

Research Article

Photoluminescence Spectroscopic Study of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ Phosphor Coated with CaF_2 via a Sol-Gel Process

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CaF_2 coatings on the surface of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (BAM) were prepared by a sol-gel process, and the optical properties and antithermal degradation properties were analyzed by photoluminescence spectra recorded under 254 nm and 147 nm excitation. The results indicate that BAM particles were successfully coated with CaF_2 and CaF_2 coatings show an interesting property to enhance the blue emission intensity of BAM. The optimum antithermal degradation properties were obtained at the weight ratio 0.4 wt% under 254 nm excitation and 0.3 wt% under 147 nm excitation, respectively.

1. Introduction

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (BAM) is widely used in plasma display panels (PDPs) and lamps, due to its high luminescence efficiency and good chromaticity [1] and also used in other displays and lighting devices, for example, white light-emitting diodes (WLED). However, luminance degradation of BAM, consisting of thermal degradation and lifetime degradation, restrains the application of BAM, especially in PDPs. In lamps, the degradation of BAM is mainly caused by thermal treatment during lamp manufacturing. In WLED, similar thermal degradation is also observed in BAM and Eu^{2+} activated nitride-based phosphors [2]. Thermal degradation occurs when the phosphors are heated to about 500–700°C in ambient atmosphere during the manufacturing of PDP and lamps, while in WLED thermal degradation is caused by the heat released by the operating devices. It is generally considered that the luminescent center Eu^{2+} is oxidized to Eu^{3+} [1–3]. However, some other potential mechanisms were proposed recently which are related with O^{2-} incorporated into the crystal lattice of BAM [4–6]. Lifetime degradation is caused by VUV radiation and ion sputtering during PDP operation, which can be explained by the formation of an amorphous surface layer [3].

One of the options to enhance thermal stability and ion resistance in BAM is the application of a closed particle coating [7]. Up to now, several inorganic materials have been reported to be selected as the coating materials such as SiO_2 [8, 9], SrO, MgO [7, 10], Al_2O_3 [8, 11], AlPO_4 , and LaPO_4 [12] and so forth. However, most of them possess strong band gap absorption in the range of 140 to 200 nm, which would thereby cause the reduction of the phosphor efficiency. Thus the option is narrowed to metal fluorides which have a wide transparency range in VUV region and high secondary electron emission coefficient which can improve the pixel brightness [7, 13]. Metal fluorides can be deposited onto the phosphor surface by conventional precipitation or emulsion-assisted precipitation [14, 15]. However, this processes result in poor adherence of the coating to the phosphor [16]. Moreover, CVD (chemical vapor deposition) and PVD (physical vapor deposition) would be good choices [17], but both are highly apparatus dependent, requiring elaborate instrumentation and careful air flow and temperature monitoring. Thus the cost of the phosphor fabrication process is increased.

In our previous report [18], BAM coated with MgF_2 was prepared via a sol-gel process which is low cost, low apparatus dependent, and convenient to operate compared with the other reported methods. The coating percentage is easy to

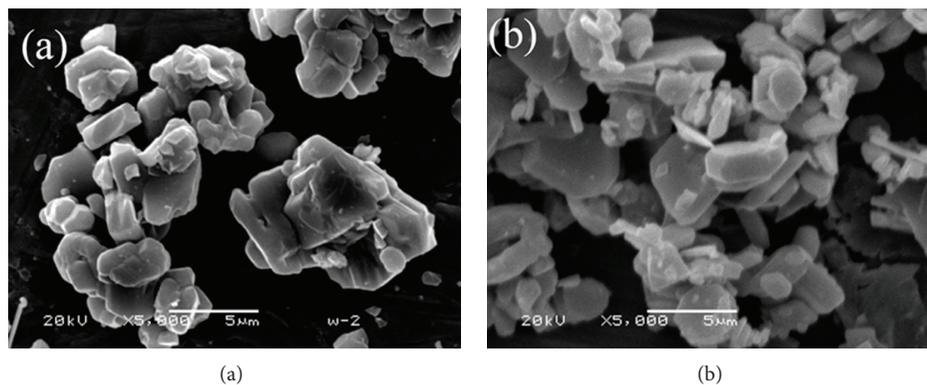


FIGURE 1: SEM images of (a) raw BAM and (b) 0.4 wt% CaF_2 -coated BAM.

control as well. The results show that appropriate MgF_2/BAM ratio can significantly improve the thermal stability of BAM without serious deterioration of emission intensity. As it is well known, CaF_2 also has wide transparency range and high secondary electron emission coefficient [19]. Thus in this paper, CaF_2 -coated BAMs were prepared using the sol-gel process, and the luminescence properties and antithermal degradation properties were also evaluated.

