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Structural and photoluminescent properties of nanosized $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ blue-emitting phosphors prepared by sol-gel method

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Abstract

We report on the photoluminescent properties of $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ (BAM) phosphors in correlation with the host crystalline structures. The phosphors were synthesized by citrate sol-gel process, followed by a sintering and a reduction step, both at elevated temperatures. We found that the phosphors were amorphous when sintered at temperatures below 900 °C. At 1000 °C, the crystalline structure was mainly that of BaAl_2O_4 phase. The $\text{BaMgAl}_{10}\text{O}_{17}$ phase appeared at 1100 °C, and became dominant with increasing temperature. At 1300 °C, the BaAl_2O_4 phase almost disappeared, and only $\text{BaMgAl}_{10}\text{O}_{17}$ features were found. The luminescent characteristics of the phosphors were closely related to the structures of the host lattice. Under the same reduction conditions, the phosphors sintered at 1000 °C showed the emission of both Eu^{3+} and Eu^{2+} . For the phosphors sintered at higher temperatures, the main features were originated from the emission of Eu^{2+} . We additionally observed the increase of emission intensity and the broadening of emission spectra with increasing reduction temperature.

Keywords: photoluminescence, BAM, phosphors, sol-gel, nanopowders

Classification numbers: 4.02, 4.04, 5.04

1. Introduction

The blue-emitting phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, which is commonly known as BAM, has been widely used in various luminescent devices in the last several decades due to its high luminescent efficiency under ultraviolet (UV) light excitation. The phosphor was first developed together with green-emitting $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ and red-emitting $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors for tricolor fluorescent lamps in 1970s [1, 2], which are still popularly used in the present time. Recently, its applications have been extended to plasma display panels (PDPs) and white light-emitting diodes (LEDs) [3–5]. The main

feature of the blue luminescence is the emission caused by the transition from the $4f^65d$ excitation state to the $4f^7$ ground state in Eu^{2+} , which is commonly reduced from the trivalent state (Eu^{3+}) [6].

The structure of $\text{BaMgAl}_{10}\text{O}_{17}$ consists of two spinel blocks ($\text{MgAl}_{10}\text{O}_{16}$) separated by one mirror plane (BaO) [7]. When Eu^{2+} is substituted into the host lattice, it can occupy three prominent locations: Beever–Ross (BR), anti-Beever–Ross (a-BR), and mid-oxygen (mO) sites in the mirror plane [8]. Under UV excitation, Eu^{2+} at a-BR sites will emit light with a wavelength in the range of 450–460 nm. At BR sites, Eu^{2+} generates a shorter wavelength (~440 nm), whereas a



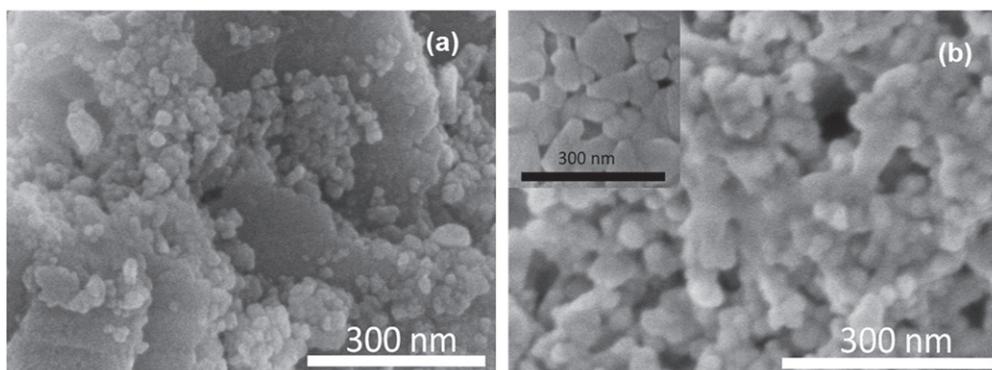


Figure 1. SEM images of grinded gel (a) and the powders sintered at 1300 °C for 3 h (b). The inset of (b) shows the morphology of the phosphors sintered at 1300 °C for 3 h and reduced at 1200 °C for 1 h.

longer wavelength (>480 nm) is observed for the ions at mO sites [3, 4]. The theoretical calculation showed that an a-BR site is energetically more stable than the others [9].

