

# Morphology control and luminescence properties of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphors prepared by spray pyrolysis

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## Abstract

Starting from the aqueous solutions of metal nitrates with citric acid and polyethylene glycol (PEG) as additives,  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  (BAM: $\text{Eu}^{2+}$ ) phosphors were prepared by a two-step spray pyrolysis (SP) method. X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectra were used to characterize the resulted BAM: $\text{Eu}^{2+}$  phosphors. The obtained BAM: $\text{Eu}^{2+}$  phosphor particles have spherical shape, submicron size (0.5–3  $\mu\text{m}$ ). The effects of process conditions of the spray pyrolysis, such as molecular weight and concentration of PEG, on the morphology and luminescence properties of phosphor particles were investigated. Adequate amount of PEG was necessary for obtaining spherical particles, and the optimum emission intensity could be obtained when the concentration of PEG was 0.03 g/ml in the precursor solution. Moreover, the emission intensity of the phosphors increased with increasing of metal ion concentration in the solution. Compared with the BAM: $\text{Eu}^{2+}$  phosphor prepared by citrate-gel method, spherical BAM: $\text{Eu}^{2+}$  phosphor particles showed a higher emission intensity.

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**Keywords:**  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ ; Phosphor; Spray pyrolysis; Luminescence; Morphology

## 1. Introduction

Inorganic luminescent materials have found many practical applications in modern lighting and display fields, such as fluorescent lamps, cathode-ray tubes, field emission displays and plasma display panels [1,2]. As a blue component,  $\text{Eu}^{2+}$ -doped barium magnesium aluminate with the typical composition of  $\text{BaMgAl}_{10}\text{O}_{17}$  (BAM: $\text{Eu}^{2+}$ ) has been widely used in fluorescent lamps and recently in plasma display panels (PDP) due to its high luminescence efficiency and good chromaticity [1–6]. Conventionally, the BAM: $\text{Eu}^{2+}$  phosphor is prepared by solid state reaction process, i.e., firing a mixture of  $\text{BaCO}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$ ,  $\text{Al}_2\text{O}_3$  together with a small amount of additional flux such as

$\text{AlF}_3$  or  $\text{MgF}_2$  at about 1600 °C in a reducing atmosphere, and the resulted phosphor contains irregularly shaped and aggregated particles (5–8  $\mu\text{m}$ ) which are not good for high screen brightness and high resolution [7]. Recently, BAM: $\text{Eu}^{2+}$  phosphors were prepared by sol-gel method, and it was found that codoping with the rare earth ions  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  could increase the luminescent intensity of the phosphor under the VUV excitation, but no morphology and its effects on the luminescent properties were reported therein [6].

It has been reported that phosphor materials must have fine size (<3  $\mu\text{m}$ ), narrow size distribution, non-agglomeration, and spherical morphology for good luminescent characteristics [8]. Oshio et al. has reported that nearly spherical morphology and uniform particle size for BAM phosphor could improve the screen brightness due to the translucent phosphor layer [9]. Additionally, high packing densities and low scattering

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of light can also be obtained by using spherical phosphors [5]. Recently, spray pyrolysis technique has been applied in the preparation of luminescent materials [5,10–13]. In general, luminescent materials derived from this method have spherical morphology and narrow size distribution. In this process, a misted stream of precursor solution is dried, precipitated, and decomposed in a tubular furnace reactor. Particles produced by the spray pyrolysis process are relatively uniform in size and composition because of microscale reaction within a droplet and the lack of a milling process. It has been reported that the luminescence intensity of phosphors derived from the spray pyrolysis process is close or higher than that of the corresponding commercial ones [10–13].

