# Preparation and Surface treatment of Spherical $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor

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**Abstract**

*Dense $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor particles with a spherical shape have been synthesized through spray pyrolysis method using basic aluminum nitrate precursor as a spray solution. Also, a thin layer of silica on the surface of $BaMgAl_{10}O_{17}:Eu^{2+}$ particles were coated by hydrolysis reaction of alkoxide sources with the particles. The correlation between PL intensity and surface treatment by coating for the dense $BaMgAl_{10}O_{17}:Eu^{2+}$ particles have been investigated.*

## 1. Introduction

Aluminate particles have been studied for applications in fluorescent lamps and plasma display panels (PDP) [1]. In PDP, $Eu^{2+}$-activated barium magnesium aluminate (BAM) phosphor has been conventionally adopted as a blue emitting component due to its availability and high quantum efficiency. Spray pyrolysis technique using an ultrasonic resonator has been applied to the preparation of $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor particles [2]. It was reported that the phosphor particles prepared from basic aluminum nitrate solution made by a precipitation method exhibit a spherical morphology [3]. But, in the method, the dissolution and concentration processes due to formation of voluminous Al precipitates in the precipitation stage, are required inevitably. To solve such problem, the spray solution with high Al concentration and low nitrate content was prepared from Al metal and aluminum nitrate. On the other hand, the BAM phosphor particles have generally problem of the decrease of PL intensity by thermal degradation during the manufacturing [4-5]. To overcome this problem, many new preparation techniques utilizing surface treatment to BAM phosphor material have been tried. In this work, a thin layer of silica was coated on the surface of BAM particles by hydrolysis reaction of alkoxide sources with phosphor particles. Also, the emission intensities of the silica-coated BAM phosphors were compared to the no-coated BAM particles.

## 2. Experimental

The BAM phosphor particles were prepared by spray pyrolysis from a mixture solution of metal salts and basic aluminum nitrate. A given amount of aluminum nitrate nonahydrate was dissolved in distilled water to form the solution with concentration of 0.75 M and then heated up to 85℃ during 30 minute. Aluminum metal powders were added into the solution by bits over two minutes. The temperature of the mixture solution was raised to between 95℃ and 100℃, and maintained at this temperature for 3 h at least, or until all the Al metal powders are dissolved completely. In next process, the spray solution for spray pyrolysis was prepared by dissolving barium, magnesium, and europium nitrate salts in the as-prepared basic aluminum nitrate solution. The viscosity of spray solutions were measured with HAAKE Viscometers VT 550. The precursor particles obtained by spray pyrolysis were fired at 900℃ for 5 h in air atmosphere and then re-fired at 1400℃ for 4 h under 5% $H_2$ gas mixed 95% $N_2$ gas flowing, and finally ground. On the other hand, the coatings of silica on the BAM particles were performed using tetraethylorthosilicate (TEOS) as a start material

