

## BaMgAl<sub>10</sub>O<sub>17</sub>:Eu blue phosphors with MgO coating and microwave irradiation

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### Abstract

Europium-activated barium magnesium aluminate (BaMgAl<sub>10</sub>O<sub>17</sub>:Eu (BAM)) phosphor particles were modified by surface coating with MgO using a polyol method. The photoluminescence (PL) properties of the MgO-coated BAM phosphors showed slightly improved blue-emission intensity compared to the unmodified ones, and reached a stronger peak intensity with 5.25% MgO coating, under vacuum ultraviolet (VUV) 147 nm excitation. Upon microwave irradiation on the MgO-coated BAM phosphors, the PL properties of the MgO-coated phosphors exhibited a much enhanced relative PL ratio, and a maximum relative PL ratio can be achieved when as high as 10.5% MgO was deposited on the phosphor surface. However, for mechanically ground phosphor powder, it was found that although the intensity of the MgO-coated BAM turned stronger with increasing MgO concentration under microwave irradiation, the purity of the resulting luminescence was slightly disrupted by the presence of a new peak near 470 nm, corresponding to BaMg<sub>3</sub>Al<sub>14</sub>O<sub>25</sub> compound. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** A. Ceramics; A. Optical materials; D. Luminescence

### 1. Introduction

Recently, plasma display panels (PDPs) have been used for large flat panel displays. However, luminescent properties such as intensity and efficiency of the resulting PDPs are still inferior to those of traditional cathode-ray tube displays. To overcome these drawbacks, optimization of phosphors becomes critical, especially for blue-emitting phosphor, i.e., barium magnesium aluminate (BaMgAl<sub>10</sub>O<sub>17</sub>:Eu (BAM)), which is currently widely used in PDPs. The vacuum ultraviolet (VUV) optical properties of BAM have been extensively studied in recent years. Color quality and luminescence efficiency of this phosphor deteriorated during both panel preparation (thermal damage) and panel operation (radiation damage) [1–6]. Surface modification of the phosphors is then a major considera-

tion for desired optical properties of the phosphors. Deposition of metal oxide such as MgO, In<sub>2</sub>O<sub>3</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> on phosphor surface has been widely investigated [7]. Address time of MgO-coated green-emitting phosphor was decreased and the address voltage was also reduced to 25 V without any misfiring problem. Furthermore, it was reported that BAM phosphors coated with MgO on the surface showed improved resistance to degradation than that without coating under VUV 147 nm excitation. Luminescence intensity of the MgO-coated phosphor was also reported to have an improvement of about 10% [8]. These results can be interpreted as a secondary electron emission coefficient ( $\gamma$ ) of MgO and irradiation-induced surface change of the BAM powders [9].

In order to avoid thermal damage on the luminescent properties of the BAM phosphor powder, a so-called polyol method was used to modify the BAM surface by coating with different amounts of MgO and a rapid microwave treatment was followed on the MgO-coated

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BAM phosphor powder. Effect of microwave irradiation and MgO coating on the surface defect and luminescent properties of MgO-coated BAM powders is elucidated in this work. Besides, BAM phosphors were also extensively mechanically ground and then modified with MgO coating on the fractured surface. The luminescent properties are also evaluated, in comparison to those as-received BAM phosphors.

## 2. Experiment

MgO precursors were prepared by polyol method. Magnesium acetate tetrahydrate ( $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , J.T. Baker, 99.99%), 18.7 g, was dissolved in 50 ml diethylene glycol (Riedel-deHaën, 99.00%). After intensive stirring, 1.0 ml of 0.1 M NaOH was added, the mixture solution turned opaque. After the MgO precursor solution became clear, different weight ratios of the as-received BAM phosphor and MgO were prepared by dispersing the phosphor powder in the MgO precursor solution. Different amount, i.e., 1.75%, 5.25%, 10.5%, 17.5%, and 35% (based on 1 g of the BAM phosphor powder) of MgO was coated on the phosphor particles. After filtration, the MgO-coated BAM powders were dried and fired at 350 °C for 30 min to enhance adhesion of the MgO coating on phosphor surface. In addition, mechanically ground phosphors were also prepared by Agitator Bead Mill (DYNO-Mill type MuITILAB, JP) with a rotation rate at 55.7 Hz for 6 h. Subsequently, the MgO-coated BAM

phosphors were treated by microwave irradiation at 300 W for various duration times. Surface morphology of the blue-phosphors powders was examined by field-emission scanning electron microscopy (FESEM, JEOL-6700). The crystallinity of BAM was analyzed by X-ray powder diffraction (XRD, MAX SCIENCE M18XHF KXY-8019-1). The photoluminescence (PL) properties of the blue-emitting phosphor were analyzed by VUV excitation at 147 and 173-nm peak wavelength, 25-ns pulse width, and 10 Hz of synchrotron radiation at room temperature.

