

Sol-Gel Preparation and Luminescence Properties of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ Phosphors

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Received 20 June 2006; revised 13 October 2006

Abstract: The synthesis of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM) phosphors using the sol-gel method and their luminescence properties were reported. The blue-light emitting BAM was synthesized using citric acid and ethylene glycol as chelating materials. Emission of blue-light was obtained from these phosphors. The luminescent intensity increases as the temperature of heat treatment is increased. This study investigated the effects of the molar ratio of ethylene glycol to citric acid (Φ value), with respect to the phase formation and luminescence properties of BAM. The variation of the Φ value resulted in the change of the sol-gel reaction mechanism and the microstructures of the resultant powders. An increase in Φ value leads to an increase in the rate of BAM phase formation. The photoluminescent intensity of the prepared phosphors increases with heating temperatures because of enhanced crystallization.

Key words: phosphors; sol-gel; synthesis; luminescent properties; rare earths

CLC number: O482.31 **Document code:** A **Article ID:** 1002 – 0721(2006)06 – 0706 – 06

Aluminate phosphors activated with rare earth are especially stable and efficient in general lighting of lamps^[1]. With the recent advancement, aluminate phosphors are intensely focused on Eu^{2+} -doped BAM phosphors for application in plasma display panels (PDPs)^[2–4]. Barium magnesium aluminate $\text{BaMgAl}_{10}\text{O}_{17}$ (BAM) is classified into β -alumina structure with a space group $P6_3/mmc$ ^[5]. The different sites occupied by the europium ions in the BAM structure have been studied by several researchers^[6–10]. Boolchand et al. reported that the Eu^{2+} sites occupy the Beevers-Ross, anti-Beevers-Ross, and the mid-oxygen sites in BAM: Eu^{2+} ^[6]. The host lattice plays an important role for varying the luminescence properties of the phosphors^[11, 12]. Howe et al.^[11] investigated the host-lattice emission and energy transfer in undoped and Eu-doped BAM. They reported that the BAM host lattice

showed an emission under vacuum ultraviolet (VUV) excitation and this result was assigned to Ba-O groups.

BAM phosphors are usually prepared by the solid-state reaction method. In this kind of process, high-temperature heating is required. It is reported that an increase in heating temperature leads to an increased particle size and the surface morphology is also varied^[13]. The Pechini sol-gel method utilizes citric acid and ethylene glycol derived polyester resin, comprising branched polymer for the synthesis. This method has the ability to synthesize multicomponent oxides with a good homogeneity at a decreased temperature of heat treatment^[14, 15]. Several researchers have used the method to prepare BAM: Eu^{2+} phosphors^[16, 17]. The effects of ethylene glycol and citric acid ratio on the phase formation and luminescent properties of BAM: Eu^{2+} phosphors have not been studied in de-

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tail. Accordingly, the purpose of this study is to investigate the effects of the molar ratio of ethylene glycol to citric acid (Φ value) on the synthesized process of BAM:Eu²⁺ phosphors. The influence of heating conditions on the microstructures and luminescent properties of the obtained phosphors was also studied here.

1 Experimental

Europium-ion-doped barium magnesium aluminate (BAM:Eu²⁺) powders were prepared by the sol-gel process using citric acid (Nacalai, guaranteed reagent grade) as a chelating agent and ethylene glycol (Nacalai, guaranteed reagent grade) as a polymerizing agent. As shown in Fig. 1, barium nitrate (Janssen Chimica; No. 20.325.42, 99%), aluminum nitrate nonahydrate (Sigma-Aldrich; No. 237973, 98%, ACS reagent grade), magnesium nitrate hexahydrate (Nacalai teaque; guaranteed reagent grade), and europium oxide (Aldrich; No. 289221, 99.9%) were used as starting materials. Europium oxide was dissolved in nitric acid solution (40% nitric acid). The nitrate compounds and europium solution were intro-

