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# Improved thermal resistance of spherical $BaMgAl_{10}O_{17}$:Eu blue phosphor prepared by spray pyrolysis

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**Abstract**

The thermal degradation characteristics of $BaMgAl_{10}O_{17}$:Eu (BAM) blue phosphor with spherical shape were investigated. In this work, we developed a strategy that is very simple, but very effective to minimize the thermal degradation of BAM blue phosphor. In order to improve the thermal degradation properties of BAM particles prepared by spray pyrolysis, the as-prepared particles were treated by a two-step post thermal treatment. That is, the particles were treated under a vacuum atmosphere at 400 °C and successively in situ reduced at 1400 °C. It was found that the two-step treatment effectively reduces the color shift of the BAM particles, which is known as a big problem generally observed in the fabrication processes of plasma display panels (PDPs). According to FT-IR analysis, the vacuum treatment produced a stable hydrophobic surface which was maintained even after the baking process. For further improving the photoluminescence intensity under VUV irradiation, in this work, the surface of BAM particles treated by the above two-step treatment was modified with alkyl and organosilane groups. As a result, the photoluminescence intensity was enhanced. Therefore, it was concluded that removing the water (OH groups) existing on the surface or in the matrix as well as making a hydrophobic surface are promised to minimize the thermal degradation of BAM particles.


*Keywords:* Phosphor; BAM; Thermal degradation; Photoluminescence; Spray pyrolysis

## 1. Introduction

Plasma display panel (PDP) is a representative flat panel display which has great potential application to large screen TV for home and a public information display. Now, most urgent task of PDP makers is to lower the production cost,

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simultaneously improving the brightness, the lifetime, and the resolution. The phosphor materials directly influence these properties of PDP. Recently more attention has been paid to blue phosphor, $BaMgAl_{10}O_{17}$:Eu (BAM) [1–6] because it is degraded most sensitively by the thermal process and VUV irradiation [7–12]. As a result, the reduction of luminescent intensity and the color shift have been the most significant shortcoming for high-quality PDP. So, the development of new candidates or the improvement of the thermal degradation characteristics is a hot issue for enhancing the luminous efficiency.

The major causes for the degradation of luminous properties of BAM are still on debate. Most acceptable and studied mechanism of the degradation is channeled into the change in the valence of europium activators during the oxidation process at 450–500 °C, which is essentially needed to seal the panel or for the adhesion of phosphor on the substrate [9,10,12,13]. The formation of defects such as oxygen deficiency, the destruction of the stoichiometric composition by high energy VUV irradiation, and the carbon contamination are also contributed to the degradation of BAM [8]. The influence of annealing in air strongly depends on the applied excitation source [9]. In the temperature range from 250 to 600 °C, the efficiency of BAM phosphor decreases for VUV excitation in which a band-gap absorption occurs, while it is not changed for 245 nm excitation in which the direct absorption on $Eu^{2+}$ occurs. This discrepancy is attributed to the penetration depth of light. Thus, the shallow penetration of VUV radiation into the phosphor grain, which is not more than several tens of nanometers, makes the luminous efficiency more strongly dependent on the phosphor surface properties, i.e., the surface composition of host materials and the state of activators in the surface layer.

The unite cell of $BaMgAl_{10}O_{17}$ consists of two spinel blocks ($MgAl_{10}O_{16}$) and one mirror plane (BaO) [14,15]. The activator $Eu^{2+}$ ions are substituted in the Ba sites in the conduction layer (mirror plane). Therefore, the change in the valence of europium is highly connected to the interaction of the conduction layer with oxygen or other oxygen source, for example water. Recently, Yokota et al. [13] reported that the thermal degradation of BAM is mainly caused by oxygen ion going in and out to the conduction layer. So, some coating to limit the access of oxygen to the conduction layer enhances the thermal stability. The coating, however, reduces the luminous efficiency. In this work, a strategy to minimize the thermal degradation of BAM blue phosphor was proposed.

## 2. Experiment

We prepared spherical BAM ($Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$) particles by spray pyrolysis using an ultrasonic nebulizer atomizer. To avoid the formation of hollow morphology, aluminum polycation was obtained by modifying the nitrate aqueous solution with ammonium solution. More details to prepare the aluminum polycation are referred to the reference [16,17]. Stoichiometically dosed barium, magnesium, and europium nitrate were dissolved in the aluminum polycation solution, which was atomized by the nebulizer and carried by air into the furnace at 900 °C. The as-prepared particles were loaded in a crucible, thereafter, which was put in aluminum tube. First, the aluminum tube was evacuated up to $\sim 10^{-1}$ torr at 400 °C for 1 h and refilled with nitrogen gas up to the atmospheric pressure. Thereafter, the furnace temperature was increased up to 1400 °C and maintained for 3 h with flowing 5% $H_2/N_2$ gas mixture.

The surface of BAM samples, which were thermally treated as mentioned above, was modified by alkyl or organosilane groups. Five grams of the BAM particles were dispersed in 100 ml ethanol or 2-propanol. This colloidal solution was heated up to 100 °C with reflux and maintained for 1 h vigorously stirring by a magnetic bar. Octyltriethoxysilane ($CH_3(CH_2)_7Si(OC_2H_5)_3$, OTES, Aldrich) was used as the precursor to attach organosilane groups to the surface. Small amount of OTES, which was changed from 0 to 0.8 wt% with respect to BAM, was dissolved in 100 ml ethanol or 2-propanol. Five grams of BAM were added in the alcohol solution containing OTES