## 3. Results and discussion

A smooth and clean surface of the as-received BAM phosphor powder was observed, as shown in Fig. 1(a). However, after deposition with various amounts of MgO, the surface of the MgO-coated phosphors showed a roughened morphology which is attributed to the formation of randomly distributed MgO particles on the surface (Fig. 1(b)). An increasing population of the MgO particles deposited on the phosphor surface was observed and is proportional to the concentration of MgO precursor used upon synthesis. A dense coating was achieved when the concentration of the MgO reached 17.5% (Fig. 1(c)) and the high-resolution TEM micrograph (Fig. 1(d)) shows an adhesive thin-film MgO coating on the phosphor surface.

The XRD patterns of the MgO precursor (Fig. 2(a)) show a well-crystalline MgO phase above 350 °C. However,

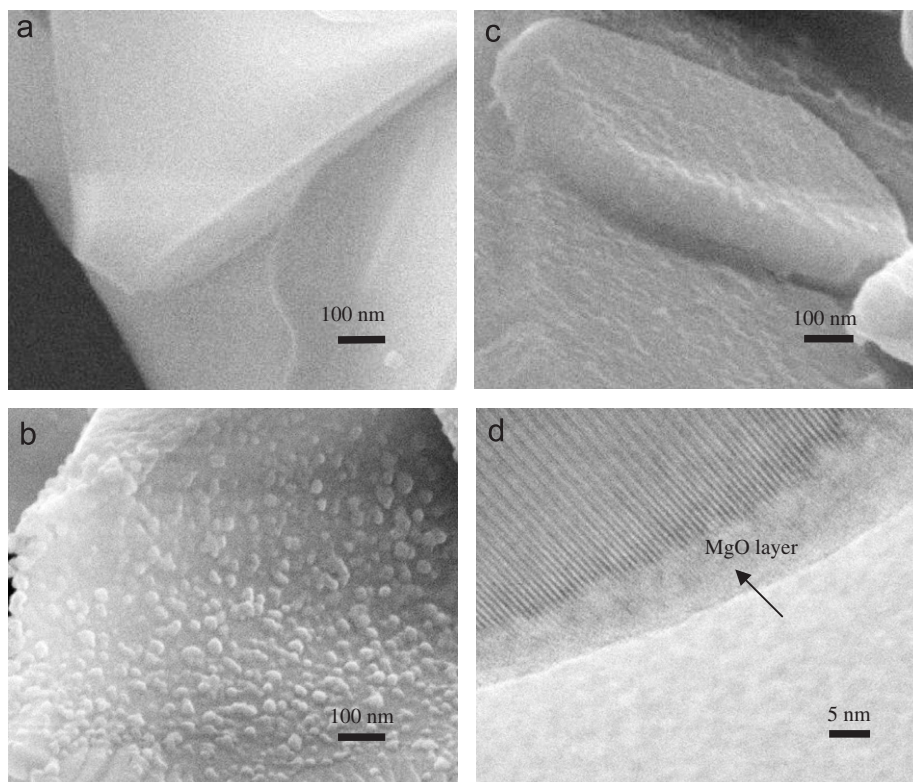


Fig. 1. SEM surface images of (a) as-received BAM phosphor and BAM phosphors coated with MgO, (b) 5.25%, and (c) 17.5%. High-resolution TEM of (c) showing the MgO layer adhesively attached on the surface of the BAM particle in (d).