Our group has been focusing on the preparation of luminescent materials via soft chemical methods, such as sol-gel process [14–16] and spray pyrolysis process [17,18], in an effort to get multiform of phosphor materials and control their morphology in an ideal shape and size. In this paper we prepared BAM:Eu<sup>2+</sup> phosphors by a two-step spray pyrolysis process (SP) using the aqueous solutions of metal nitrates with citric acid and polyethylene glycol (PEG) as additives for the first time. The effects of experimental conditions, such as metal ion concentrations, ratios between citric acid and metal ions, molecular weight and concentration of PEG on the morphology and luminescence properties of the BAM:Eu<sup>2+</sup> phosphors were investigated. Furthermore, the performance of the SP-derived BAM:Eu<sup>2+</sup> phosphors was compared with that of the ones prepared by citrate gel (CG) process.

## 2. Experimental

The starting materials for the preparation of BAM:Eu<sup>2+</sup> phosphors were Ba(NO<sub>3</sub>)<sub>2</sub> (Analytical reagent, A.R., Beijing Fine Chemical Company), Mg(OH)<sub>2</sub>·4MgCO<sub>3</sub>·6H<sub>2</sub>O (A.R., Beijing Fine Chemical Company), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (A.R., Beijing Fine Chemical Company), Eu<sub>2</sub>O<sub>3</sub> (99.99%, Shanghai Yuelong Non-Ferrous Metals Limited). The doping concentration of Eu<sup>2+</sup> is 10 mol% of Ba<sup>2+</sup> in BaMgAl<sub>10</sub>O<sub>17</sub>, i.e., all samples have a composition of Ba<sub>0.9</sub>Eu<sub>0.1</sub>MgAl<sub>10</sub>O<sub>17</sub>, which has been optimized before [4]. The stoichiometric amount of the starting materials were weighted, dissolved in water or diluted HNO<sub>3</sub>, and mixed under stirring and heating. Subsequently, certain amount citric acid mono-hydrate (citric acid/metal ion = 0.5:1, 1:1, 2:1, 3:1) and polyethylene glycol (PEG, molecular weight = 600, 1000, 6000, 10,000) were added and dissolved in the above solution, and the resulting mixtures were stirred for 2 h. For the spray pyrolysis (SP) process, the above solution was loaded to a spray pyrolysis apparatus (BÜCHI Mini Spray Dryer B-191)

to obtain SP precursor particles. For the CG process, the above solution was concentrated by slow evaporation at 75 °C and dried in an oven at 110 °C overnight to obtain the gel powder. Such gel powder was finely ground in an agate mortar to obtain the CG precursor particles. Finally, the above precursor particles were annealed at 1400 °C for 6 h under a reducing atmosphere of CO in order to reduce Eu<sup>3+</sup> to Eu<sup>2+</sup> which replaces Ba<sup>2+</sup> in the host lattices.

Phase development in the post-annealed powder samples were checked by X-ray diffraction (Rigaku, D/max-II B) using Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm). The morphology of the samples was inspected using scanning electron microscope (JEOL JXA-840). The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature (RT).

## 3. Results and discussion

### 3.1. Morphology control in the spray pyrolysis process

Our spray pyrolysis method includes two steps. The first step is to prepare the precursor particles by spray drying process. Subsequently, the obtained precursor particles were sintered at certain temperature to yield the phosphor samples. The as-formed precursor particles by the spray drying process were amorphous. Fig. 1 shows the XRD patterns of the SP-derived BAM:Eu<sup>2+</sup> sample annealed at 1400 °C. It can be seen that all the diffraction peaks of the sample are in an excellent agreement with those of the standard BAM phase (JCPDS card 26-163). No second phase and Eu<sup>3+</sup> (Eu<sub>2</sub>O<sub>3</sub>) are detected, indicating that all Eu<sup>3+</sup> ions have been reduced to Eu<sup>2+</sup> ions which have entered the host lattices of BAM after annealing at high temperature (1400 °C) in the reducing atmosphere (CO). It is well