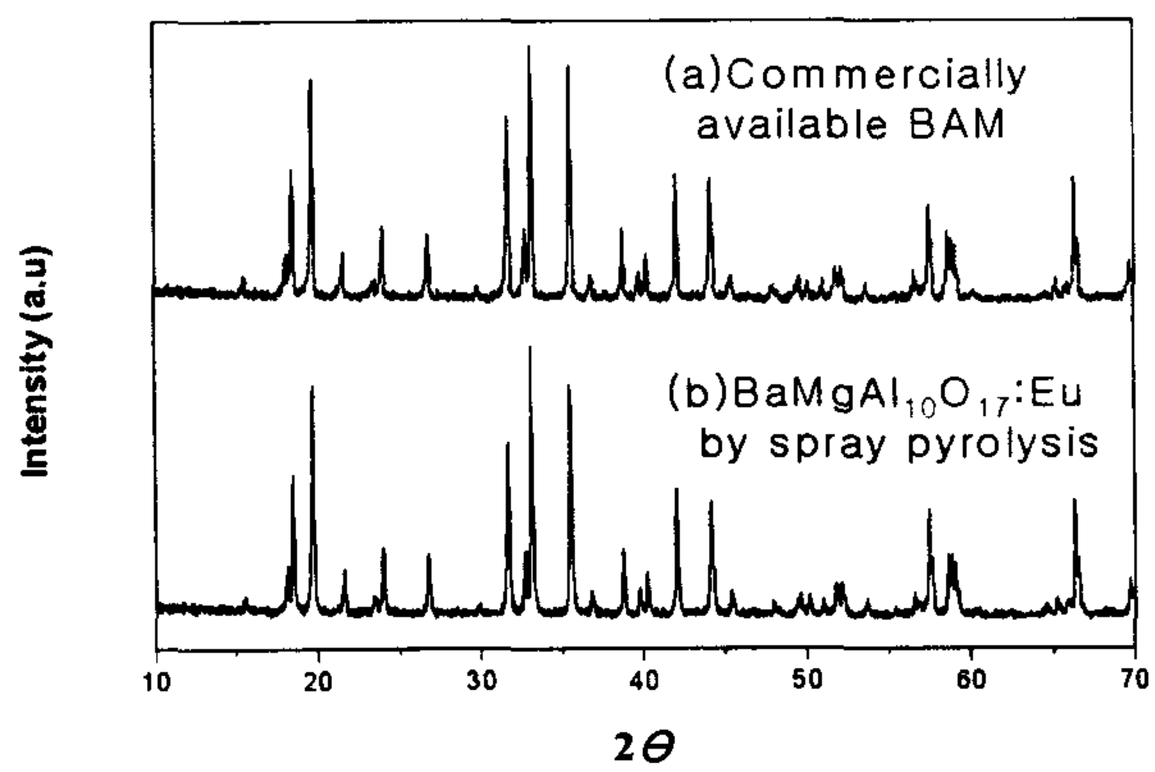


**Figure 1. XRD patterns of the commercial BAM phosphor and the BAM phosphor particles prepared by spray pyrolysis.**

based on hydrolysis reaction of alkoxide. The ratio of silica to the phosphor was changed from 0.05% to 1% (in weight). The required amount of phosphor particles were firstly dispersed in ethanol. Then TEOS was added and kept on about 25℃ for 1 h. The coated particles were filtered and dried. The crystallinity and morphology of particles were investigated using X-ray diffractometer (XRD) and scanning electron microscope (SEM), respectively. The PL characteristics of the prepared particles were measured under vacuum ultraviolet (147 nm) by $D_2$ lamp.

## 3. Results and Discussion

As the particles in the spray pyrolysis equipment had too short residence time, the post-heat treatments in air ambience and 5% $H_2/N_2$ gas flowing are needed. Figure 1 shows the XRD patterns of commercially-available $BaMgAl_{10}O_{17}:Eu^{2+}$ and the BAM phosphor particles prepared by spray pyrolysis. The crystalline phases of both BAM phosphor particles are exactly accordance with each other. Therefore, both the samples have the single phase of β-alumina structure. In order to prepare spherical BAM particles, the effective manufacturing method of the basic aluminum nitrate solution have been modified, as described in the experimental section. The mean size of particles produced by spray pyrolysis can be controlled by changing the concentration of spray solution.

