

Effect of SiO₂ coating on photoluminescence and thermal stability of BaMgAl₁₀O₁₇: Eu²⁺ under VUV and UV excitation

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Abstract

The BaMgAl₁₀O₁₇: Eu²⁺ (BAM) phosphors used as blue component of tricolor fluorescent lamps (FLs) and plasma display panels (PDPs) have the problems of thermal degradation in the process of fabrication. In this work, the nanometer SiO₂ was homogeneously coated on it. The luminescence and thermal stability are investigated for the excitation in both the UV and the VUV regions. The results demonstrate that after coating, there is an increase in the luminescence intensity in the UV region, while no obvious increase is observed in the VUV region. In addition, the thermal stability was largely improved under both UV and VUV excitations. The underlying mechanism is elucidated.

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1. Introduction

BaMgAl₁₀O₁₇: Eu²⁺ (BAM), as an efficient blue phosphor, was developed and firstly used in tricolor fluorescent lamps (FLs) since 1974 [1]. Recently, BAM has also been used in plasma display panels (PDPs) [2] because it can efficiently absorb the vacuum ultraviolet (VUV) light coming from the resonance radiation line of Xe atoms (147 nm) and from the excited state of molecular Xe (172) [3]. However, numerous studies indicated that the thermal stability of BAM is poor, compared with red and green phosphors [3–9]. This becomes a critical problem in the application of BAM in FLs and PDPs, since the BAM spreads on the insides of a glass tub, and is then heated at 700–750 °C in air for FLs manufacturing, and at 500–600 °C

in air for PDPs manufacturing [6]. Numerous studies have been devoted to improve the thermal stability and operation life of BAM: Eu [10–17].

In recent years, surface modification, i.e., the fabrication of core–shell structure, has attracted extensive attention. Initially, this idea was applied in semiconductor nanoparticles, around which a suitable bandgap material was grown to increase the quantum efficiency by suppressing the energy-loss processes at the particles surface [18–27]. Very recently, this strategy has been extended to the inorganic luminescent systems [28–32]. Examples of such core–shell structures are Y₂O₃: Eu/Y₂O₃ [25], (La, Tb 20%) PO₄–xH₂O/CePO₄–xH₂O [33]. Results indicated that the formation of core–shell structure is an effective way to improve the photoluminescence efficiency also for rare-earth-doped inorganic luminescent systems.

It is assumed that a suitable shell grown around the surface of BAM phosphors probably acts as a protection

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against the thermal degradation, since the surface is a place where the reaction takes place first between air and phosphors. Based on this consideration, in this work, we attempt the coating of nanosized SiO_2 on the surface of BAM phosphors by sol–gel route. The effects of SiO_2 coating on the photoluminescence and thermal stability of BAM were investigated.

2. Experimental

Preparation of BAM: Eu was synthesized employing conventional solid-state reaction method. The stoichiometric mixture of BaCO_3 , MgCO_3 , Al_2O_3 , and Eu_2O_3 was ground with 1.5% AlF_3 as a flux and then fired at 1200°C in air for 10 h. After grinding, it went through a reduction process at 1400°C for 10 h under a reducing atmosphere (CO) and then the BAM is obtained.

Coating SiO_2 on BAM: six grams of the freshly prepared BAM phosphors was placed into a 500 ml conical flask with 150 ml ethanol, and then vigorously stirred for 1 h at 60°C . Water 40 ml and NH_4OH 30 ml were added to the above suspension. After the temperature was stabilized to 60°C , 10 ml tetraethyl orthosilicate (TEOS) was rapidly injected into the reaction system and the reaction was continued. Three hours later, the powders separated from the mother liquid were washed for three times with ethanol and dried at 80°C for 2 days to obtain SiO_2 -coated BAM.

All the measurements were conducted at room temperature. XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation. SEM images were taken on an S-4800 field emission electron microscopy. The emission spectra under 147 nm excitation were measured by using a vacuum monochromator and a deuterium (D_2) lamp and were normalized to that of sodium salicylate. The emission spectra under 254 nm excitation were measured with a Hitachi F-4500 fluorescence spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of BAM powders synthesized by solid-state reaction method. It is seen that all the diffraction peaks are well indexed to the hexagonal alumina structure of BAM phase.