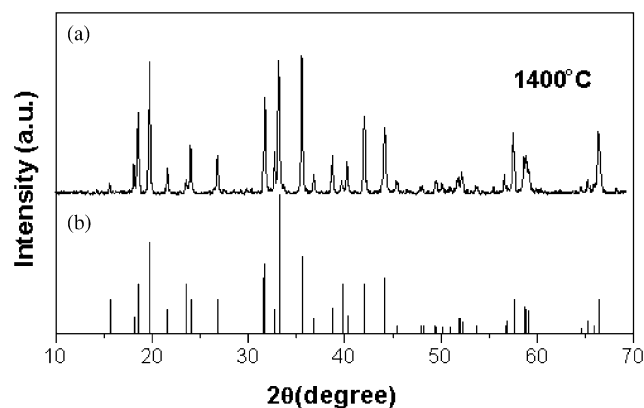


Fig. 1. XRD patterns of BAM:Eu<sup>2+</sup> phosphor derived from SP method (a) and the JCPDS card 26–163 for BAM (b).

known that the BAM adopts a  $\beta$ -alumina structure consisting of a spinel block ( $\text{MgAl}_{10}\text{O}_{16}$ ) and a mirror plan ( $\text{BaO}$ ) [13]. In  $\text{BAM:Eu}^{2+}$  phosphor, the  $\text{Eu}^{2+}$  activator ions are partially substituted for  $\text{Ba}^{2+}$  sites of the mirror plan based on their same valence state (+2) and close ionic radii ( $\text{Ba}^{2+}$ –0.142 nm,  $\text{Eu}^{2+}$ –0.125 nm) [19], which will not affect the structure of BAM. In the following sections we will focus on the effects of various parameters in the spray pyrolysis process on the morphology of the phosphor particles.

### 3.1.1. The effects of PEG concentration

It is found that the PEG concentrations in the precursor solutions have great effects on the morphology of the  $\text{BAM:Eu}^{2+}$  phosphor particles. Fig. 2 shows SEM images of  $\text{BAM:Eu}^{2+}$  phosphor particles derived from the precursor solutions with different PEG concentrations. Without PEG in the precursor solution ( $[\text{PEG}] = 0 \text{ g/ml}$ ), most of the obtained phosphor particles have an irregular morphology (Fig. 2a). With low PEG concentration in the precursor solution ( $[\text{PEG}] = 0.01 \text{ g/ml}$ ), the obtained phosphor particles have spherical morphology with size 0.5–2.50  $\mu\text{m}$ , but some broken pieces coexist (Fig. 2b). When the PEG concentration was increased to 0.03 g/ml, spherical solid particles with size of 0.5–3.0  $\mu\text{m}$  were obtained, and no obvious broken pieces can be observed (Fig. 2c). Further increasing the PEG concentration resulted in more narrow size distribution of the spherical solid

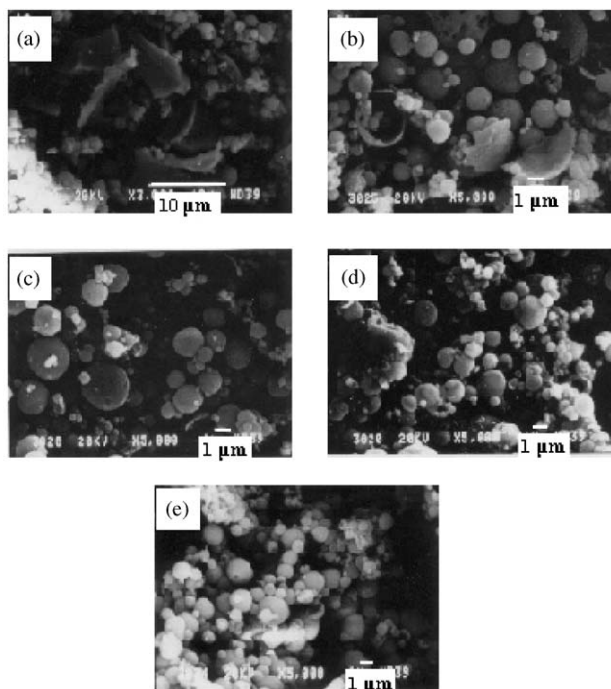


Fig. 2. SEM micrographs of  $\text{BAM:Eu}^{2+}$  phosphors prepared by SP method with different PEG concentrations in the precursor solutions. (a)  $[\text{PEG}] = 0$ , (b)  $[\text{PEG}] = 0.01 \text{ g/ml}$ , (c)  $[\text{PEG}] = 0.03 \text{ g/ml}$ , (d)  $[\text{PEG}] = 0.05 \text{ g/ml}$  and (e)  $[\text{PEG}] = 0.10 \text{ g/ml}$ .