2. Experimental

The starting materials were TFA (CF_3COOH , CP), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), and iso- $\text{C}_3\text{H}_7\text{OH}$ (AR). BAM was provided by IRICO Group Corporation. 0.005 mol $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 15 mL of isopropanol with the addition of 2 mL of TFA and 2 mL of distilled water. The solution was stirred for 2 h and then diluted to 300 mL with isopropanol. BAM phosphor particles were added to the solution at the weight ratio $\text{CaF}_2/\text{BAM} = 0.1\text{--}1.4$ wt% and stirred for 15 min. Then the solution mixed with BAM was dried at 80°C for 24 h so that dry gel containing BAM samples was obtained. After being calcined at 350°C for 15 min, BAM particles coated with CaF_2 were obtained. In order to investigate the antithermal degradation properties, all samples were heat-treated at 600°C for 30 min.

X-ray photoelectron spectroscopy (XPS) was carried out on a MICROLAB VG 210 instrument for surface components analysis. Surface morphology was observed with a scanning electron microscope (SEM, Model JSM-5600LV). The photoluminescence properties were measured by an FLS920T spectrophotometer equipped with a VM504 vacuum monochromator (Acton Research Corporation) at room temperature.

3. Results and Discussion

The SEM images of coated (0.4 wt%) and uncoated BAMs are shown in Figure 1. The surfaces of pure BAM and CaF_2 -coated BAM are both smooth, although the coated samples' corners and edges are slightly less sharp. It is suggested that the phosphors may be covered by continuous CaF_2 coatings,

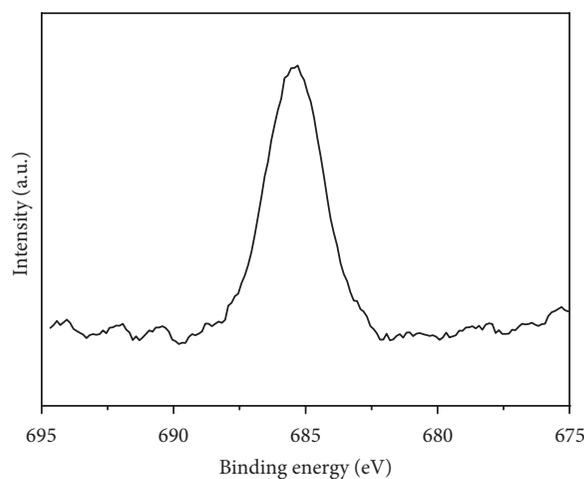


FIGURE 2: XPS spectrum of F1s.

TABLE 1: Binding energies of the elements of uncoated and coated BAM phosphor surfaces.

| Sample | Ba3d5 (eV) | Mg2p (eV) | O1s (eV) | Al2p (eV) | F1s (eV) | Ca2p3/2 (eV) |
|----------------|---------------|--------------|-------------|--------------|-------------|-----------------|
| BAM (uncoated) | 780.41 | 49.94 | 531.08 | 74.08 | — | — |
| BAM (coated) | 780.41 | 50.00 | 531.09 | 74.08 | 685.0 | 347.3 |

which should be beneficial to prevent the access of oxygen to the phosphors, rather than particles.

The XPS analysis of a series of samples shows that BAM phosphors were coated with CaF_2 via this sol-gel process. As an example, Figure 2 exhibits the F1s peak of the sample with 0.4 wt% CaF_2 . Table 1 shows the $\text{Ca}2p_{3/2}$ and F1s checked in the coated samples. It indicates that they are close to that of CaF_2 standard, in which $\text{Ca}2p_{3/2}$ is 347.5 eV and F1s is 684.9 eV [20], respectively. Combined with the analysis of SEM, it can be confirmed that the surfaces of BAM phosphors are covered with CaF_2 coatings.