Fig. 2 shows SEM images of the BAM before and after coating. It is easily observed that the uncoated BAM has a clean surface and the edges and corners are clearly observed, as shown in Fig. 2a. However, the coated BAM (see Fig. 2b) has a coarse surface with blurred edge and corners. This indicates that the nano- SiO_2 particles were formed on the BAM phosphors and the thickness of the coating is 20 nm.

Fig. 3 depicts the photoluminescence spectra of BAM before and after coating under 254 nm excitation, which consist of a wide band peaking at 450 nm, corresponding to $5d \rightarrow 4f$ transitions of the Eu^{2+} [34]. It is worth noting that the BAM phosphor with SiO_2 coating shows an

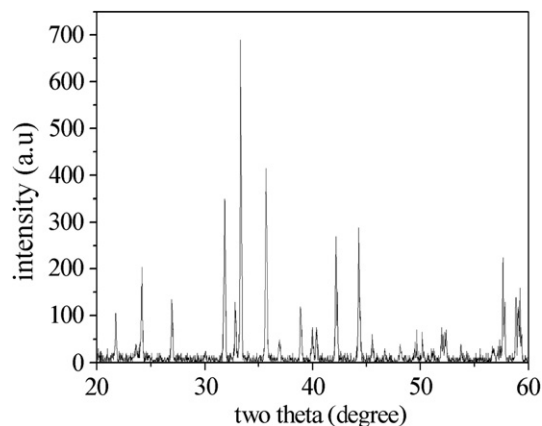


Fig. 1. X-ray diffraction pattern of BAM synthesized by solid-state reaction method.

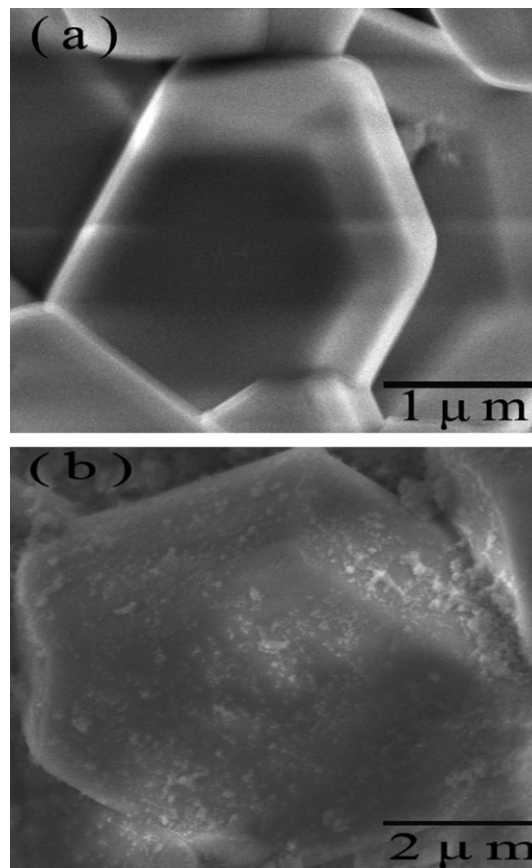


Fig. 2. SEM images of BAM phosphors of (a) before and (b) after coating.

increase in the luminescence intensity under 254 nm excitation. However, no obvious increase in the luminescence intensity is observed for the 147 nm excitation (see Fig. 4). As is well known, a part of the photons reaching the BAM is reflected to the air and the other part is absorbed by BAM. Only those absorbed can be converted to the visible light. After coating, the photons must transmit the SiO_2 coating and then get to the BAM surface. In

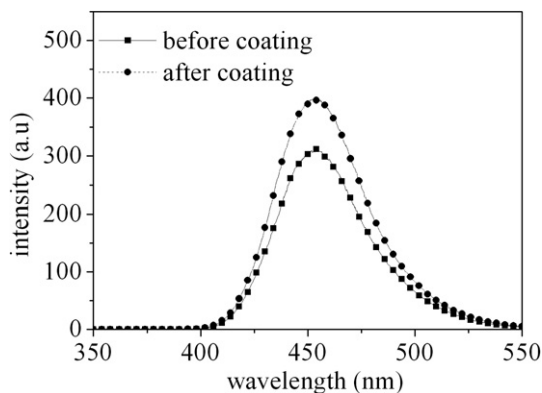


Fig. 3. The emission spectra of BAM before and after coating under 254 nm excitation.

