powder was heated from room temperature to 1000, 1200 and 1450 °C at a heating rate of 573 K/h<sup>-1</sup> in a 5% H<sub>2</sub>/95% N<sub>2</sub> atmosphere.

The emission and excitation spectra were measured at room temperature using a xenon lamp (500 W) as a source for a PL spectrophotometer (PLE/PL Drasa PRO 5300, Korea) over the range of 350–700 nm, and 220–380 nm. Powder X-ray diffraction (XRD, Cu K $\alpha$ , 30 kV, 100 mA, Rigaku) was used to determine the crystalline phases of the synthesized specimens. The surface morphology and crystallinity of the resulting particles were observed by scanning electron microscopy (FESEM, XL-30, Philips) and high resolution transmission electron microscopy (HR-TEM, JEOL 300 kV).

## Results and Discussion

Fig. 1 shows a schematic diagram of a possible mechanism of particle formation in cellulose pulp using the LPP method. In this method, cellulose pulp was used to synthesize the nanoparticles due to the distinct porous structure of cellulose fibrils. It is expected that these pores may allow physical absorption of the metal ions contained in solution into the cellulose inner space. Most of the metal ions incorporated were bound to the cellulose chains probably via electrostatic (ion-dipole) interactions because the electron-rich oxygen atoms of the polar hydroxyl groups on the cellulose chains are expected to interact with the electropositive metal ions [10–12]. Subsequently, particle formation began on the cellulose fibrils and its cavities when the impregnated cellulose pulp was fired. In this study, various morphologies, such as spherical, rod, and hexagonal types, were obtained depending on the firing temperature and flux concentration. These particle morphologies can be explained by considering the pyrolysis mechanism of cellulose. Cellulose is an organic compound with the



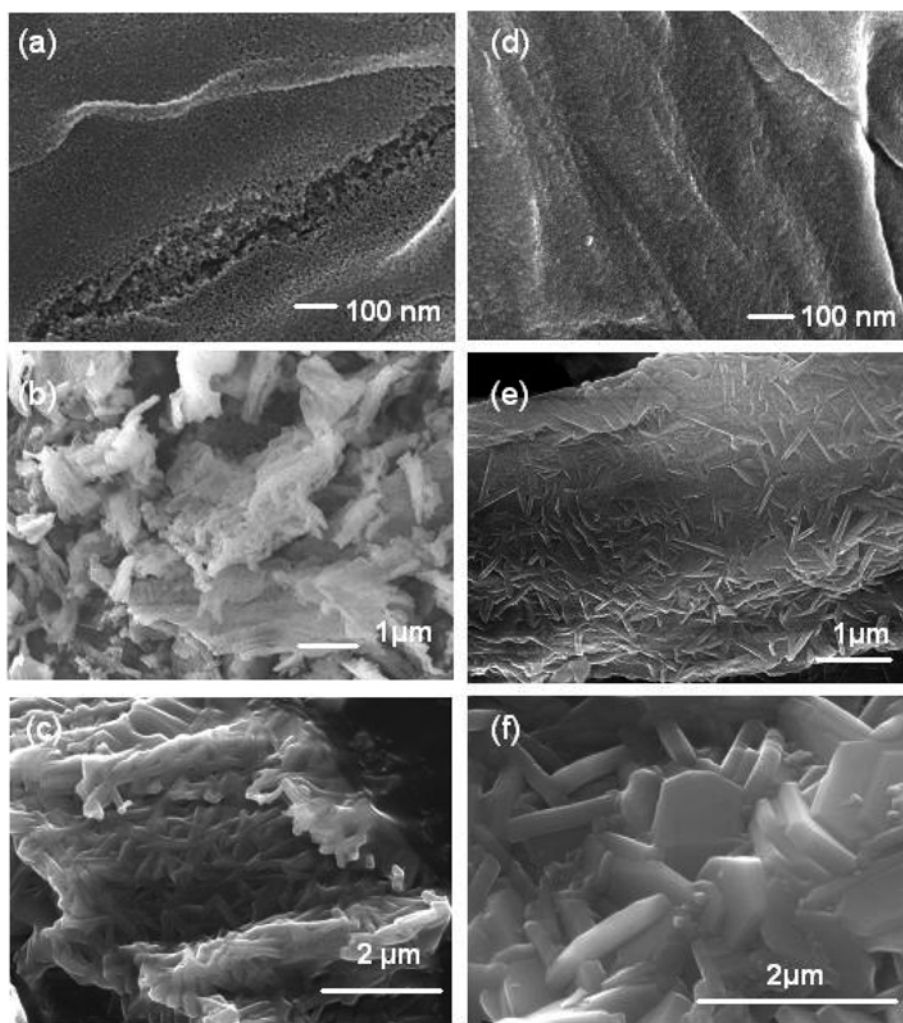
**Fig. 1.** Schematic diagram of particle formation on the cellulose fiber cell wall.