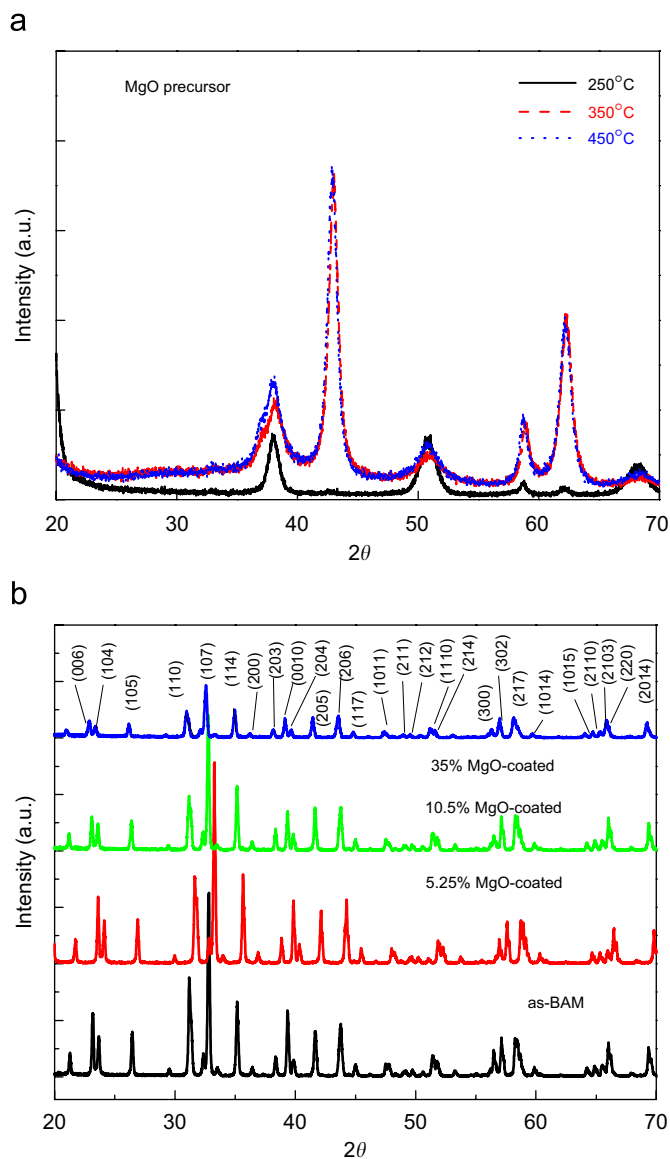


Fig. 2. XRD patterns of (a) MgO precursor and (b) coated and uncoated BAM phosphors.

MgO phase were non-detectable on the MgO-coated BAM powders (Fig. 2(b)) which is suggestive of too thin the MgO layer or probably an amorphous nature as a result of poor crystallization. However, excessive deposition of the MgO may reduce the crystallinity of the BAM itself which may further de-stabilize or reduce the luminescence property. A peak-shift was observed in Fig. 2(b), which is believed to attribute as a host-lattice distortion induced by a chemical interaction between MgO and BAM host.

Fig. 3(a) shows the PL intensity of the MgO-coated and -uncoated BAM excited by 147 nm VUV. The blue-emission intensity of the MgO-coated BAM is slightly increased compared to that of the uncoated (as-received) BAM. This may be attributed to the fact that more secondary electrons which were generated by the MgO layer promoted luminescence of the phosphor under VUV excitation. However, after microwave irradiation treatment

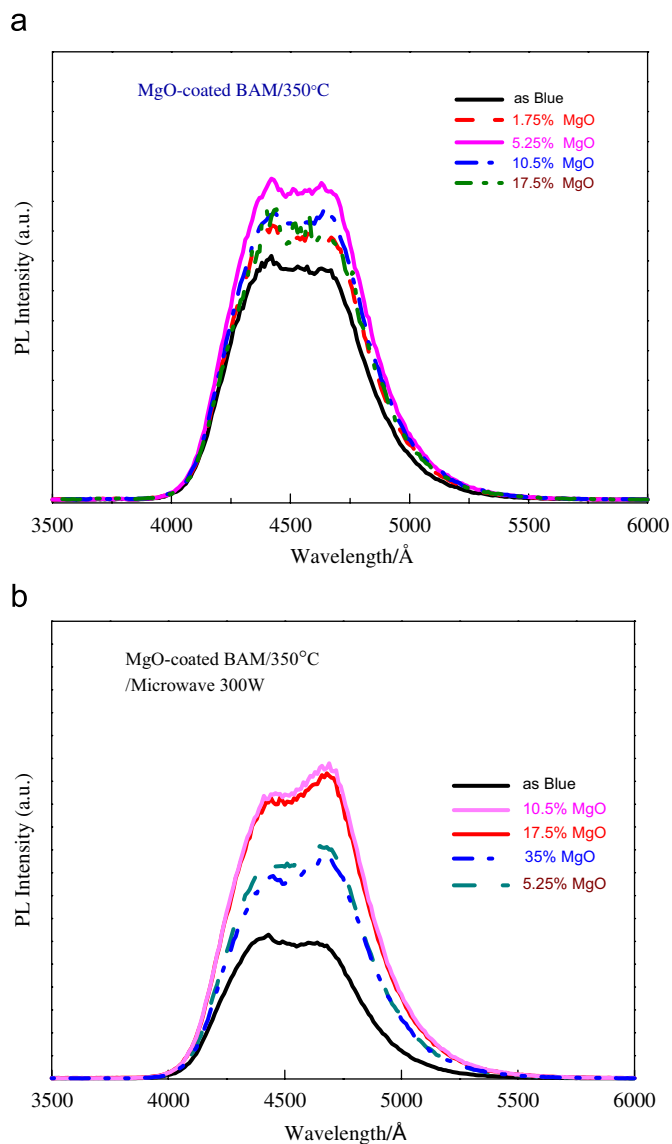


Fig. 3. PL intensities of (a) coated and uncoated BAM phosphors, and (b) MgO-coated BAM with microwave irradiation treatment.