Figure 2 is SEM photographs of BAM phosphors

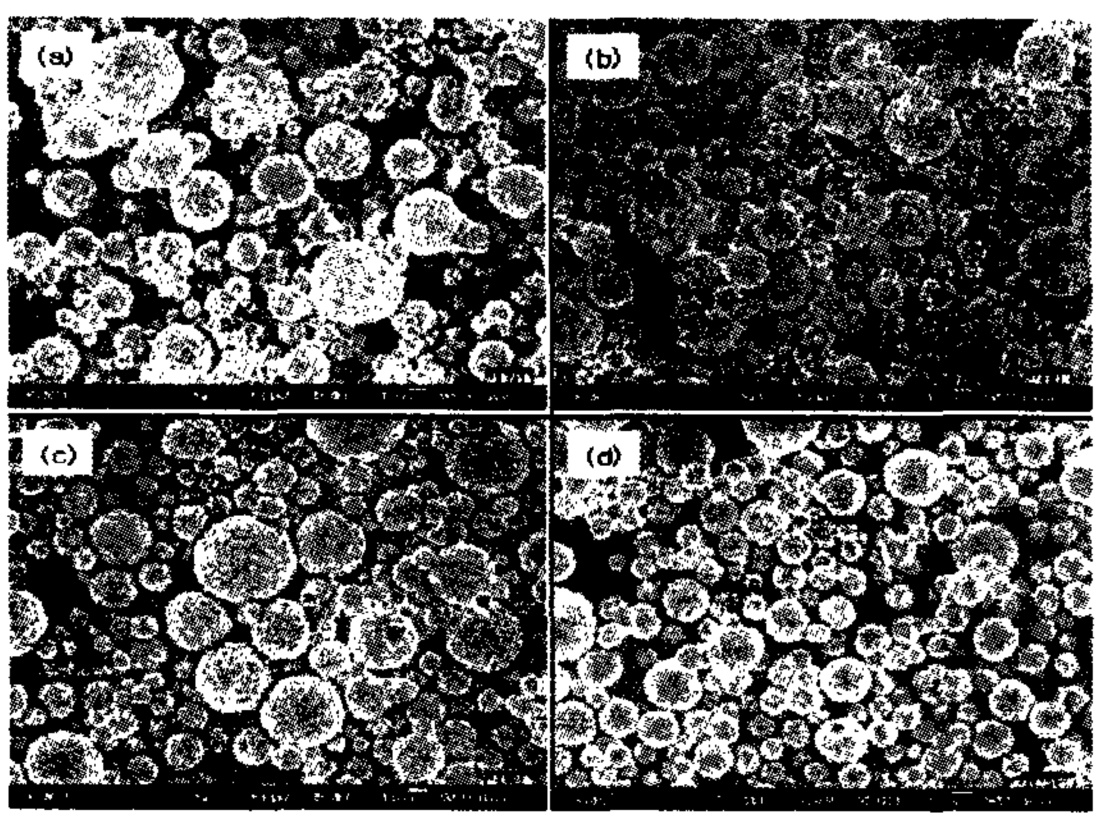


**Figure 2. Scanning electron micrographs of BAM phosphor particles prepared by spray from Al concentration of (a) 0.75 M (b) 1.0 M (c) 1.25 M (d) 1.5 M, respectively.**

