



Double Surface Coating to Improve the Photoluminescence Performance of BaMgAl₁₀O₁₇ : Eu²⁺ Phosphors

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Europium-doped barium magnesium aluminate was double-coated with silicon dioxide and alumina by a sol-gel method. X-ray diffraction patterns show no phase change for coated phosphors. The scanning electron microscope and energy dispersive X-ray spectrophotometer result that the single coated material was uniform silicon dioxide thin film and the double coated surface was consisted of silicon dioxide and alumina hybrid films. The transmission electron microscope images revealed that the thickness of the first layer and the second layer was 60 and 15 nm, respectively. The results of thermal stability test indicated that relative-brightness loss of un-coated, single coated and double coated phosphors was 18.29, 6.83 and 2.76 %, respectively. Colour coordinate shift (Δx , Δy) of these samples was (0.0003, 0.0082), (0.0001, 0.0042) and (0.0001, 0.0028), respectively. Barium magnesium aluminate phosphor's colour coordinate shift was reduced while thermal stability was improved by double coating, which was better than that of single coated sample, because the double coating method overcame the problem of luminescence intensity decline in the process of thickening the single coated layer.

Key Words: BaMgAl₁₀O₁₇ : Eu²⁺, Sol-gel method, Double-coating, SiO₂ and Al₂O₃.

INTRODUCTION

Europium-doped barium magnesium aluminate (BaMgAl₁₀O₁₇:Eu²⁺, BAM) has been widely used in tri-colour fluorescent lamps, plasma display panels and near-ultraviolet excited light emitting diodes due to high emission efficiency and good chromaticity¹. However, luminance degradation and colour coordinates shift were two bottlenecks which have restricted its wider applications. In recent years, surface coating to barium magnesium aluminate has attracted extensive attention. Examples of such surface coated materials are SiO₂²⁻⁶, Al₂O₃⁷⁻¹⁰, MgF₂¹¹⁻¹³, MgO¹⁴, ZnO¹⁵ and Y₅SiO₅¹⁶. Reports in the literature suggested that that coating is an effective way to improve the stability of barium magnesium aluminate. It is assumed that a suitable shell grown around the surface of barium magnesium aluminate probably acts as a protection layer against the thermal degradation, since the surface is a place where the reaction takes place first between air and phosphors¹⁴. The relationship between the thickness of the coating layer and the optical properties were investigated. The results indicated that thin film coating could not cover the phosphor particles completely to prevent barium magnesium aluminate from oxidation effectively, but thicker coating layer results in high reflectance and low transmission ratio, which causes low

luminescent intensity¹¹. In order to more effectively protect barium magnesium aluminate, coating layer should be as thick as possible in the range of zero reflectance¹², but the single layer can not increase absolute-ness because of the above limitation.

However, double coating method was reported by Hu¹⁷ and Seo¹⁸ for the better protection. They coated green phosphor BaMgSrAl₁₀O₁₇: Mn and red phosphor (Y, Gd) BO₃: Eu³⁺ with SiO₂/Al₂O₃, respectively. Results of their reports indicated that double coating phosphors have a better performance than single coating one. Aim with the same goal, we coated barium magnesium aluminate phosphor with SiO₂ single layer and SiO₂/Al₂O₃ double layers in this work, investigated their crystal structure and morphology, finally compared the luminescence intensity and colour shift after thermal treatment.

EXPERIMENTAL

The commercial blue phosphor barium magnesium aluminate (provided by Hunan Steady New material company) was coated with SiO₂ by sol-gel method and colloidal silica (Tianjin Fengchuan, AR) was used as precursor. The colloidal SiO₂ with concentration of 0.084 mol/L was dropped into the barium magnesium aluminate solution (50 g BAM in 500 mL de-ionized water). The pH value was adjusted to 7 with nitric

acid. The solution was kept stirring for 2 h at 80 °C, washed with ethanol and water and dried at 120 °C for 2 h. After calcination at 300 °C for 2 h, the SiO₂ coated phosphors were obtained. The obtained SiO₂ coated phosphor was used as core material for subsequent coating with colloidal Al₂O₃ (Tianjin Damao, AR). The process was the same as the first coating except the concentration of colloidal Al₂O₃ was 0.010 mol/L and pH value was adjusted to 8.

In order to compare the luminescence properties among un-coated, single coated and double coated samples, the thermal stability tests were investigated. After calcination of these samples at 600 °C for 0.5 h, the relative brightness and colour coordinate of the samples before and after the test were measured by the relative brightness meter (JY-2003, EVERFINE) and the photocolourimeter (PMS-50, EVERFIN), respectively. The morphology of material was examined by Nova Nano230 scanning electron microscope (SEM) and JEOL-1230 transmission electron microscope (TEM). X-ray diffraction (XRD) measurements were conducted by Rigaku-D/max X-ray diffractometer with condition of Cu K α at 40 kV tube voltage and 250 mA tube current. The distribution of the element was determined by EDAX energy dispersive spectrophotometer (EDS).