The thermal stability of Eu^{2+} , and therefore the luminescent stability of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ are strongly dependent on its site occupancy. Even at a-BR sites, Eu^{2+} can be oxidized to the trivalent state, causing the luminescence degradation of the phosphors [4, 10–13]. This occurs when the temperature of BAM is raised up to 500 °C during baking up in PDP processing, and is a critical problem that can cause, for example, the modification of the red, green and blue sub-pixel size in the panel design of PDPs [14]. To avoid the degradation, several methods have been introduced, including coating the phosphors with oxide materials (MgO , SiO_2), or mixing BAM with an ultraviolet emitting material [15–17].

BAM has been synthesized by conventional solid state method [12, 14, 18, 19], combustion [20, 21], spray pyrolysis [22, 23], and citrate sol-gel [3, 24]. In all these methods, the phosphors must be annealed at elevated temperatures, i.e. from 1200 °C to 1800 °C to obtain good crystallinity and high luminescent intensity. As the emission of the Eu^{2+} is strongly affected by its surroundings, understanding the influence of the host lattice structure on the emission properties is of importance in tailoring the experimental conditions to obtain desired phosphors.

In this work we investigated the luminescent properties of $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ phosphors in correlation with the host crystalline structures. The powders were prepared by citrate sol-gel method, followed by sintering and reduction processes at elevated temperatures. We observed the evolution of the host crystalline structures when increasing the sintering temperature from 900 °C to 1300 °C, and found strong influence of the crystalline structures on luminescent properties of both as-sintered and reduced phosphors.

2. Experimental

The $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM) blue phosphors were prepared by citrate sol-gel process using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), $\text{Ba}(\text{NO}_3)_2$ (99%), MgO (99.99%) and Eu_2O_3 (99.99%) as starting reagents. A stoichiometric amount of the materials

was used to obtain the mole ratio of $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$. In the first step, Eu_2O_3 and MgO were dissolved in HNO_3 (69%) at room temperature to produce $\text{Eu}(\text{NO}_3)_3$ and $\text{Mg}(\text{NO}_3)_2$ solutions. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ were then added, and the mixture was stirred continuously using a magnetic stirrer until the solution became transparent. Next, citric acid was added, and the solution was heated at 80 °C. The water evaporation converted the solution into a white viscous gel, which was then dried at 120 °C for 2 h, grinded and sintered at a temperature in the range of 900–1300 °C for 3 h in air. Until this point, the europium ions were in the form of Eu^{3+} , which emitted light in the wavelength range of 600–700 nm (red-emitting phosphors) upon excitation. To obtain blue-emitting phosphors, the powders were further annealed in a reducing ambient (90% Ar, 10% H_2) at a temperature in the range of 900–1200 °C for 1 h.

The phosphor morphology was observed by scanning electron microscopy (SEM) using a Hitachi S-4800 FE-SEM. The crystalline structures of the powders were studied using a Siemens Brucker D8-Advance XRD system with $\text{Cu-K}\alpha$ radiation. The emission spectra were recorded using a He-Cd laser (325 nm) as excitation source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Morphology of synthesized phosphors

Figure 1 shows the morphology of the grinded gel after drying at 120 °C (a) and the powders sintered at 1300 °C for 3 h (b). Clusters of phosphors with various shapes and sizes are seen for the grinded gel. However, nanosized particles can also be found on the clusters. The powders sintered at 1300 °C exhibit granular morphology with sub-micrometer clusters of nanoparticles with average size of about 20–30 nm. Upon anneal in reducing ambient (to reduce Eu ions from Eu^{3+} to Eu^{2+}), the size of the particles increased slightly, possibly due to the agglomeration of the powders during the reduction (the inset of (b)).

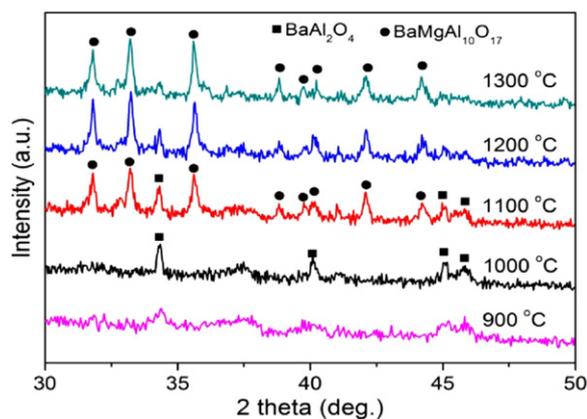


Figure 2. XRD patterns of the phosphors sintered at different temperatures.