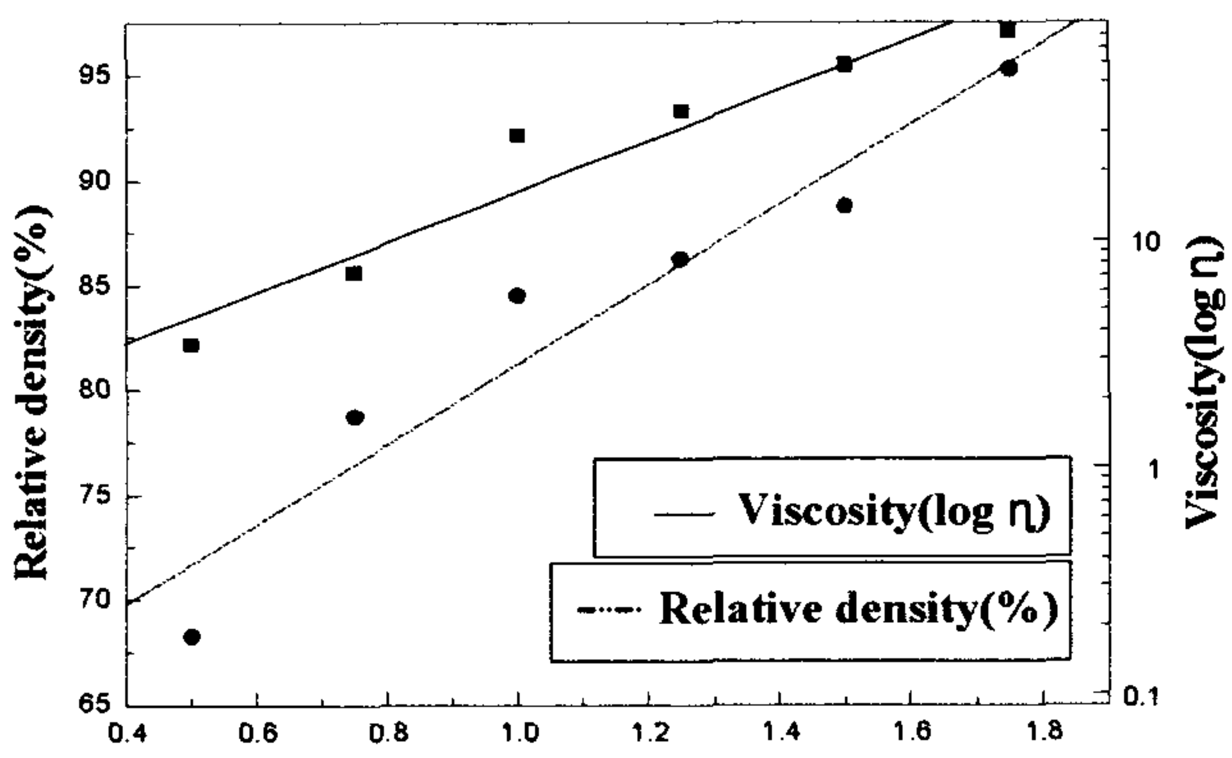


**Figure 3. The relative density of phosphor and the viscosity of precursor solution on the concentration change.**

synthesized by using the 0.75, 1.0, 1.25, and 1.5 M of aluminum concentrations in aqueous basic aluminum nitrate solution. As the Al concentration in the spray solution increases from 0.75 M to 1.5 M, the mean particle size of the phosphors decreases from 2.7 ㎛ to 1.2 ㎛. Although a majority of as-prepared particles have spherical shape, a few of non-spherical particles are observed in case of lower Al concentration than 1 M. From the comparison of the photographs, therefore, it could be concluded that the post-heat treatment at 1400℃ changes the shape of the particles prepared from the nitrate solution, whereas the spherical shape of BAM particles prepared from the basic aluminum nitrate solution is maintained without variation of the shape. In view of the results, the formation of spherical and filled-structured particles from high concentration of solution is essential for production of phosphor particles using spray pyrolysis.

Figure 3 shows the relative density of spherical BAM phosphor and the viscosity of spray solution with the concentration changes. With increasing Al content, the viscosity of spray solution and the relative density of BAM phosphor increase linearly. As the concentration of Al ingredient in the spray solution increases from 0.5 to 1.75 M, the relative density of the phosphor increases. The 1.5 M of concentration results in about 95% of relative density. Accordingly, the most dense phosphor particles can be made at 1.5 M of Al concentration.

Figure 4 shows SEM photographs for silica-coated BAM particles. As can be seen, a hexagonal surface