RESULTS AND DISCUSSION

The scanning electron microscope images of the un-coated (a), single coated (b) and double coated (c) phosphors have represented in Fig. 1. As shown in Fig. 1(a) the surface of un-coated blue phosphor is 2-3 μ m in size. Particles coating on the surface of single coated phosphors and double coated phosphors can also be observed in Fig. 1(b) and 1(c). But there is no clear difference exists between the single coated and double coated one. The burrs-like surface reported by other researcher⁸ has not found in this study, probably because the coated material was too thin to be observed. Results of TEM also confirmed this.

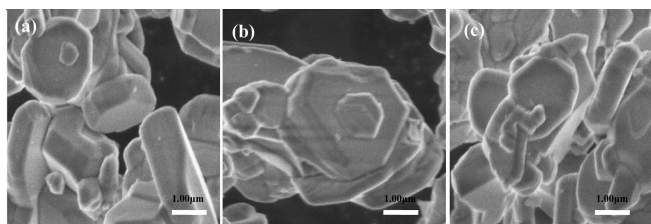


Fig. 1. Scanning electron microscope images of un-coated (a), single coated (b) and double coated (c) phosphors

The energy dispersive spectrophotometric analysis of the un-coated, the single coated and the double coated phosphors were shown in Fig. 2. As shown in Fig. 2(b), the silicon related peak was observed. Thus it confirmed that the particle on the surface of single coated sample was consisted of SiO₂. The peaks related to Si and Al were appeared in Fig. 2(c) and the content percentages of Al was increased from Fig. 2(b) to 2(c), which can explain that the material coated on the surface of the barium magnesium aluminate phosphor was composed of SiO₂ and Al₂O₃. The results above illuminated that the material coated on the surface of sample (b) was SiO₂ and both SiO₂ and Al₂O₃ coated on the surface of sample (c), double coated barium magnesium aluminate.

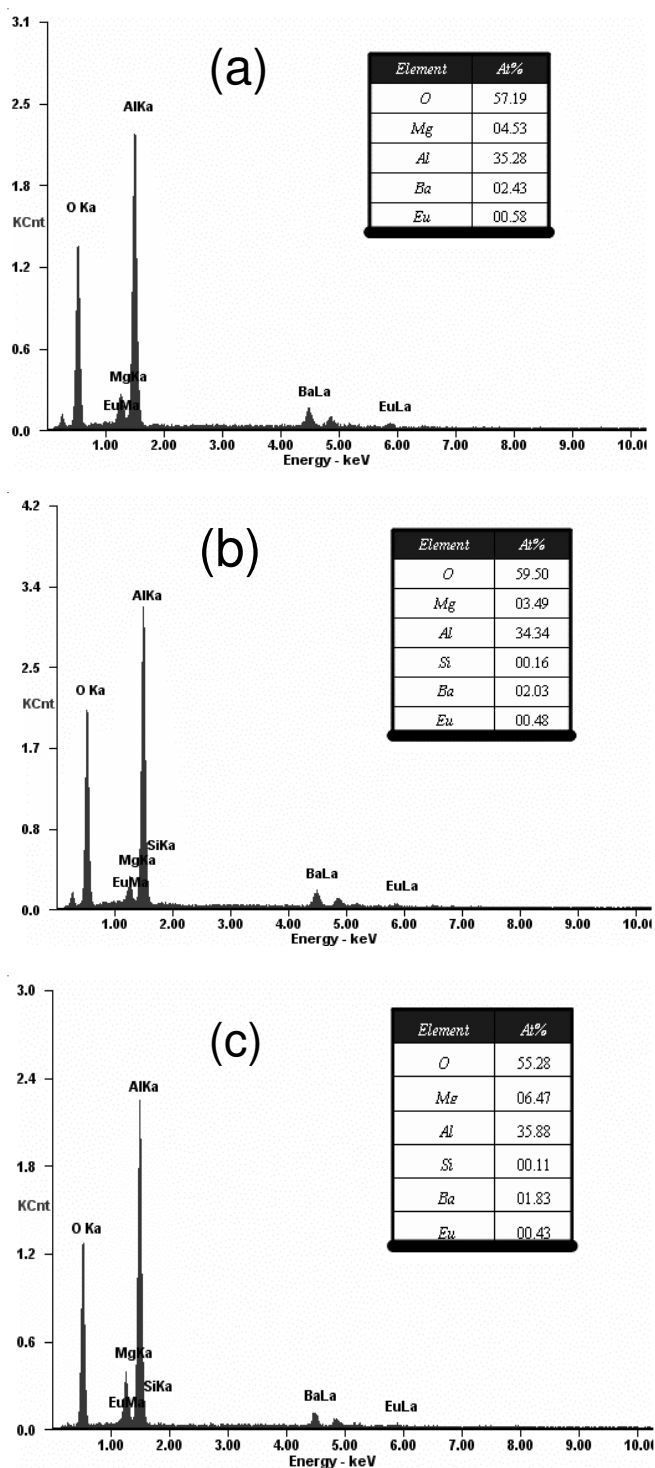


Fig. 2. Energy dispersive spectrophotometric data of un-coated (a), single coated (b) and double coated (c) phosphors