formula, (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, which is formed by linking D-glucose molecules with a  $\beta(1 \rightarrow 4)$  glycosidic bond in a well-ordered repeating unit. Generally, the pyrolysis of cellulose occurs in several stages and results in the formation of char and gas species, such as H<sub>2</sub>O, CO or CO<sub>2</sub>. These stages involve the desorption of physically combined water (~150 °C), dehydration of cellulose (150–240 °C), radical cleavage of the main chains and the scission of C–O or C–C bonds (240–400 °C), and aromatization and polymerization (> 400 °C) [13–15]. A large weight loss accompanying the release of gaseous species during radical cleavage leads to rapid shrinkage of the cellulose fibers. The metal oxide particles attached to functional groups on the cellulose chain diffuse towards neighboring particles. This can explain the rod-shaped morphology due to the oriented aggregation of metal oxide particles in one dimension during fiber shrinkage. The cellulose pulp evaporates completely at higher temperatures and particles grow in free space without restriction. This results in a transformation of the particle morphology to a hexagonal shape due to the hexagonal crystal system of BAM.

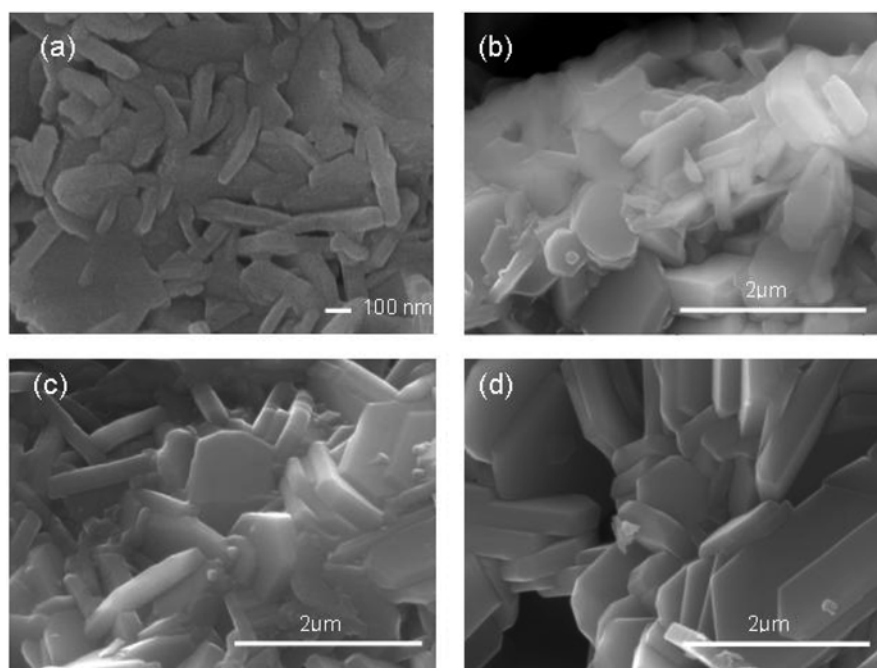
Fig. 2 shows FE-SEM images of the phosphor particles fired at various temperatures (1000, 1200 and 1450 °C). While the left hand side (Fig.2(a), Fig.2(b), and Fig.2(c)) exhibits the morphology of specimens not containing flux, the right hand side (Fig.2(d), Fig.2(e), and Fig.2(f)) were taken on specimens having 2 wt% H<sub>3</sub>BO<sub>3</sub> flux. Approximately 10 nm spherical grains were obtained at 1000 °C (Fig.2(a)) and (d)). With an increase in the process temperature from 1000 to 1200 °C the particle morphology transformed to a rod shape and the particles size increased to ~60 nm in diameter and 500–700 nm in length and ~100 nm in diameter and 600–800 nm in length for flux containing and fluxless specimens as shown in Fig. 2(b) and Fig. 2(e). When phosphor particles were prepared at 1450 °C, larger rod-shaped particles (~100 nm in diameter and 800–1  $\mu$ m in length) and micrometer-sized hexagonal plate-like particles were obtained as shown in Fig.2(c) and (f), respectively.