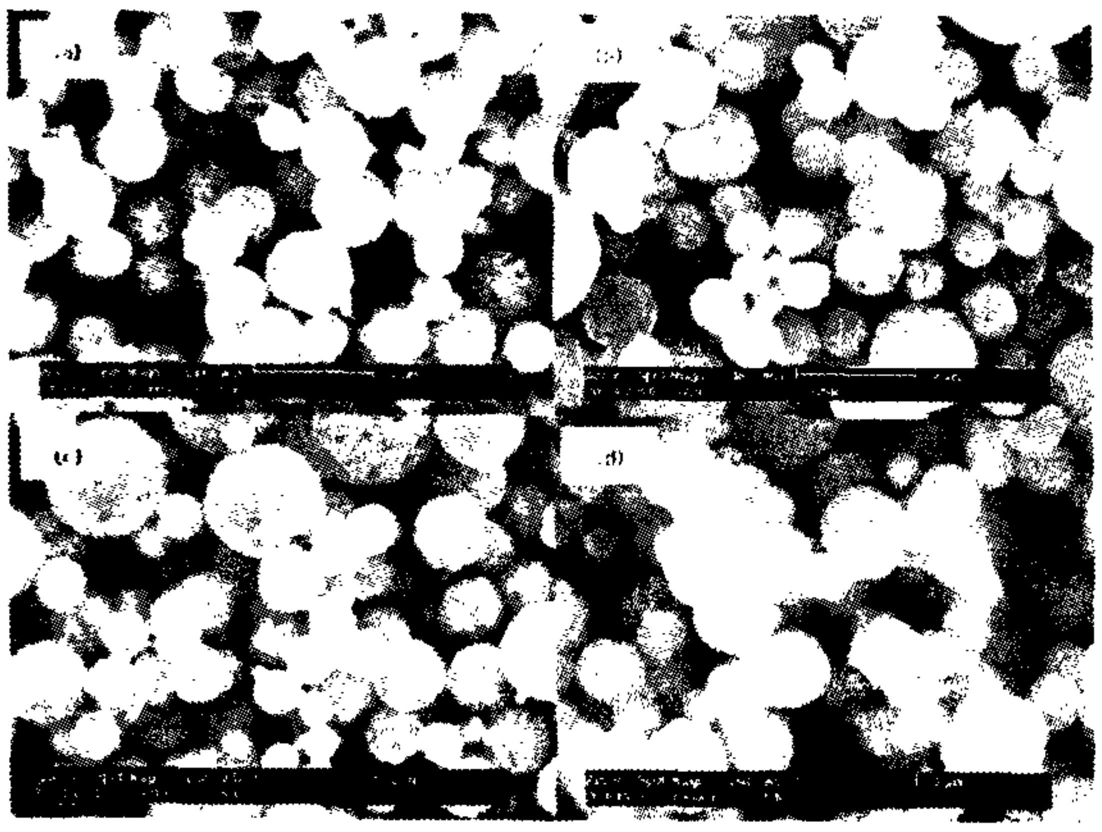

**Figure 4. Scanning electron micrographs of the BAM phosphors with (a) no-coated, (b) coated 0.05%, (c) coated 0.1% and (d) coated 1%, respectively.**

of pure BAM phosphor is observed obviously in Fig. 4(a). However, the surface of phosphor particles is gradually smoother with the increasing content of silica. This indicates that the synthesized BAM particles were uniformly silica-coated by using TEOS. On the other hand, TEM photograph for a BAM particle coated by 0.1% silica is presented in Figure 5. It is confirmed from TEM observation that the surface of BAM particle is well-coated with a thin layer (20±5 nm) of silica.

Table 1 expresses relative emission intensities of BAM particles. It is shown that the emission intensity of BAM phosphor was abruptly decreased with the increasing thickness of silica layer on the phosphors. Before heat treatment at 500℃, the pure BAM particles exhibit the higher PL intensity compare to


**Figure 5. TEM image of a BAM particle coated by silica.**

**Table 1. The comparison of relative emission intensities for the BAM phosphors**

| Sample | Relative Intensity | | Thermal degradation (%) |
|---|---|---|---|
| | Before ($I_0$) | After (I) | $(1-I/I_0) \times 100$ |
| Commercial | 100 | 77 | 23 |
| No-coated | 101.3 | 78.2 | 22.8 |
| $SiO_2$ 0.05% | 97 | 84 | 13.4 |
| $SiO_2$ 0.1% | 92..6 | 85.5 | 7.7 |
| $SiO_2$ 1% | 88.1 | 82.1 | 6.8 |

the silica-coated BAM particles. After heat treatment at 500℃ for the BAM phosphor particles, on the contrary, the relative emission intensity of the silica-coated particles was less decreased than that of pure BAM. In other words, the degree of thermal degradation of 0.1% silica-coated BAM was 7.7%, while that of no-coated particles was around 23%. Therefore, it is concluded that the thermal degradation of the BAM phosphor could be improved by forming uniform silica layer on the surface of BAM particles.

## 4. Conclusion

Blue-emitting BAM phosphor particles for plasma display panels were fabricated by spray-pyrolysis from spray solution containing basic aluminum nitrate. The BAM phosphor particles exhibit a completely spherical shape and filled morphology even after post-heat treatment at 1400℃. The optimum Al concentration in spray solution was 1.5 M, which can be result in high productivity of BAM phosphor particles. On the other hand, the silica-coated BAM phosphor was prepared and the thermal degradation was improved.

## 5. Acknowledgments

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