phosphor particles (0.5–2.0  $\mu\text{m}$  for  $[\text{PEG}] = 0.05 \text{ g/ml}$ , Fig. 2d; 0.8–2.0  $\mu\text{m}$  for  $[\text{PEG}] = 0.1 \text{ g/ml}$ , Fig. 2e). It was reported that starting with a colloidal solution in the spray pyrolysis process had advantages on avoiding the formation of hollow particles, and the addition of PEG can increase the viscosity of spray solution to obtain solid particles [20]. From the above results, it can be known that the suitable PEG concentration in the current system is 0.05–0.10 g/ml for obtaining spherical solid phosphor particles with narrow size distribution.

### 3.1.2. The effects of PEG molecular weight

PEG is a kind of polymer which has different molecular weight (MW). Here we tried to add PEG with different MW in the precursor solution, and found that the MW of PEG also has great effects on the morphology of resulted phosphor particles. Figs. 3a–d show SEM images of phosphor particles derived from PEG with MW of 600, 1000, 6000 and 10,000 in the precursor solutions, respectively. First, from Fig. 3 it can be seen that all the phosphor particles have spherical shape independent of the MW of PEG, but the average size of the phosphor particles increases with the increase of the MW of PEG (1.20  $\mu\text{m}$  for MW = 600, 1.40  $\mu\text{m}$  for MW = 1000, 1.60  $\mu\text{m}$  for MW = 6000, 2.30  $\mu\text{m}$  for MW = 10,000). Additionally, it can be seen that the least amount of hollow phosphor particles with narrow size distribution can be obtained for  $\text{MW}(\text{PEG}) = 600$ , which will result in a higher emission intensity for this sample (see below for luminescent properties).

### 3.1.3. The effects of citric acid/metal ion molar ratios

Keeping the PEG concentration as 0.1 g/ml, we used different amount of citric acids with citric acid/metal ions molar ratios of 0.5:1, 1:1, 2:1, 3:1 to obtain the  $\text{BAM:Eu}^{2+}$  phosphors by the spray pyrolysis process.

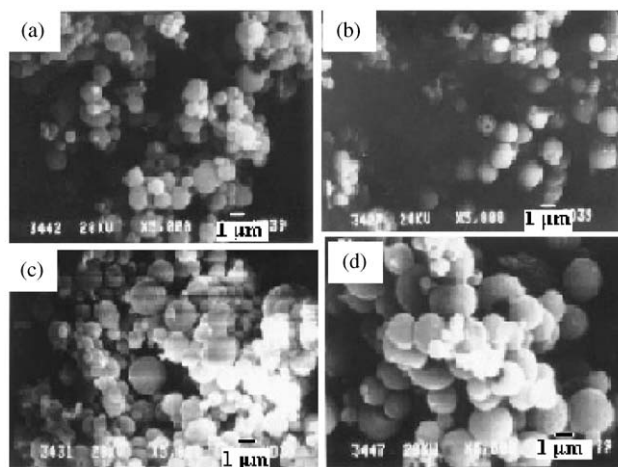


Fig. 3. SEM micrographs of  $\text{BAM:Eu}^{2+}$  phosphors prepared by SP method using PEG with different molecular weight (MW) in the precursor solutions. (a) MW = 600; (b) MW = 1000; (c) MW = 6000; (d) MW = 10,000.