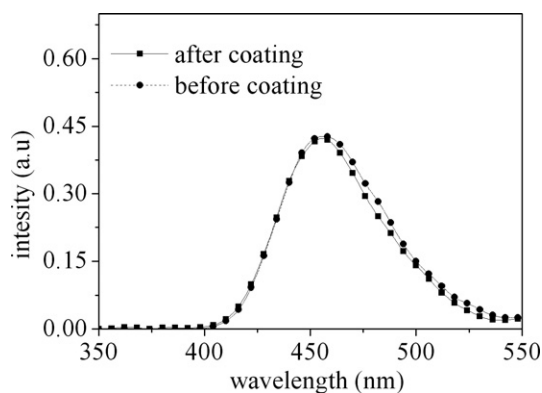


Fig. 4. The emission spectra of BAM before and after coating under 147 nm excitation.

this process, multiple reflectance, absorption, and refraction occurred. For the excitation in the UV region, considering the refractive index of the air ($n = 1$), SiO_2 ($n = 1.5$), and the BAM phosphors (1.7) around 254 nm [35], Jung et al. [35] have obtained the reflectivity of UV between air and BAM surface which is about 0.067, while the total reflectivity of air– SiO_2 and SiO_2 –BAM layers sums to 0.044. That is, after SiO_2 coating, there will be more photons reaching the BAM surface compared with the uncoated BAM phosphors. As a result, this contributes to the increase of emission intensity. But we must also consider the other aspect, the absorption of SiO_2 , because the thickness of SiO_2 shell cannot be negligible. When the light transmitted the SiO_2 coating, considering the absorption of SiO_2 , the light is weakened. It can be expressed as [36]

$$I(d) = I_0 e^{-\alpha d}$$

where $I(d)$ is the light intensity at a given thickness d , I_0 is the light intensity entering the medium and α is the intensity absorption coefficient of the material (cm^{-1}), which depends on the excitation wavelength and increases with decreasing the wavelength [36]. For the 254 nm excitation, α is relatively small compared with the excitation in the VUV region. So considering both anti-reflection effect

(the positive effect) and absorption effect (the negative effect) of SiO_2 , our results (see Figs. 3 and 7a) indicate that the positive effect is dominant for the excitation in the UV region, that is, more excitation light is transmitted into the BAM phosphor after being coated with SiO_2 under 254 nm excitation compared with the non-coated BAM phosphor; therefore the luminescence intensity is increased. This is consistent with the conclusion obtained by Jung and his co-workers [35]. This indicates that the SiO_2 coating has a positive effect on the application of FLs. But for the excitation in the VUV region, there is no obvious increase in the emission. This can be explained as follows: the absorption index (α) for VUV is larger compared with UV, so, when the light reaches the SiO_2 coating, relatively large number of photons are absorbed and therefore, the number of absorbed photons into the crystal is smaller compared with the ones absorbed into the coating. In this case, the negative effect is dominant. So the luminescence intensity of BAM with SiO_2 coating is decreased compared with the uncoated ones.

In order to investigate the thermal stability after SiO_2 coating, SiO_2 -coated and uncoated BAM were annealed simultaneously at 700 °C for 1 h in air. The PL measurements were performed to evaluate the degree of thermal degradation in SiO_2 coated and uncoated BAM. Fig. 5 shows the effect of thermal treatment on the emission intensity of uncoated and SiO_2 -coated BAM under 147 nm excitation. From Fig. 5 we can easily find that after heat-treatment, the emission intensity decreased in these two samples, but the decreasing rate is different. The integrated emission intensity is 93.05% of its original value for the SiO_2 -coated samples and 86.67% for the uncoated samples.