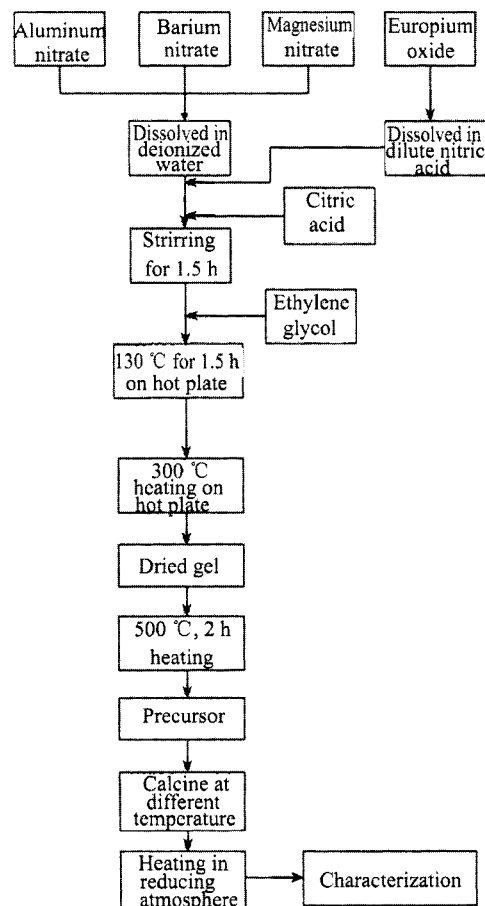


Fig. 1 Experimental procedure of (Ba_{0.9}Eu_{0.1})MgAl₁₀O₁₇ phosphors prepared by sol-gel method

duced into deionized water under stirring. When the nitrate compounds had completely dissolved in the solution, citric acid was added. After stirring for 1.5 h, ethylene glycol was added in a controlled manner (Φ is defined as the molar ratio of ethylene glycol to citric acid). The solution was heated at 130 °C on a hot plate for 1.5 h. This was followed by the heating of the solution at 300 °C until formation of dried gels. The dried gels or xerogels were heated at 500 °C for 2 h and then were ground thoroughly. The precursor powders were calcined in air at different temperatures for 4 h, followed by heating in reducing atmosphere for 4 h.

The elimination of water and decomposition of residual species contained in the dried gels were examined by the thermal gravimetric analysis (TGA) coupled with differential thermal analysis (DTA) (UL VAC TGD 7000). The DTA-TGA measurements were made in air at a scan rate of 10 °C·min⁻¹. The structural evolution was recorded by XRD using Cu K α radiation (MAC Science, MXP3). The photoluminescence measurement was carried out with the Hitachi F-4500 fluorescence spectrophotometer using a Xenon lamp at room temperature. The reflectance measurement was done using a synchronous scan of two monochromators in the Hitachi F-4500 fluorescence spectrophotometer (PMT voltage was 400 V, and response time was 2 s). Reflectance spectra were corrected using BaSO₄ as a standard. The reflection data were expressed in terms of the percent reflectance (%R):

$$\%R = \frac{I_S}{I_R} \times 100\%$$

where I_S is the intensity of the beam reflected from the samples and I_R is the intensity from a reference standard (barium sulfate, BaSO₄)^[19].

2 Results and Discussion

2.1 Differential thermal and thermogravimetric analyses of BaMgAl₁₀O₁₇:Eu gels

The pyrolysis process of the dried gels was monitored by DTA and TGA as shown in Figs. 2 and 3. The samples with Φ values (ratio of ethylene glycol to citric acid) of 0.5, 1.0, 2.0, and 3.0 exhibit broad exothermic peaks at 453, 470, 605, and 682 °C respectively (Fig. 2) as a result of the decomposition of the gels. The DTA results show that the decomposition temperature is associated with the Φ values. Increase in Φ values will lead to an increase in the polymerization of metal-complexes with growing polymer nets, and this effect results in an increase in the pyrolysis

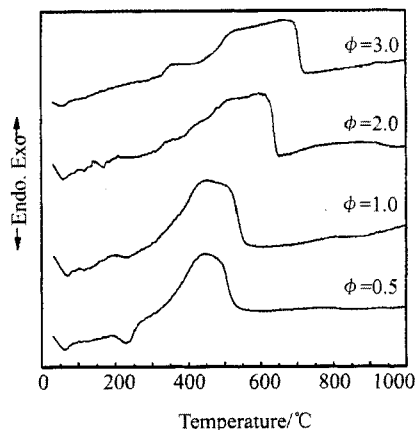


Fig. 2 DTA curves showing the decomposition with various Φ values of $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ dried gels

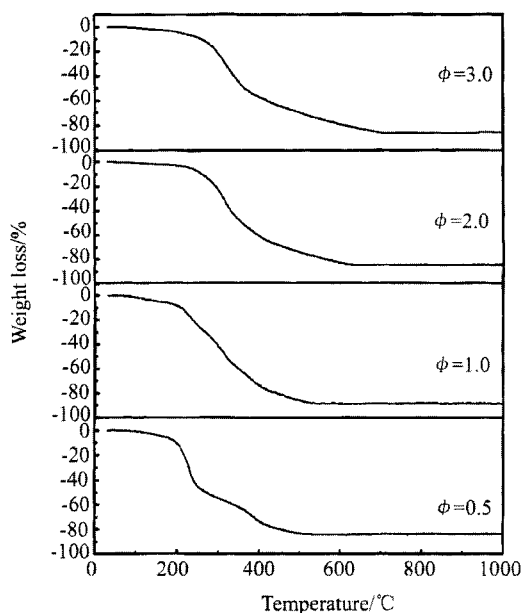


Fig. 3 Thermogravimetric curves for $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ dried gels with various Φ values of samples

energy. As a result, the pyrolysis temperature region gets shifted to a higher temperature as Φ values increase.