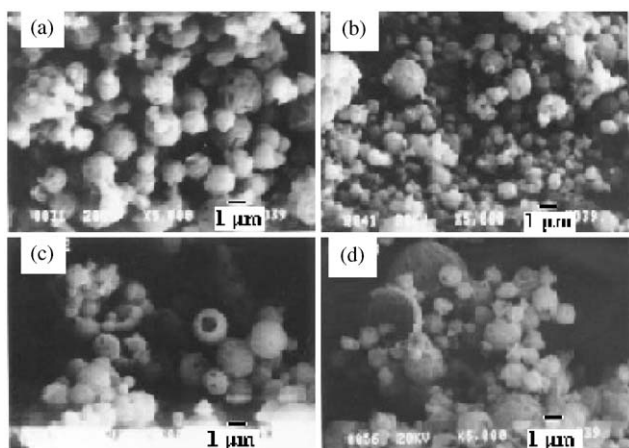


Fig. 4. SEM micrographs of BAM:Eu<sup>2+</sup> phosphors prepared by SP method with different molar ratios between citric acid and metal ion in the precursor solutions. (a) Citric acid/metal ion = 0.5:1; (b) citric acid/metal ion = 1:1; (c) citric acid/metal ion = 2:1; (d) citric acid/metal ion = 3:1.

Fig. 4 shows the SEM images of these BAM:Eu<sup>2+</sup> phosphor particles. It can be seen that nearly spherical particles (1.0–3.0 μm) with rough surface were obtained with low amount of citric acid (citric acid/metal ions = 0.5:1, Fig. 4a). When the citric acid was increased (citric acid/metal ions = 1:1), spherical solid particles with an average size of 0.94 μm were obtained (Fig. 4b). However, further increasing of the amount of citric acid (citric acid/metal ions = 2:1, 3:1) resulted in many hollow phosphor particles, which are not good for luminescence. Therefore, the suitable molar ratio between citric acid and metal ions is 1:1 in current system, which gives the strongest emission intensity (see below for luminescent properties).

#### 3.1.4. The effects of total metal ion concentration

The morphology of the phosphor particles can be tuned by changing the molar concentration of the metal ions in the precursor solution. Figs. 5a–c show the SEM images of the phosphor particles derived from the precursor solutions with different metal ion concentrations ( $C_M$ ) from 0.01 to 0.04 M. When the metal ion concentration in the precursor solution is low ( $C_M = 0.01$  M, 0.02 M), some of the phosphor particles are in irregular shape (Fig. 5a) and the particle surfaces are rough, (Fig. 5b). When the metal ion concentration is increased to 0.04 M, spherical solid particles with smooth surface and an average size of 1.27 μm are obtained (Fig. 5c).

#### 3.2. Luminescence properties

Generally, the luminescence properties of phosphors depend on the characteristics of the phosphor particles, such as size, shape, crystallinity, defects and so on. The

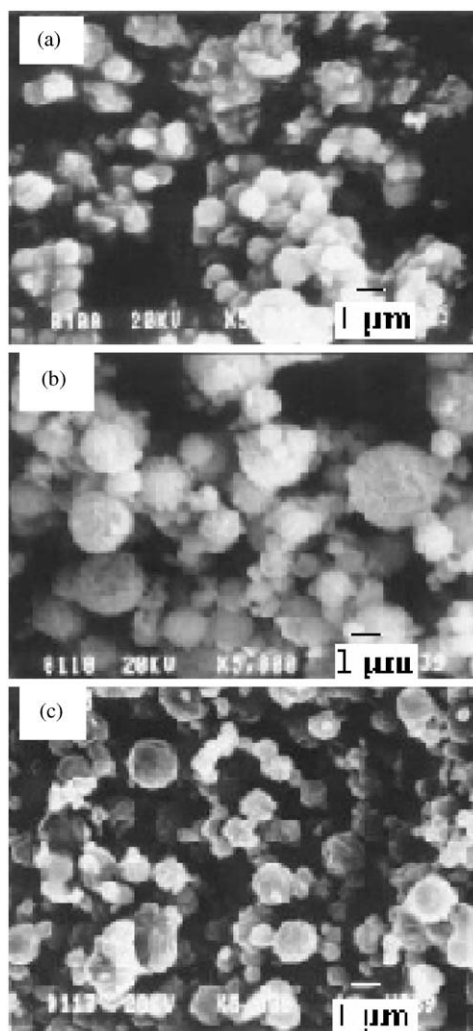


Fig. 5. SEM micrographs of BAM:Eu<sup>2+</sup> phosphors obtained from different metal ion concentrations in the precursor solutions: (a)  $C = 0.01$  M; (b)  $C = 0.02$  M; (c)  $C = 0.04$  M.