Fig. 6 shows the effect of thermal treatment on the emission intensity of uncoated and SiO_2 -coated BAM under 254 nm excitation. From Fig. 6 we can easily find that after heat-treatment, the emission intensity decreased in these two samples, but the decreasing rate is different. After heat-treatment, the integrated emission intensity of BAM is 95.5% of its original value for the SiO_2 -coated samples and 88.7% for the uncoated samples.

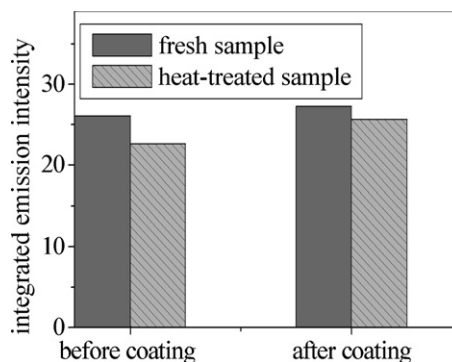


Fig. 5. The integrated emission intensity of the fresh and heat-treated sample before and after coating SiO_2 under 147 nm excitation.

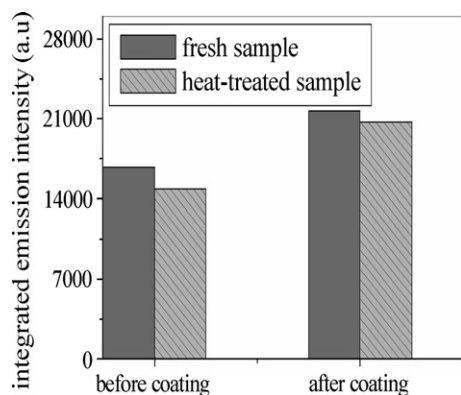


Fig. 6. The integrated emission intensity of the fresh and heat-treated sample before and after coating SiO_2 under 254 nm excitation.

As expected, surface coating is an effective way to improve the thermal stability of BAM phosphors. In order to elucidate the underlying mechanism, the coated and uncoated samples were simultaneously heated at 900°C for 1 h in air. Fig. 7 compares the excitation spectra of uncoated and SiO_2 -coated BAM phosphor. We can easily find that there are two wide bands, which originate from the transitions from the $4f^7$ ground state of the Eu^{2+} to the T_{2g} and E_g excited states of the $4f^65d$ configuration [37]. As is well known, the structure of $\text{BaMgAl}_{10}\text{O}_{17}$, or

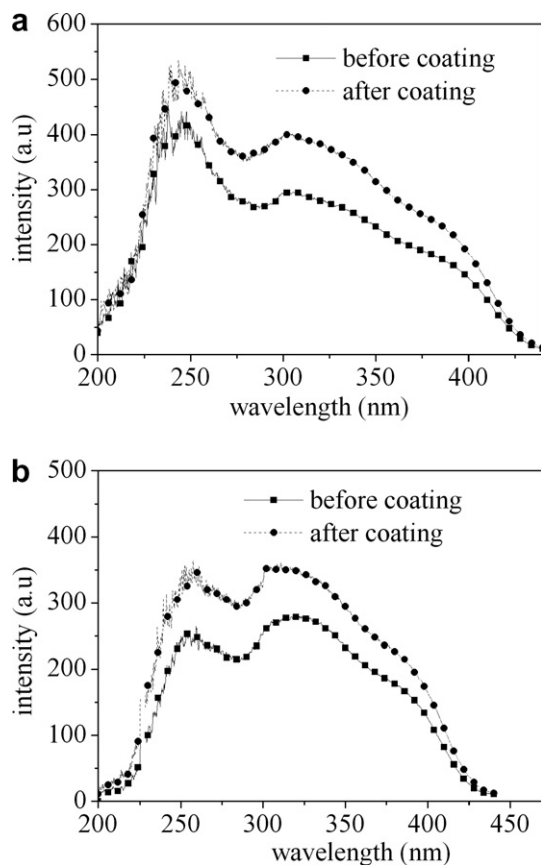


Fig. 7. The excitation spectra of coated and uncoated BAM (a) before and (b) after heat-treatment.