Fig. 3 shows FE-SEM images of the BAM particles fired at 1450 °C. Rod shaped particles, 50 nm in diameter and 300–500 nm in length, were obtained without a H<sub>3</sub>BO<sub>3</sub> addition at 1450 °C, as shown in Fig. 3(a). Hexagonal shaped particles were obtained from all H<sub>3</sub>BO<sub>3</sub> containing specimens fired at 1450 °C. There was no significant difference in the particle size (~ 1  $\mu$ m) of the 1 and 2 wt% of boric acid containing specimens, as shown in Fig. 3(b) and (c). However, the particle size increased to 2  $\mu$ m when the flux concentration was increased to 5 wt% (Fig. 3(d)). It is expected that the addition of flux affected the particle size and morphology because a large amount of boron melts at low temperatures and produces a liquid interface between the crystal grains. This results in grain growth on the surface and promotes the formation of larger crystallites with a smooth surface [16].

In order to support this assumption, TEM and selected area electron diffraction (SAED) analyses of the BAM

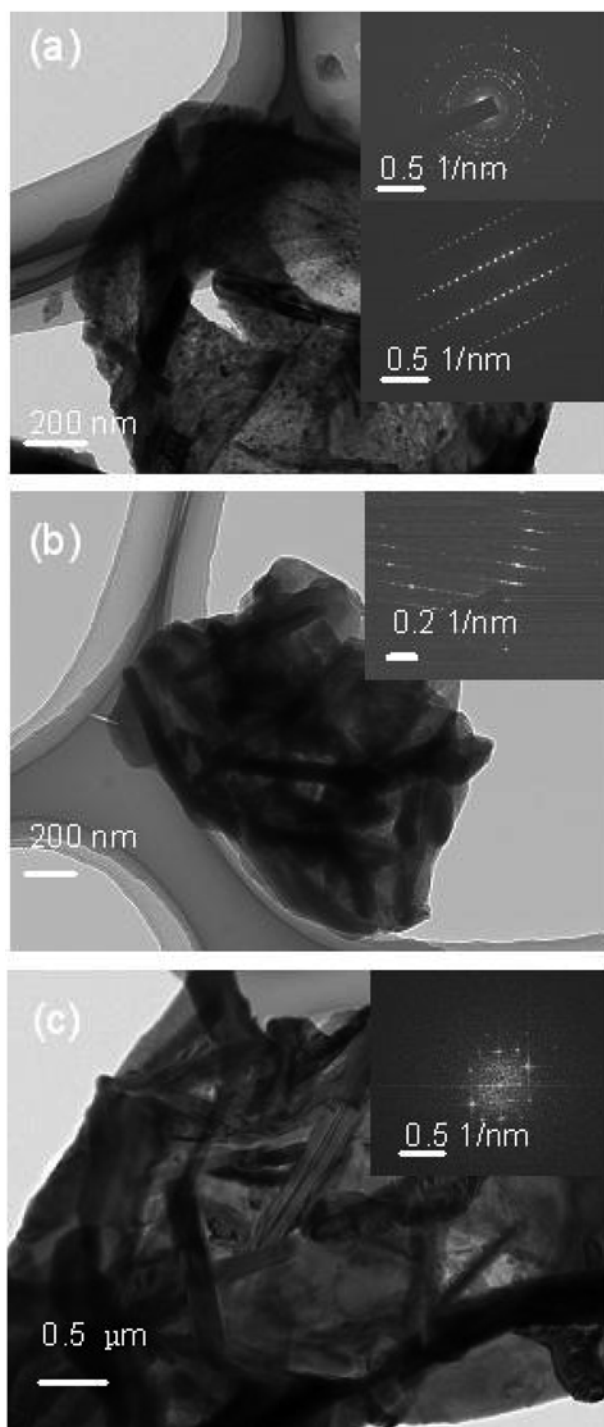


**Fig. 2.** FE-SEM images of BAM phosphor particles prepared at 1000, 1200 and 1450 °C with absence (left hand side) and presence (right hand side) of 2 wt% of H<sub>3</sub>BO<sub>3</sub> flux.



**Fig. 3.** FE-SEM images of BAM particles with the absence (a) and presence of 1 (b), 2 (c), and 5 wt% H<sub>3</sub>BO<sub>3</sub> (d).

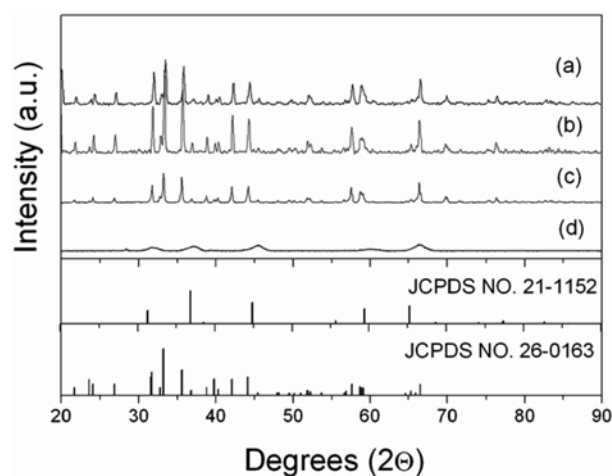