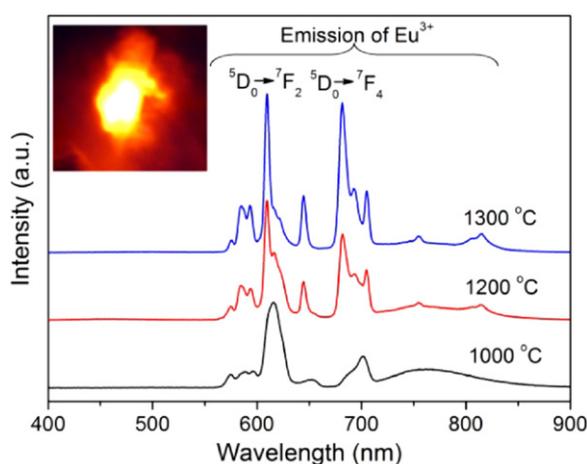


Figure 3. PL spectra of BAM powders sintered at different temperatures. The inset shows the photograph of the phosphors sintered at 1300 °C during the excitation by a 325 nm wavelength He-Cd laser.

3.2. Crystalline structures of synthesized phosphors

Figure 2 shows the XRD patterns of BAM powders sintered at different temperatures. No XRD peaks were found for the powders sintered below 900 °C. The powders sintered at 1000 °C revealed the XRD patterns of mainly BaAl_2O_4 phase (the squares) [25, 26]. The peaks of $\text{BaMgAl}_{10}\text{O}_{17}$ phase (the circles) appeared from 1100 °C, including the featuring peaks located at 31.78°, 33.18° and 35.60° which correspond to the (110), (107) and (114) planes, respectively [27]. The $\text{BaMgAl}_{10}\text{O}_{17}$ phase exhibited its predominance with increasing temperature. At 1300 °C, BaAl_2O_4 phase almost disappeared, and only the XRD patterns of $\text{BaMgAl}_{10}\text{O}_{17}$ were found [3, 27]. This indicates that single phase $\text{BaMgAl}_{10}\text{O}_{17}$ phosphors were obtained.

3.3. Luminescent properties of the phosphors

Figure 3 shows the photoluminescence (PL) spectra of as-synthesized phosphors sintered at temperatures in the range of 1000–1300 °C. The plots show the featuring emission spectra of Eu^{3+} ions with the main peaks at 610 nm and 681 nm (red

emission, see the inset of the figure). These wavelengths correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively, of electrons upon the excitation and relaxation processes [3]. The intensity of the longer wavelength emission increased with increasing sintering temperature relatively compared to that of the shorter wavelength. It is known that the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is strongly affected by the surroundings. When Eu^{3+} ions occupy the sites with higher asymmetry, the emission from $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is very weak, and vice versa [3]. The intensity difference of the 610 nm and 681 nm peaks at different temperatures is therefore attributed to the difference of Eu^{3+} occupancy in the host lattice, which is strongly temperature dependent, as shown in figure 2. For all samples, extremely low signal of blue emission was detected. The results indicate that in the pre-reduction BAM phosphors, the europium exists mainly in trivalent state (Eu^{3+}).

In order to obtain the blue-emitting phosphors, the powders were then annealed in reducing ambient containing 90% Ar and 10% H_2 at different temperatures. Figure 4(a) shows the emission spectrum of the phosphor sintered at 1000 °C for 3 h, followed by a reduction at 1100 °C for 1 h. At this temperature, the emission of Eu^{3+} can still be observed. The broad emission band in the short wavelength range represents the emission of Eu^{2+} with the peak at 455 nm, corresponding to the transition from the $4f^65d$ excitation state to the $4f^7$ ground state [3, 28]. This indicates that Eu^{3+} was partially reduced. For the phosphors sintered at 1200 °C and 1300 °C and reduced under the same conditions, the emission of Eu^{2+} was totally dominant with a broad peak at 455 nm (blue colour) and only a minor contribution of Eu^{3+} was detected, as shown in figures 4(b) and (c). The PL spectra suggest that almost all trivalent ions were reduced to Eu^{2+} . However, a small shoulder was found at a wavelength of about 510 nm for the phosphors sintered at 1200 °C, possibly due to the emission of Eu^{2+} located at mO sites [3, 4]. This shoulder was not observed for the phosphors sintered at 1300 °C. We ascribe the observed trend of PL spectra with increasing sintering temperature to evolution of crystalline structure of the phosphors shown in figure 2. With increasing sintering temperature from 1000 °C to 1300 °C, the crystalline structure changed from the predominance of BaAl_2O_4 to $\text{BaMgAl}_{10}\text{O}_{17}$. This means that in the phosphor sintered at 1000 °C, the Eu^{3+} ions possibly incorporated into the lattice of BaAl_2O_4 . At 1200 °C, these ions could occupy in the lattice of either BaAl_2O_4 or $\text{BaMgAl}_{10}\text{O}_{17}$, whereas at 1300 °C only the latter was possible. The results suggest that Eu^{3+} ions incorporated into the BaAl_2O_4 lattice are more stable than those in the $\text{BaMgAl}_{10}\text{O}_{17}$ phase.