β -alumina consists of two spinel blocks ($\text{MgAl}_{10}\text{O}_{16}$) separated by one mirror plane (BaO) [6]. When Eu^{2+} is substituted into the host lattice, it can have three possible locations: Beever–Ross (BR), anti-Beever–Ross (a-BR), and mid-oxygen (mO) sites in the mirror plane [7], in which the a-BR site is more stable [38]. Since $4f-5d$ is largely affected by the crystal field, relative rate of transition to T_{2g} and E_g should be different for these sites because the environment surrounding the Eu^{2+} ions is different. The position of the d bands is sensitive to the crystal field, but their rate does not change so much since there are parity allowed transitions. In our previous work [39], we have demonstrated that the BR site excitation is more efficient in the long wavelength peaking at 310 nm, but the a-BR site is more efficient in the short wavelength peaking at 250 nm. From Fig. 7a, we can find that the short wavelength excitation peaking at 250 nm is more efficient than the long wavelength peaking at 254 nm both for coated and uncoated BAM. After heat-treatment, the overall intensity decreases at the same time, but the short wavelength peaking at 250 nm decreases more dramatically than the long wavelength excitation peaking at 310 nm. This leads to the decrease of excitation efficiency at 254 nm. In the process of oxidation, because the Eu^{2+} occupy the BR and mO sites were relatively unstably, these two sites must be firstly oxidized, and then those which occupy the a-BR site might migrate to the BR and mO sites. For the SiO_2 -coated sample, short wavelength excitation peaking at 254 nm is more efficient than long wavelength excitation peaking at 310 nm; however, for the uncoated BAM, the long wavelength excitation is more efficient. In our previous work [39], we have demonstrated that in the process of oxidation, Eu^{2+} firstly migrate to the Al (2) site, and then change to Eu^{3+} . In this work, the SiO_2 coating as a protective layer can prevent the migration of Eu^{2+} and oxidation; therefore, the SiO_2 coated BAM is more stable.

To further confirm the improved thermal stability of SiO_2 -coated BAM phosphor, the coated and uncoated BAM were simultaneously annealed at 1100°C in air for

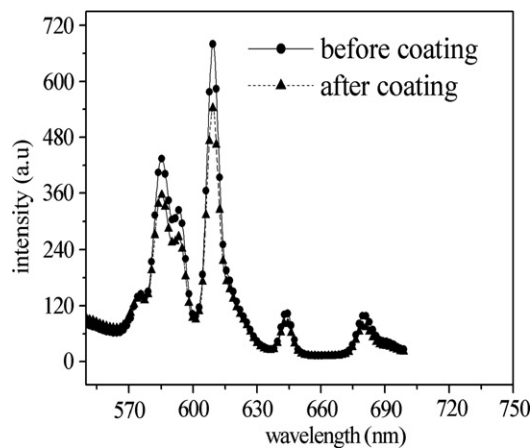


Fig. 8. Emission spectra of coated and uncoated BAM annealing at 1100°C in air for some time under 254 nm excitation.

5 h, the peaks observed in Fig. 8 are characteristic of the $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) transition of Eu^{3+} [4]. We can easily find that more emission of Eu^{3+} is observed for uncoated BAM. This further confirms that the SiO_2 -coated BAM is more stable compared with the uncoated BAM under thermal treatment.

Therefore, we can conclude that the SiO_2 coatings protect the phosphor surface by prohibiting migration of Eu^{2+} and oxidation during the firing process. This enhances the thermal stability of phosphors, which is critical in PDP and FL manufacturing.

4. Conclusion

The $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ was synthesized by conventional solid-state method and the SiO_2 was homogeneously coated on it employing sol–gel route. SEM images show that nanometer SiO_2 was homogeneously coated on it. After coating, the photoluminescence is enhanced under 254 nm excitation, but no obvious increase is observed under 147 nm excitation. This related to the change of reflectivity and absorption coefficient with changing of wavelength. The most important thing is that the thermal stability is improved after coating. SiO_2 as a protective layer can prohibit the oxidation and migration of Eu^{2+} . Therefore, a surface coating that could prohibit a surface chemical reaction would improve the phosphor's longevity and thermal stability.

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