The weight loss under varied Φ values from 0.5 to 3.0 can be explained by the behavior between the Pechini and citrate sol-gel process. The Pechini process (using citric acid and ethylene glycol producing a polyester resin comprising a branched polymer), exhibited two stages of decomposition^[20]. The $\Phi = 3.0$ and 2.0 samples exhibited a two-stage weight loss profile. In the sample of $\Phi = 3.0$, the first and second stages occurred at 200 ~ 360 °C and 360 ~ 705 °C ranges respectively. In the sample of $\Phi = 2.0$, the first and second stages occurred at 200 ~ 336 °C and 336 ~ 622 °C ranges respectively.

The first stage of decomposition can be associated

with the evaporation of ethylene glycol and traces of water. The second stage was because of the decomposition of the metal citrate complex and the residual organics^[20]. In contrast, in the citrate sol-gel process, which uses a citric acid forming concentrated metal complex, weight loss can be found at three temperature regions. As shown in Fig. 3, the $\Phi = 0.5$ sample exhibited a three-stage weight loss at three temperature ranges of 153 ~ 243 °C, 243 ~ 366 °C, and 366 ~ 519 °C. The first weight loss can be assigned to the loss of the coordinated water molecule, whereas the second and third weight losses can be attributed to the decomposition of citric acid complex and other organic materials formatting a pure oxide system^[21].

The three-stage weight loss profile of the samples prepared by the citrate gel method was reported by Zhang et al.^[14] The TGA curve of the BAM sample, which was prepared by the sol-gel method under $\Phi = 0.5$, showed a weight loss profile of typical citrate gels because of the few ester linkages caused by polymerization reactions. On the other hand, the TGA curve of BAM prepared under $\Phi = 1.0$ exhibited a one-stage weight loss profile having a heating span of 200 ~ 558 °C, whereas three smooth stage profiles were observed in the differential thermogravimetry (DTG) curve (Fig. 4). This profile of TGA and DTA curves can be explained by the pyrolysis reaction occurring between the Pechini polymerizable gels and citrate gels. As a result of increase in Φ value-the precursor being rich in ethylene glycol-leads to an increase in the polymeric branches. Increase in polymeric branches indicates that the polymeric complex structure may be formed by the Pechini reaction process and this structure leads to an increase in the range of decomposition temperature.

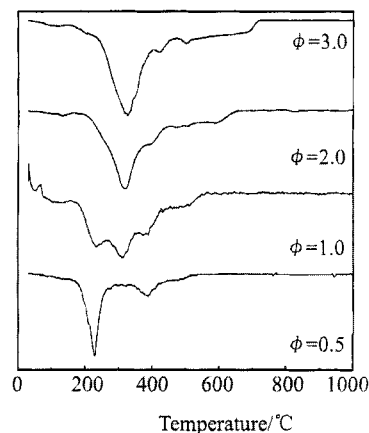


Fig. 4 Differential thermogravimetry (DTG) curves for $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ dried gels with various Φ values of samples

2.2 X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) patterns of quenched BaMgAl₁₀O₁₇:Eu (BAM:Eu) powders are shown in Fig. 5. The precursor powder was initially crystallized to give the BaAl₂O₄ (BAL) phase at 1000 and 1100 °C. Upon heating to 1100 °C for 4 h, both BAL and BAM phases were observed. The amount of BAM phase increased where the ϕ value increased. It shows that the increase in BAM phase was because of the improved level of mixing, which decreased the crystallization temperature. These results could be explained by the mechanism of Pechini-type sol-gel method, where polymeric resin might improve the level of molecular-scale mixing of cations in both resins and their precursors. Improved level of mixing causes the crystallization temperature to decrease^[15].

The XRD pattern obtained after heating the precursor powder at 1200 °C indicates BAM to be the only crystalline component. Further heating at a higher temperature may lead to an improvement in the crystallinity and grain growth (Fig. 6).