The optical properties and antithermal degradation properties of the coated samples were found to be highly dependent on the coating percentage. As it is shown in Line (a)

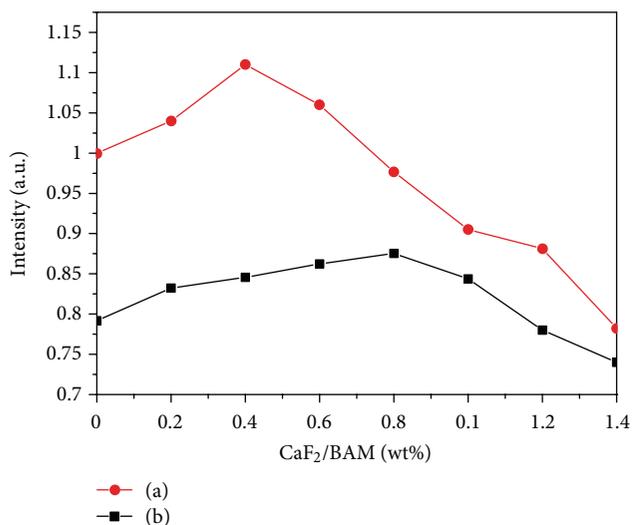


FIGURE 3: Emission intensities of CaF₂-coated BAM phosphors as a function of the weight ratio CaF₂/BAM (a) before heat treatment and (b) after 600°C heat treatment ($\lambda_{\text{ex}} = 254 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$).

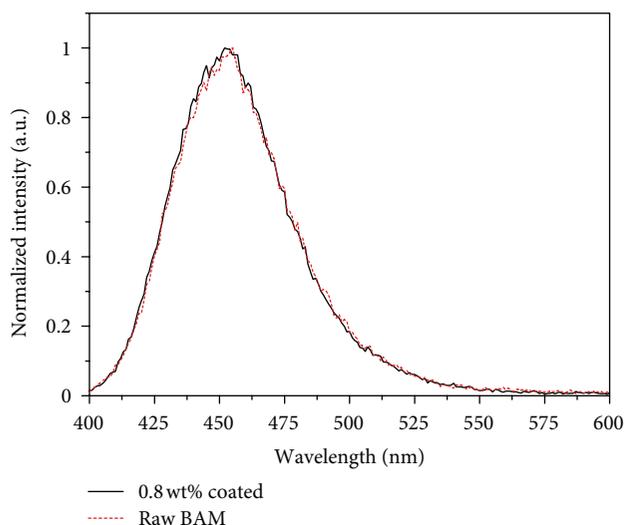


FIGURE 4: Emission spectra of 0.4 wt% CaF₂-coated BAM and raw BAM.

of Figure 3, the emission intensities of CaF₂-coated BAMs under 254 nm excitation show a maximum at 0.4 wt% (Line a) which is about 11% higher than that of uncoated BAMs before heat treatment. This phenomenon is rather different from the cases of oxides or MgF₂-coated samples [14, 17] and may be due to the reduction of the reflectivity of the excitation UV light from the surface of the BAM phosphor [9], caused by the CaF₂ coating, whose refractive index is 1.32, smaller than 1.38 of MgF₂. This effect results in the less loss of UV light passing through the coating layers. Thus the emission intensity is thereby enhanced.

After heat treatment, the emission intensity at 0.8 wt% becomes the maximum (Figure 3, Line (b)), which is about 10% higher than the uncoated counterparts. This may be

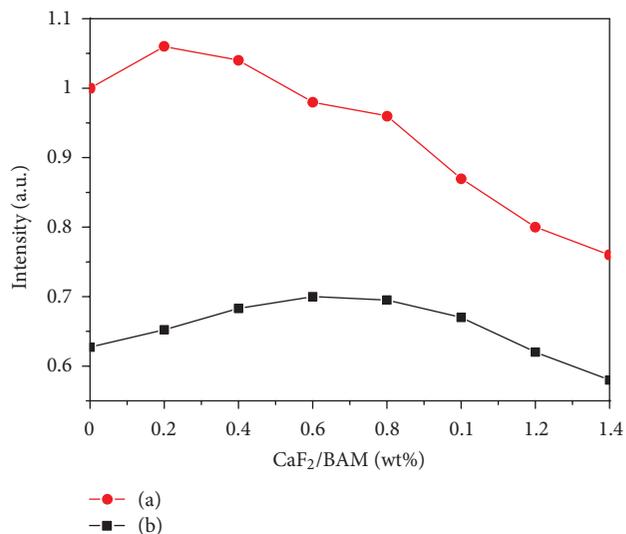


FIGURE 5: Photoluminescent intensities of CaF₂-coated BAM phosphors as a function of the weight ratio CaF₂/BAM (a) before heat treatment and (b) after 600°C heat treatment ($\lambda_{\text{ex}} = 147 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$).