particles fired at 1000, 1200 and 1450 °C without a  $\text{H}_3\text{BO}_3$  addition were carried out, as shown in Fig. 4. TEM revealed that the crystallinity of the particles increased with an increase in the temperature from 1000 to 1200 °C, and the morphology transformed from a rod shape to a hexagonal shape. At 1200 °C, rod-shaped crystalline particles (the darker part) and spherical-shaped grains were observed, as shown in Fig 4(a). The SAED patterns of this specimen



**Fig. 4.** TEM analyses and SAED patterns of the resulting particles obtained at (a) 1000, (b) 1200 and (c) 1450 °C without a  $\text{H}_3\text{BO}_3$  addition.

were obtained in two different parts of this specimen. A ring pattern (upper inset) was observed with spherical amorphous grains and a spot pattern (lower inset) was observed with the rod shaped particles. The number of rod shaped particles increased significantly as the temperature was increased from 1200 to 1450 °C (Fig 4(b)). This morphological transformation can be assigned to the oriented aggregation of polycrystalline particles in one dimension. High resolution TEM analysis of the rod shaped particles revealed similar features with an interlaced structure of cellulose fibers. This suggests that during the calcination process, dense BAM spherical grains form along the cellulose chains via functional groups diffused through the neighboring particles until the cellulose template is completely evaporated. The spherical grains, which were formed in the cavities, diffuse through the side part of the rod shaped particles as the temperature is increased further to 1450 °C. This may allow the formation of larger hexagonal crystallites, and might be a plausible explanation for the rod and hexagonal shaped morphology.