3.4. Influence of reduction temperature on PL properties

Figure 5 shows the PL spectra of the phosphors sintered at 1300 °C and reduced at different temperatures ranging from 900 °C to 1200 °C. We found that the emission intensity increased significantly with increasing temperature. This can be due to the contribution of increasing particle size of the phosphors. As mentioned above, the agglomeration occurred

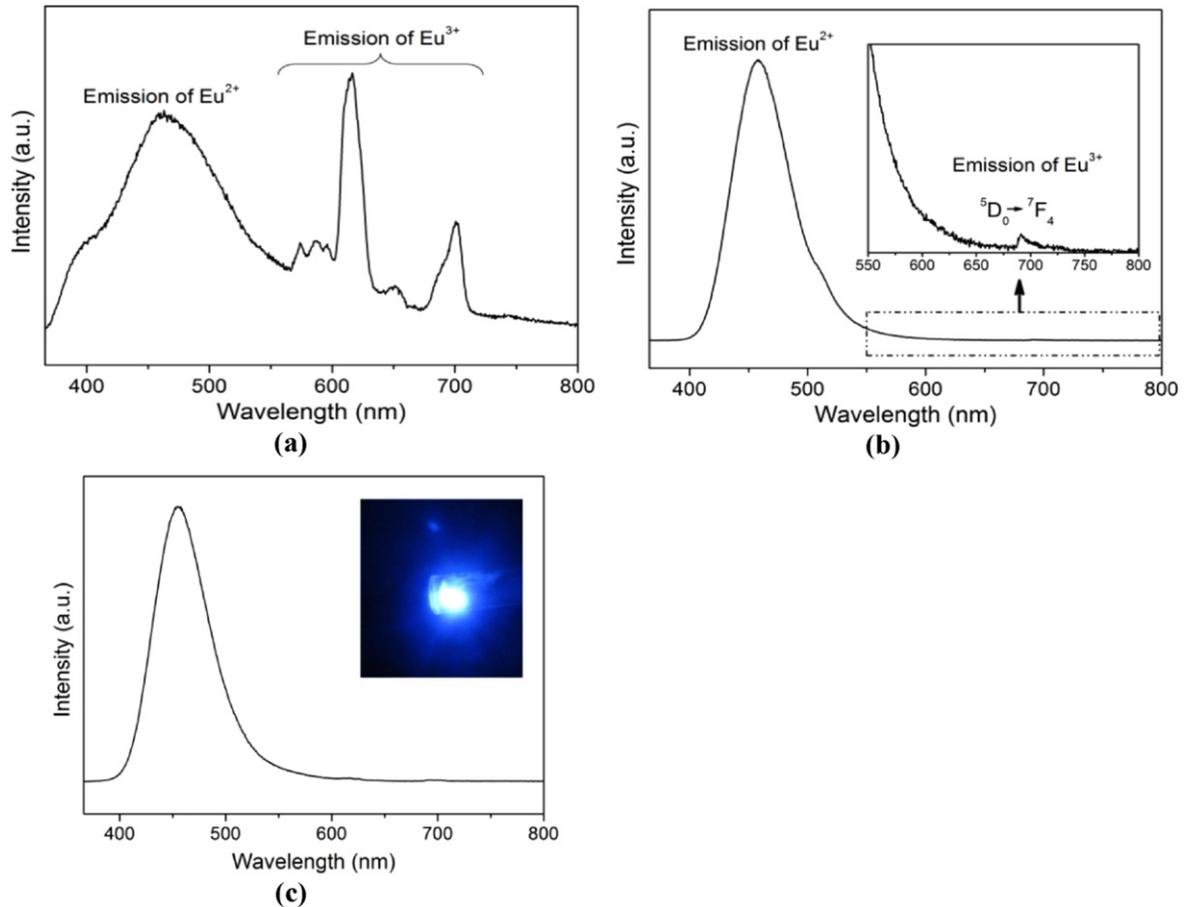


Figure 4. Photoluminescence spectra of the phosphors sintered at 1000 °C (a), 1200 °C (b) and 1300 °C (c) and reduced in (90% Ar, 10% H_2) ambient at 1100 °C for 1 h. The inset of (b) shows a zoomed-in view of the spectrum in the wavelength range of 550–800 nm. The inset of (c) shows the photograph of the phosphors reduced at 1200 °C during the excitation by a 325 nm wavelength He-Cd laser.

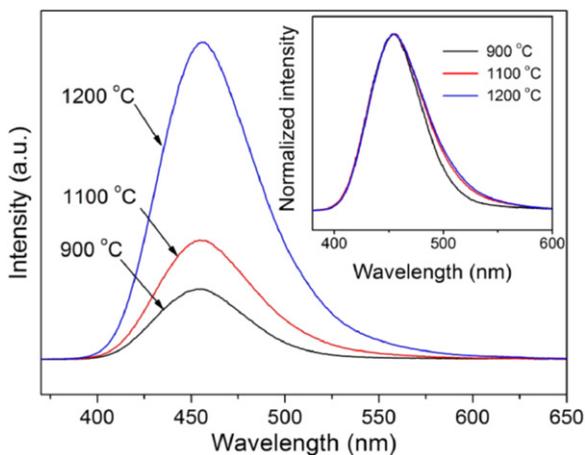


Figure 5. Emission spectra of the phosphors sintered at 1300 °C and reduced at different temperatures. The inset shows the normalized emission intensity.

during the reduction at high temperatures, forming bigger grains (see figure 1(b)) and better crystallinity. In addition, a broadening of the emission spectra to the longer wavelength range was observed when increased the reduction temperature from 900 °C to 1100 °C (see the normalized intensity shown

in inset of figure 5), whereas it is very small when the temperature raised from 1100 °C to 1200 °C. Generally, the broadening of emission spectra of $\text{BAM}:\text{Eu}^{2+}$ arises from Eu^{2+} occupying different sites [4]. When Eu^{2+} is substituted into the host lattice, it can occupy three prominent locations corresponding to BR, a-BR and mO sites (see above). The peak at 455 nm is caused by the Eu^{2+} at a-BR sites. When the ions are at mO sites, the emission peak will shift to a longer wavelength, whereas a shift to the other direction is attributed to