(Fig. 3(b)), 10.5% MgO-coated BAM shows the best luminance intensity compared to that of the BAM coated with MgO of other concentrations. The actual reason is not clearly understood at present but it is believed that an optimally efficient absorption of microwave irradiation by MgO would transfer energy to BAM host, resulting in an increased PL intensity. The relative intensity ratio of blue emission of the MgO-coated BAM powders to uncoated BAM powders under microwave irradiation is summarized in Fig. 4. It can be observed that without microwave irradiation, the 5.25% MgO-coated BAM phosphor exhibited higher luminance intensity and a maximum relative PL ratio appeared in the 10.5% MgO-coated BAM following a subsequent microwave irradiation treatment. Furthermore, one special feature was noted that the peak intensity near 470 nm was enhanced after microwave irradiation. This indicates that a strong

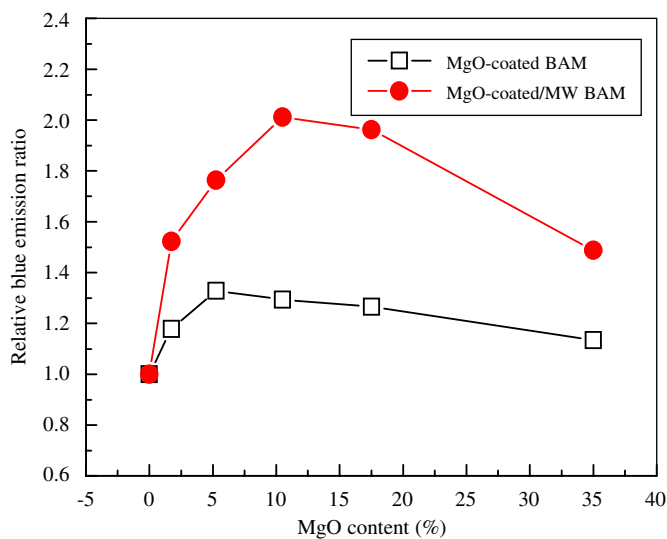


Fig. 4. Relative emission ratio of MgO-coated BAM phosphors with and without microwave irradiation.

interaction took place between the BAM powder and MgO thin layer under microwave treatment.

For those BAM phosphor powder subjected to mechanically ground, more defects were introduced and the crystallinity of BAM host reduced. The emission intensity of the ground BAM phosphor can be adversely affected. This is clearly evidenced by a reduction of the luminescent intensity of the ground phosphor powder compared to that of the as-received BAM. However, after the ground BAM phosphor powder was coated with MgO and then fired at 350 °C, the blue emission intensity was increased (Fig. 5(a)). The maximum emission intensity was detected for those ground BAM powder treated with 10.5% MgO. Furthermore, a characteristic peak near 470 nm starts to appear for the ground BAM powder after surface modification. However, when the MgO-coated ground BAM phosphor powder was subjected to microwave treatment, an enhanced PL is observed and the characteristic peak near (470 nm) becomes stronger and sharper, as shown in Fig. 5(b). This may suggest that particle reduction and microwave irradiation provide an effective surface modification with improved luminescence properties on those MgO-coated ground BAM powder.

The peculiar behavior of the development of 470 nm peak may be related to an improvement in the orderness of crystalline structure or chemical modification on the surface of the MgO-coated BAM phosphors after microwave irradiation treatment. The newly developed BAM host shows a composition slightly different from the as-received BAM phosphor ( $\text{BaMgAl}_{10}\text{O}_{17}$ ), synthesized at a high temperature, which emits at 449 nm (BAM-I) [10]. This observation is supported by earlier studies in which Ravichandran et al. reported that as the BAM powder was prepared from hydrothermal synthesis, a newly developed BAM compound was obtained. The new  $\text{BaMg}_3\text{Al}_{14}\text{O}_{25}$  (BAM-II) activated with  $\text{Eu}^{2+}$  produced new BAM phase