The influence of the firing temperature and boric acid addition on the crystallinity was examined by XRD. Fig. 5 shows the XRD patterns of BAM particles fired at different temperatures (1000, 1200, and 1450 °C). All the main diffraction peaks of the phosphor powders fired above 1000 °C were well indexed to a hexagonal structured  $\text{BaMgAl}_{10}\text{O}_{17}$  according to the JCPDS card (no. 26-0163). Fig. 5(a) and (b) shows the crystallinity of the BAM particles fired at 1450 °C in the absence and presence 2 wt% of boric acid, respectively. In this figure, the effect of boric acid in enhancing the particle crystallinity was confirmed with the higher peak intensity with no extraneous phase belonging to the boron content. Fig. 5(b)-(d) shows the particle crystallinity and purity at different processing temperatures. The crystallinity decreased with a decrease in the firing temperature, and no diffraction peaks belonging to barium magnesium aluminate were detected



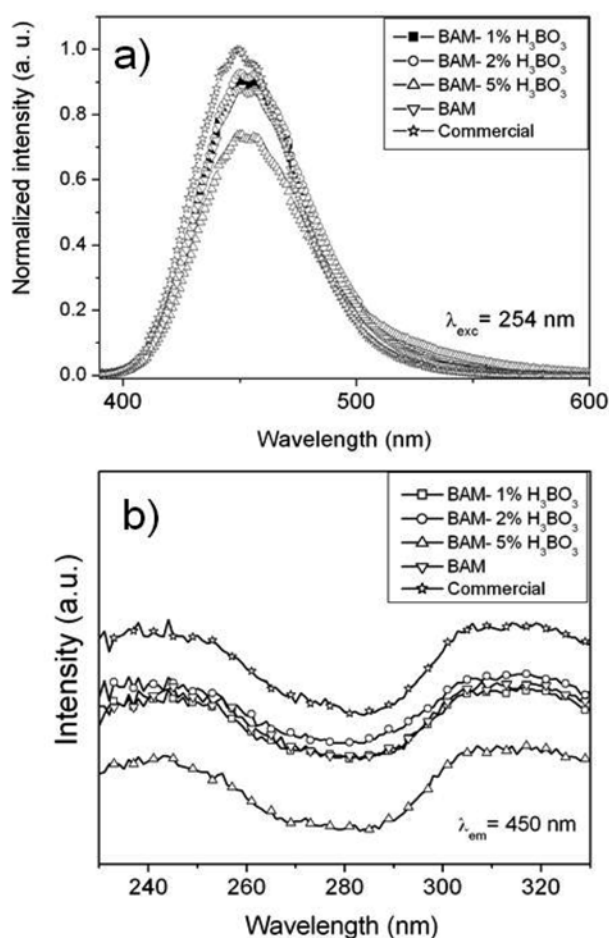
**Fig. 5.** The XRD pattern of the  $\text{Ba}_{0.88}\text{Mg}_{0.93}\text{Al}_{10}\text{O}_{16.96}:\text{Eu}_{0.1}$  specimens prepared at 1450 °C with absence (a) and presence (b) of 2 wt% of flux. The crystallinity of 2 wt% of flux containing specimens at lower temperature such as (c) 1200 and (d) 1000 °C.

at 1000 °C. At this temperature, all the main peaks were well matched with magnesium aluminate according to the JCPDS card (no.21-1152).

Apart from the efficiency of crystallization, boric acid has another function in controlling the particle size through its contribution to cellulose decomposition. The LPP method can be assumed to be a self combustion process due to the extra thermal energy released during cellulose decomposition. This thermal energy is reduced when boric acid is introduced into the reaction because boric acid and related flame retardant compounds decrease the dehydration temperature of cellulose and enhance the formation of char, water and other intermediate products instead of flammable volatiles [16]. Consequently, in the case of the specimens with boric acid additions, there was less explosive gases released, resulting in a larger particle size.