The typical diffraction curves were shown in Fig. 3. The X-ray diffraction patterns illustrated that no phase change for coated phosphor, which kept hexagonal crystal structure and all peaks agreed well with Ba_{0.956}Mg_{0.912}Al_{10.088}O₁₇ as the JCPDS-084-0818 shown. The diffraction peaks of Al₂O₃ and SiO₂ was not observed in Fig.3, indicating that Al₂O₃ and SiO₂ might only exist on the surface of the phosphor without any separate second phase. No crystalline was detected in the composite oxide of coating of Al₂O₃ and SiO₂, which meant that Al₂O₃ and SiO₂ all exist in the form of amorphism.

TABLE-1
RESULT OF THERMAL STABILITY TEST

	Before thermal treatment			After thermal treatment			ΔBr (%)	Δx	Δy
	*Br	x	y	Br	x	y			
Un coating	103.9	0.1420	0.1383	84.9	0.1423	0.1301	18.29	0.0003	0.0082
Single coating	102.5	0.1418	0.1386	95.5	0.1419	0.1344	6.83	0.0001	0.0042
Double coating	101.3	0.1418	0.1379	98.5	0.1417	0.1351	2.76	0.0001	0.0028

*Br: brightness

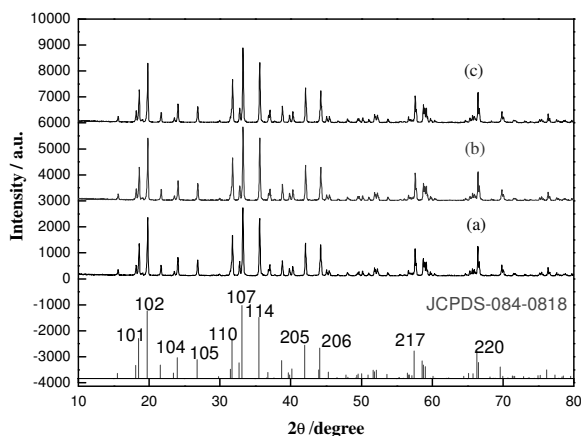


Fig. 3. X-ray diffraction patterns of un-coated (a), single coated (b) and double coated (c) phosphors

The transmission electron microscope images of the un-coated (a), single coated (b) and double coated (c) phosphors were shown in Fig. 4. The surface of un-coated barium magnesium aluminate phosphor was smooth and clean from Fig. 4 (a). After coated with SiO₂, a continuous coating layer with burr-like surface could be seen in Fig. 4(b). The reason that the burr-like layer could not be seen from the SEM images is possibly because the layer was not three-dimensional and it could only be observed from the side view. So there were not have too much different between coated and un-coated phosphors in SEM images. Fig. 4(c) revealed that barium magnesium aluminate have been coated with SiO₂ and Al₂O₃ layer successfully, also illustrated the thickness of first layer and second layer were 60 and 15 nm, respectively.

The results of the thermal stability test were presented in Table-1 and the relative brightness changed before and after the thermal treatment exhibited in Fig. 5. The results shown that relative brightness loss of un-coated, single coated and double coated phosphors was 18.29, 6.83 and 2.76 %, respectively. Double coated phosphors present much better performance than that of single coated phosphors. The performance of the un-coated sample was worst among all these samples. On the other side, colour coordinates shift (Δx , Δy) of un-coated, single coated and double coated was (0.0003, 0.0082), (0.0001, 0.0042) and (0.0001, 0.0028), respectively, which demonstrated that x coordinates did not change as much as the y coordinates after thermal treatment. The biggest shift for y coordinate was appeared at un-coated phosphors, then single coated barium magnesium aluminate, the double coated barium magnesium aluminate did the best performance in all these samples.