BAM:Eu<sup>2+</sup> phosphors show a strong blue emission under the irradiation of UV light. Fig. 6 shows the typical excitation (a) and emission (b) spectra of BAM:Eu<sup>2+</sup> phosphor prepared by spray pyrolysis process with different MW of PEG added in the precursor solutions. The excitation spectrum consists of a broad band with a maximum 324 nm with two shoulders at 270 and 380 nm, respectively, which are due to the transitions from the ground state  $^8S_{7/2}$  of Eu<sup>2+</sup> with  $4f^7$  configuration to the different crystal field splitting components of the Eu<sup>2+</sup> with  $(4f^6)5d$  configuration in the excited states. The emission spectra, obtained by excitation into the band at 324 nm, includes a broad band with a maximum at 450 nm, which corresponds to the transition from lowest  $(4f^6)5d$  excited component to the  $^8S_{7/2}$  ground state of Eu<sup>2+</sup> ion [1]. The emission from Eu<sup>3+</sup>, which in general consists of sharp lines in the red spectral region (580–750 nm), has

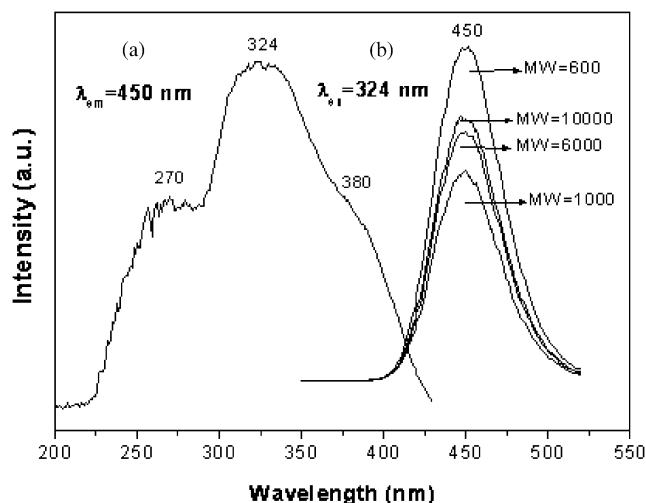


Fig. 6. Excitation (a) and emission (b) spectra of BAM:Eu<sup>2+</sup> phosphors prepared by SP method using PEG with different molecular weight in the precursor solutions.

not been detected. This indicates all the Eu<sup>3+</sup> ions in the starting material (Eu<sub>2</sub>O<sub>3</sub>) have been built into the host lattices as Eu<sup>2+</sup> ions to replace the Ba<sup>2+</sup> after annealing under the reducing atmosphere of CO.

The BAM:Eu<sup>2+</sup> phosphors show different emission intensity with different MW of PEG added in the precursor solutions, as shown in Fig. 6b. It can be seen that the phosphor has highest emission intensity when PEG with MW of 600 is used in the precursor solution. This is because the phosphor contains the least amount of hollow particles in this case (Fig. 3a). The phosphor derived from MW=1000 shows the lowest emission intensity due to many hollow particles existing in it. However, the phosphors derived from PEG with MW of 6000 and 10,000 show higher emission intensity again due to the increase in size of the phosphor particles.

Since the particle morphology is affected by PEG concentrations, it is expected that the luminescent properties of the phosphors are also dependent on the PEG concentration in the precursor solution. Fig. 7 shows the emission intensity of BAM:Eu<sup>2+</sup> phosphor as a function of the PEG concentration in the precursor solutions. It can be seen that the emission intensity of BAM:Eu<sup>2+</sup> increases with the increase of the PEG concentration. These results are in agreement with the change of the morphology of the phosphor particles, as shown by the SEM in Fig. 2. It seems that the emission intensity increases as the morphology of phosphor particles becomes better, i.e., from non-spherical to spherical, with the decrease of hollow pieces, finally to the solid spherical with narrow size distribution.