Fig. 6 shows the PL emission (a) and excitation (b) spectra of the BAM specimens fired at 1450 °C in the absence and presence 1, 2, and 5 wt% of boric acid. Fig. 6 (a) shows the emission spectra of a commercial BAM and these specimens under excitation of 254 nm at room temperature. The commercial BAM phosphor has a broad emission band with a maximum of approximately 450 nm corresponding to the blue emission in the visible

region of the electromagnetic spectrum. This broad band originates from the transitions of  $\text{Eu}^{2+}$  ions from the  $4f^65d^1$  excitation state to the  $4f^7$  ground state. However, the peaks for all the BAM specimens shifted slightly towards a longer wavelength. This composition-dependent shift was reported to depend on the excesses or deficiencies of  $\text{Ba}^{2+}$  ions. In other words, the crystal structure may distort and the band position can shift in both directions. This can also lead to a slight decrease in the observed maximum emission intensity due to the crystal field of  $\text{Eu}^{2+}$  activator ions [17-20]. The 1 wt% boric acid containing specimen had a slightly higher PL emission intensity than the specimen prepared with no flux, as shown in Fig. 6(a). The observed increase in emission intensity originated from the larger crystallite size of the 1 wt% flux containing specimen. The PL intensity increased further when the flux concentration was increased to 2 wt%, even though the particle size and crystallinity of the 1 and 2 wt% of boric acid containing specimens were similar. This improved emission intensity may have originated from the amount of activated  $\text{Eu}^{2+}$  ions involved in luminescence. When  $\text{H}_3\text{BO}_3$  was introduced into the reaction, it produced a liquid interface between the neighboring particles to promote diffusion leading to rapid crystallization and a uniform activator ion distribution. The emission intensity decreased with an increase in the flux concentration to 5 wt%. The reason for this decrease may be due to the affect of boron on the crystal field or absorption of defect layers on the particle surface due to the extraneous product. During heat treatment, a small amount of B can become incorporated into the crystal structure through the Al sites because the diameter of a boron atom is smaller than an Al atom. The number of boron atoms on the Al sites should increase with an increase in the flux concentration. This will affect the crystal field of the surrounding  $\text{Eu}^{2+}$  and may cause a shift in the maximum peak position [20]. However, none of the specimens showed a peak shift towards a higher or lower energy regardless of the amount of  $\text{H}_3\text{BO}_3$  added. In addition, the band shape and width remained the same irrespective of the boron content. Therefore, boron is not necessarily incorporated into the crystal to affect the crystal field. When the flux concentration was increased to 5 wt%, the boric acid produced a defect layer originating from the extraneous product remaining from cellulose decomposition. This defect layer may be the reason for the loss of emission intensity. Fig. 6(b) shows the excitation spectra of the commercial and BAM specimens synthesized in this study monitored at 450 nm. The spectral shape of all the specimens was similar and there were two peaks located at ~240 and 320 nm, corresponding to excitation of the 5d levels of  $\text{Eu}^{2+}$  ions.



**Fig. 6.** The emission (a), and excitation (b) spectra of the BAM specimens.

## Conclusions

In this study, phosphor particles with high crystallinity and efficiency were synthesized by adding boric acid as a

flux. Phosphor particles, 60 nm in diameter and 500-700 nm in length, were obtained without adding the flux. The particle size increased (from ~1 to 2  $\mu\text{m}$ ) when 1, 2 and 5 wt% of boric acid was introduced. Photoluminescence analysis performed under UV excitation ( $\lambda_{\text{ex}} = 254 \text{ nm}$ ) revealed that the 2 wt% flux containing specimen exhibited the maximum PL intensity (93% of the commercial product). When the flux concentration was increased further to 5 wt%, a defect layer produced by the extraneous products resulted in a loss of emission intensity.

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