because the coating could not cover the phosphor particles completely at lower weight ratios. High weight ratios resulted in high reflectance and low transmission ratio, which caused low luminescent intensity. These two factors are combined to cause the optimum CaF₂/BAM ratio which is 0.8 wt% for antithermal degradation property. The normalized emission spectra of 0.4 wt% CaF₂-coated BAM and raw BAM are presented in Figure 4, which clearly shows the emission band shapes are similar. Neither obvious band broadening nor peak shift is observed.

As shown in Line (a) of Figure 5, when irradiated by 147 nm, a maximum was observed at about 0.2 wt% before heat treatment. And the emission intensity at 0.2 wt% is about 6% higher than that of the raw BAM. The increase of the PL intensity is associated with the decrease of the reflectivity at as mentioned above. After heat treatment, the maximum at about 0.6 wt% is 12% higher than the uncoated's (Figure 5, Line (b)). This phenomenon may be explained by the mechanism proposed in the discussion of Figure 3, that is, the confluence of the requirements of low reflectance and coverage. The enhancement of thermal stability of CaF₂-coated BAMs is less efficient than that of MgF₂-coated samples prepared via the same sol-gel process [18], which may be due to the higher porosity of CaF₂ coating layers synthesized by this sol-gel process mentioned in [19].

It is known that one of the most important factors regarding BAM for application in PDPs is its color purity. The normalized emission spectra of 0.6 wt% CaF₂-coated BAM and raw BAM after heat treatment are presented in Figure 6. The bandwidth of raw BAM is obviously bigger than that of the sample with 0.6 wt% CaF₂, which may be attributed to the migration of Eu²⁺ from mirror planes to spinel blocks [5], indicating the more severe thermal degradation of raw BAM. Furthermore, the chromaticity coordinates of the samples

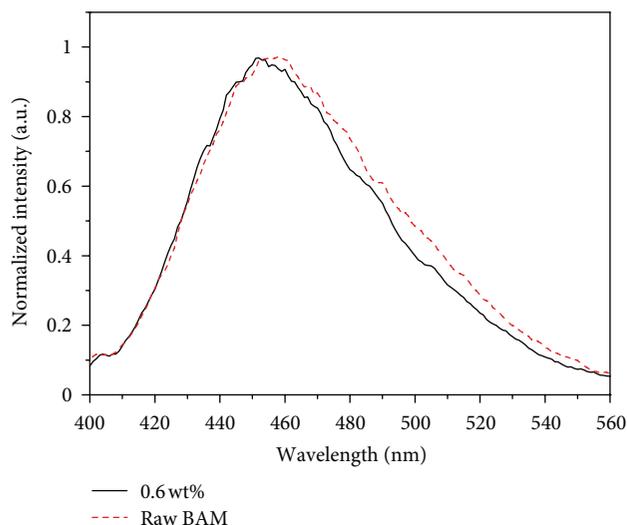


FIGURE 6: Emission spectra of 0.6 wt% CaF_2 -coated BAM and raw BAM after 600°C heat treatment ($\lambda_{\text{ex}} = 147 \text{ nm}$).

TABLE 2: The chromaticity coordinates of the 0.6 wt% CaF_2 -coated BAM and raw BAM.

| | Before heat treatment | | After heat treatment | |
|-----|-----------------------|---------|----------------------|---------|
| | Raw | 0.6 wt% | Raw | 0.6 wt% |
| x | 0.14 | 0.14 | 0.14 | 0.14 |
| y | 0.09 | 0.10 | 0.13 | 0.11 |

are listed in Table 2. Obviously, the y value of raw BAM deteriorates more severely than that of coated BAM.

4. Conclusions

BAM phosphors were successfully coated with CaF_2 coatings by a sol-gel process. The results indicated that the luminescence intensities are effectively improved before heat treatment and the antidegradation properties were also improved. As a conclusion, this sol-gel coating process is a promising method to improve not only the phosphors' thermal stability but also the luminescence properties under UV and VUV excitation for application in displays and lamps. Further works regarding the correlation between the coating process parameters and the optical properties of phosphors for PDPs are currently ongoing.

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