All these results above revealed that the double coated modification method improved the thermal stability effectively. The problems of luminance intensity decrease and colour shift

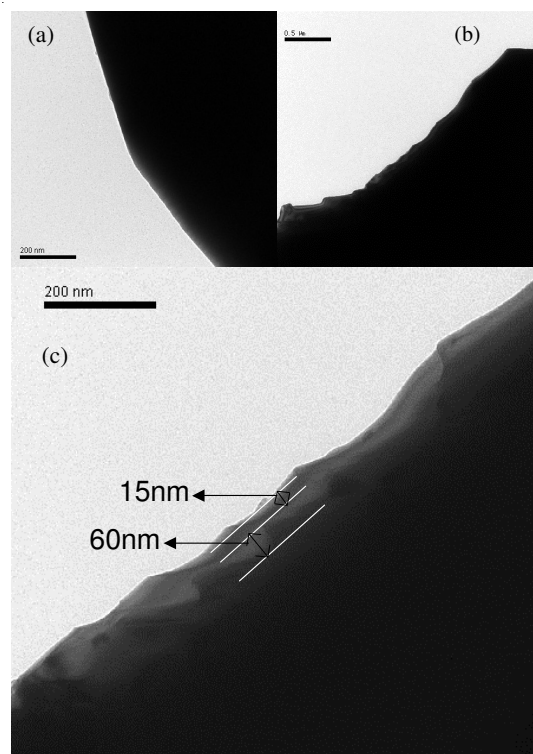


Fig. 4. Transmission electron microscope images of un-coated (a), single coated (b) and double coated (c) phosphors

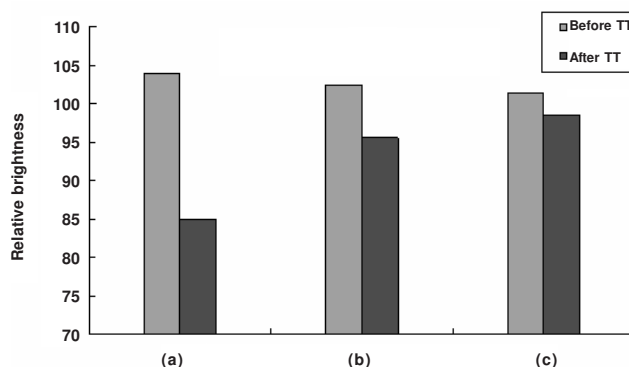


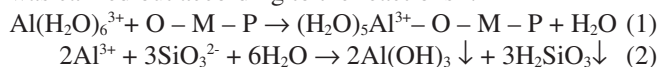
Fig. 5. The relative brightness before and after the thermal treatment of un-coated (a), single coated (b) and double coated (c) phosphors
**TT: Thermal Treatment

have been mitigated by double coated method, which might be used to modify other types of phosphor with different coating material combination.

Bizarri and Moine¹ have proposed three mechanisms for the barium magnesium aluminate phosphors degradation, the oxygen vacancy adsorbed oxygen atom from the atmosphere, divalent europium ion diffused along with conduction layer and dopant ions transferred electron to the adsorbed oxygen

ions. Coated material represented as a shield to barium magnesium aluminate phosphors. Different kinds of material with different refractive index and reflectivity decided the quantity of the excitation UV light arrived to the phosphors surface. Coated process kept the oxygen out of the layer, so as to reduce the adsorption of oxygen, which minimized the degradation of the phosphor. The layers also protected the Eu^{2+} ions from high temperature environment, which avoided turn divalent europium to trivalent and reduced the luminescence intensity of barium magnesium aluminate samples.

Double coating method could overcome the problem of luminescence intensity decline in the process of thickening the single coated layer. SiO_2 and Al_2O_3 have been chosen for the double coating, which avoid the limitation of single coated. The double coating process of barium magnesium aluminate was carried out according to the reactions¹⁷.



wherein, M are Ba, Mg and Al, P represents phosphor particle and O - M - P represents metal-oxygen chemical bonds suspended on the surface of phosphor particle. $\text{Al}(\text{H}_2\text{O})_6^{3+}$ presents the existing form of Al^{3+} in aqua solution. Thus, a thin homogeneous and amorphous coating layer of Al_2O_3 and SiO_2 were formed by controlling pH value of the solution. The interaction between SiO_2 and Al_2O_3 films might be the reason for single coating method has better performance than single coating method both decreasing the relative brightness loss and reducing the colour coordinate shift.

Conclusion

In this study, we have coated BAM phosphors with silicon dioxide and alumina by a sol-gel method. The thickness of SiO_2 and Al_2O_3 layers were 60 and 15 nm, which improved the thermal stability of the samples effectively. The relative-brightness loss of un-coated, single coated and double coated phosphors was 18.29, 6.83 and 2.76 %. Colour coordinates shift (Δx , Δy) of these samples was (0.0003, 0.0082), (0.0001, 0.0042) and (0.0001, 0.0028). The problems of luminance intensity decrease and colour shift have been solved by double

coated method in a certain extent, which might be used to modify other types of phosphor with different coating material combination. The reason for the results above might cause by the interaction between silicon dioxide and alumina. Furthermore, the mechanism between these two films affect each other still need more research.

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