Fig. 8 shows the emission intensity of BAM:Eu<sup>2+</sup> phosphors as a function of the molar ratios between citric acid and metal ions. It can be seen that the emission intensity first increased with increase of the

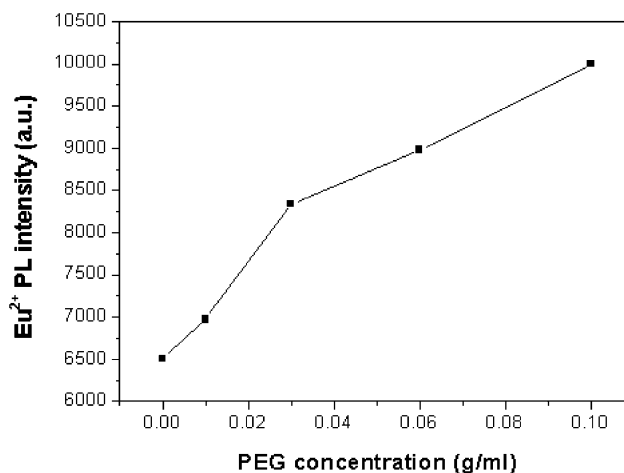


Fig. 7. Emission intensity of BAM:Eu<sup>2+</sup> phosphors as a function of PEG concentration in the precursor solution.

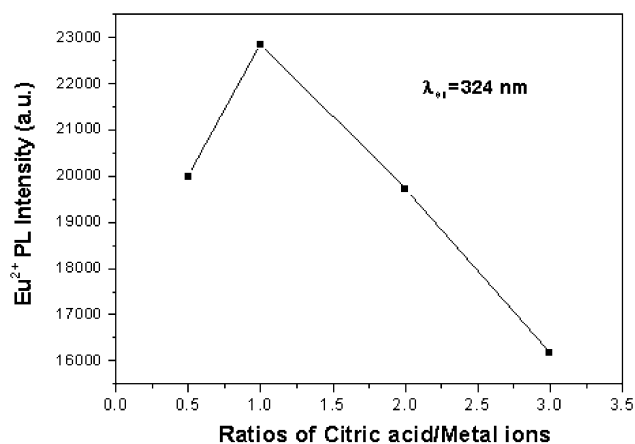


Fig. 8. Emission intensity of BAM:Eu<sup>2+</sup> phosphors as a function of the molar ratios between citric acid and metal ion in the precursor solutions.

ratio between citric acid and metal ions, reached the largest intensity when the ratio is 1:1, then decreased with further increase of the ratio between citric acid and metal ions. This indicates that the optimum ratio between citric acid and metal ions is 1:1 for obtaining the highest emission intensity of BAM:Eu<sup>2+</sup> phosphors by the spray pyrolysis process. In this case, the phosphor contains the least amount of hollow particles with a narrow size distribution, as shown by the SEM in Fig. 4(b).

The influence of metal ion concentration in precursor solution on the luminescent properties of BAM:Eu<sup>2+</sup> has been also studied. Fig. 9(a) shows the emission spectra of BAM:Eu<sup>2+</sup> particles prepared with different metal ion concentrations in the precursor solution. It can be seen that the emission intensity increased with increasing the metal ion concentration.