the Eu^{2+} ions occupying at BR sites [3, 4]. Therefore, the broadening to the longer wavelengths in figure 5 (the inset) is attributed to the increasing contribution of Eu^{2+} at mO sites, which suggests that more Eu^{2+} ions occupied at mO sites when temperature raised from 900 °C to 1100 °C. Above this temperature, the amount of Eu^{2+} at mO sites remained nearly constant.

4. Conclusion

We have successfully synthesized BAM phosphors by citrate sol-gel process. The $\text{BAM}:\text{Eu}^{2+}$ blue-emitting phosphors were obtained by annealing the $\text{BAM}:\text{Eu}^{3+}$ as-sintered powders in reducing ambient at elevated temperatures. The

phosphor morphology, crystalline structure, and luminescent properties were studied. Clusters with arbitrary shapes and sizes were found for as-prepared gel. The sintered powders showed quite uniform granular morphology with grain sizes of about 20–30 nm. The anneal in reducing environment caused the agglomeration of the phosphors, resulting in slightly larger grains. We found that the powders were amorphous when sintered at temperatures below 900 °C. At 1000 °C, the crystalline structure was mainly BaAl₂O₄ phase. The BaMgAl₁₀O₁₇ phase appeared at 1100 °C, and became dominant with increasing temperature. At 1300 °C, the BaAl₂O₄ phase almost disappeared, and only BaMgAl₁₀O₁₇ features were found. The PL characteristics of the phosphors were closely related to the structures of the host lattice. In each phase of the crystalline structures, the phosphors exhibited featuring PL properties, both as-sintered and reduced phosphors. Increasing reduction temperature resulted in the increase of emission intensity and the broadening to the longer wavelength range of emission spectra, possibly due to the contribution of grain size, crystallinity and the emission of Eu²⁺ ions at mO sites in the host lattice.

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