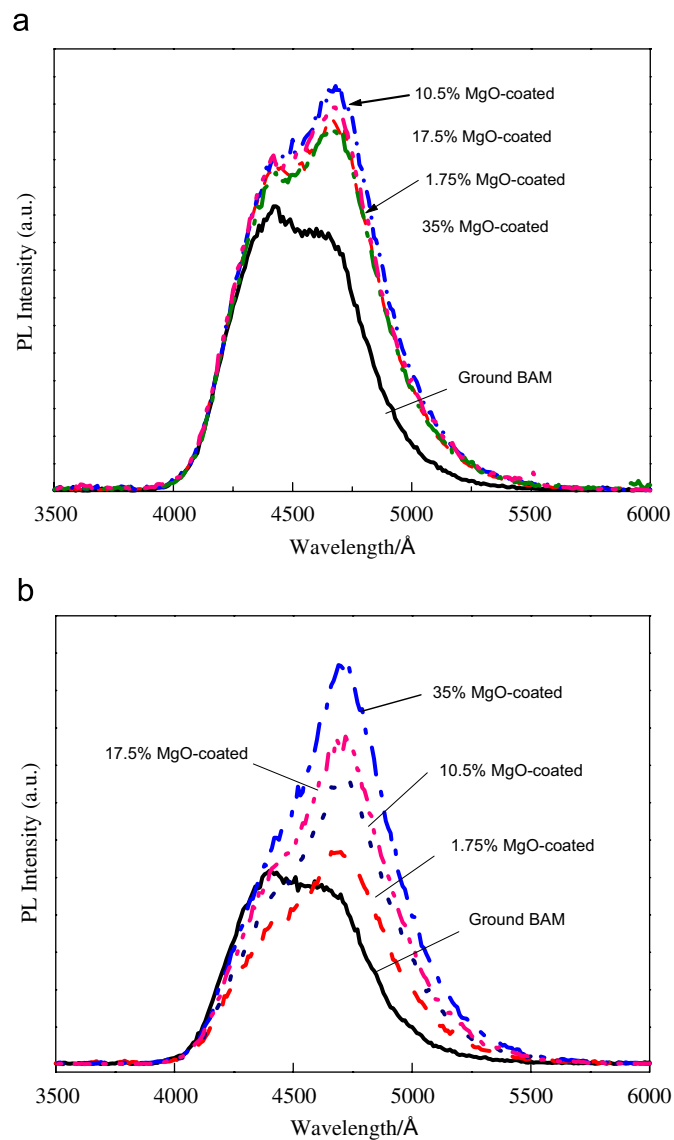


Fig. 5. PL intensities of (a) ground BAM phosphors with MgO coated and (b) ground phosphors with both MgO coated and microwave irradiation treatment.

with a peak at 467 nm [11]. A comparison between BAM-I and BAM-II reveals that the ratio of Mg relative to Ba in the latter composition is higher than that in the former. Therefore, it can be inferred that as the MgO-coated ground BAM powder was treated with microwave irradiation, the microwave energy may induce a chemical interaction along the interface between the MgO and BAM surface. Consequently, an Mg-rich BAM phase was probably formed near the surface of the as-received BAM particles. As evidenced in Fig. 5(a), with the increase of MgO on the BAM particle surface, a 470 nm peak corresponding to a new BAM compound becomes stronger in intensity. The spectrum of microwave-treated MgO-coated BAM was distinctly different from the spectrum of the as-received BAM phosphor powder, suggesting a change in the distribution of activator ions over the possible  $\text{Ba}^{2+}$  sites in BAM host.

#### 4. Concluding remarks

In this work, it was found that MgO-coated BaMgAl<sub>10</sub>O<sub>17</sub>:Eu blue phosphor showed an improvement in the luminescent efficiency, compared to uncoated phosphor. The concentration of the MgO used on the coating is critically important, and experimental results showed that 5.25% (in weight) of MgO coating is sufficiently enough for a uniform surface coverage on the blue phosphor powder without loss of luminescence brightness. An optimal amount of the MgO coating is characterized to be 10.5% for the mechanically ground BAM phosphor powders. Microwave irradiation treatment is able to enhance the luminance properties of the phosphors, ground and as-received, but induce the formation of a crystalline phase, namely BaMg<sub>3</sub>Al<sub>14</sub>O<sub>25</sub>, which has an emission peak near 470 nm, especially for the MgO-coated ground BAM powder.

#### Acknowledgments

The authors gratefully acknowledge the financial support of Central Research Institute, Chungwha Picture Tubes Ltd., Taoyuan, Taiwan, ROC.

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