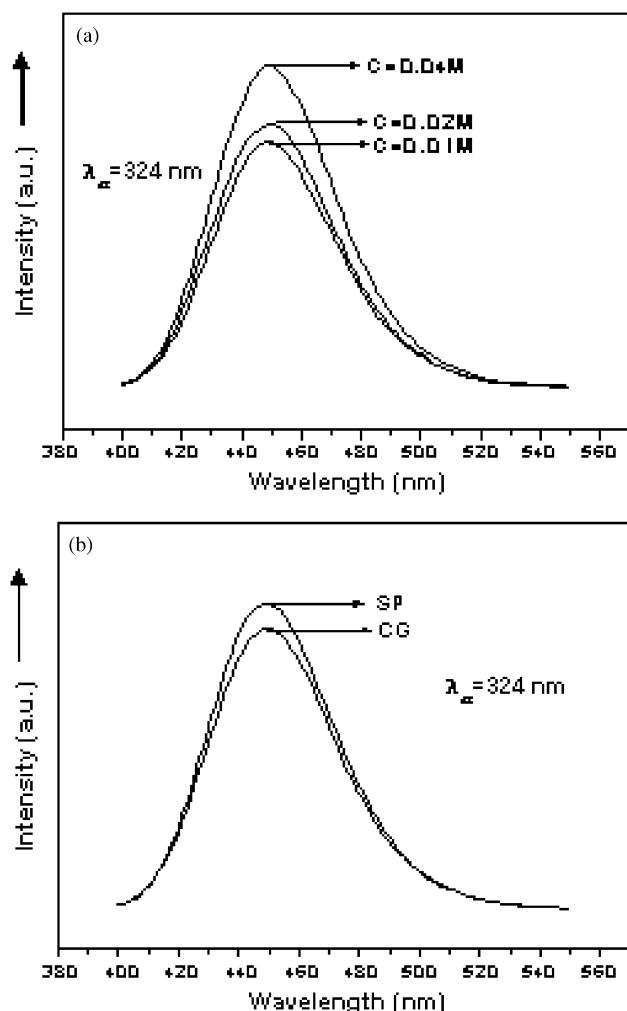


Fig. 9. Emission spectra of BAM:Eu<sup>2+</sup> phosphors prepared by SP method with different metal ion concentrations in the precursor solutions (a) and a comparison of the emission spectra prepared by the SP and CG methods (b).

The luminescent properties of BAM:Eu<sup>2+</sup> phosphor particles derived from the SP method (with spherical morphology) were compared with those derived from CG method. The latter phosphor particles had irregular morphology [16]. Fig. 9(b) shows the comparison of emission spectra for BAM:Eu samples prepared by the SP and CG methods, respectively. It can be observed that the BAM:Eu phosphors prepared by SP process had higher emission intensity than those by CG process. This can be ascribed to the better morphology (spherical morphology, non-aggregation and narrow size distribution) of the SP-derived phosphors.

Finally, we can simply discuss the reasons for the dependence of the morphology and luminescence intensity on the additives, PEG (concentration, molecular weight) and citric acid. Citric acid can form chelates with the metal ions (Ba<sup>2+</sup>, Al<sup>3+</sup>, Eu<sup>3+</sup>) in the precursor solution. These chelates can bond together to

form a polymer when PEG is added (the –OH groups in PEG can react with the –COOH groups in citric acid to form polyester, making them more homogeneously distributed in the solution). The PEG concentration and its molecular weight will affect the viscosity of the polymer solution. The morphology of the resulted particles, such as shape and size, filled or hollow, depends strongly on the viscosity of the spray polymer solution. This will further influence the luminescence properties of the final phosphors.

#### 4. Conclusions

BAM:Eu<sup>2+</sup> phosphors have been successfully prepared by spray pyrolysis technique from metal nitrate solutions containing citric acid and PEG. Thus prepared phosphor particles have spherical shape, submicron size and narrow size distribution. Furthermore, the morphology of the phosphor particles can be controlled by the addition of citric acid, PEG with different molecular weights, the metal ion and PEG concentration in the precursor solution. The emission intensity of BAM:Eu<sup>2+</sup> phosphors increased with increasing of PEG and metal ion concentration in the precursor solution. The optimal morphology and emission intensity can be obtained using PEG with molecular weight of 600, and citric acid/metal ion molar ratio of 1:1 in the precursor solution. The BAM:Eu<sup>2+</sup> phosphors prepared by the spray pyrolysis method show higher emission intensity than those derived directly from the citric gel method.

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