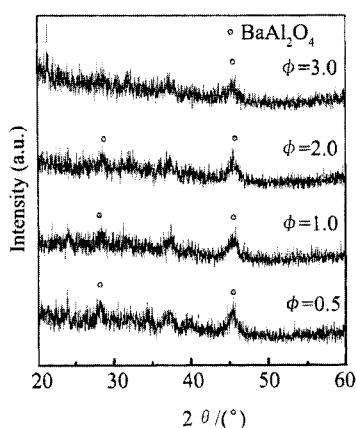


Fig. 5 XRD analysis for (Ba_{0.9}Eu_{0.1})MgAl₁₀O₁₇ prepared by sol-gel with various Φ values, with quenching at the temperature of 1100 °C

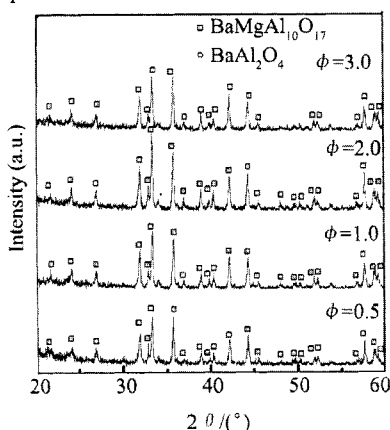


Fig. 6 XRD analysis for (Ba_{0.9}Eu_{0.1})MgAl₁₀O₁₇ prepared by sol-gel with various Φ values, with heating at 1400 °C in air for 4 h

For all samples heated at 1200 °C or higher temperatures, followed by heating in reducing atmosphere (Fig. 7), the XRD patterns agree well with those of the standard pattern reported by the Joint Committee on Powder Diffraction Standard (ICDD Card No. 26-0163) for BAM.

2.3 Photoluminescence properties of europium-ion doped BaMgAl₁₀O₁₇ phosphors

Fig. 8 shows the excitation and emission spectra of BAM samples, which were prepared by sol-gel method using a variety of Φ values and heated at 1200 °C. The BAM samples showed a uniform blue color, indicating a homogeneous doping. The emission at 453 nm was because of the 4f⁶5d¹→4f⁷ transition of Eu²⁺ in the BAM^[6]. BAM samples having a Φ value between 0.5 and 3.0 showed a similar type of photoluminescence spectra. For samples heated at higher temperatures, as shown in Fig. 9, these spectra did not show

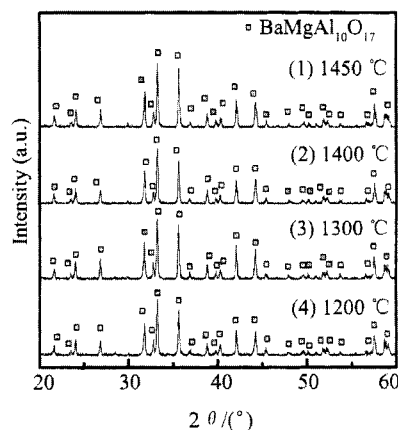


Fig. 7 XRD analysis for (Ba_{0.9}Eu_{0.1})MgAl₁₀O₁₇ precursors heated at various temperatures for 4 h

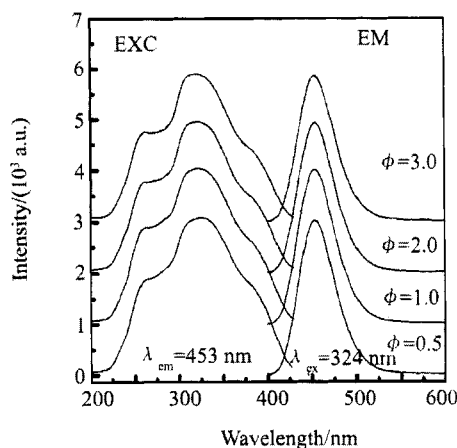


Fig. 8 Excitation (EXC) and emission (EM) spectra of (Ba_{0.9}Eu_{0.1})MgAl₁₀O₁₇ precursors heated at 1200 °C for 4 h in air followed by heating at 1200 °C for 4 h in reducing atmosphere

any noticeable change for the Φ value between 0.5 and 3.0. This result indicates that the effect of the Φ value is weak at high temperatures. The emission spectra of BAM heated at different temperatures ($\Phi = 2.0$) are shown in Fig. 10. The luminescent intensity of these samples increases as the temperature of heat treatment is increased. This effect can be explained by the improvement in the crystallinity and grain growth. A similar result was reported earlier for YAG materials^[22].

The absorption properties of excitation source can be observed via excitation spectra and reflection spectra. The reflection spectra are obtained by a synchronous scan (scanning both the excitation and emission monochromators), using BaSO_4 as a standard.

As shown in Fig. 11, the reflection spectra showed absorption around 250 ~ 340 nm. The reflection spectra contained two valleys at 254 and 311 nm. It was clear that two absorption bands were observed. In contrast, the excitation spectra (Fig. 9) showed two

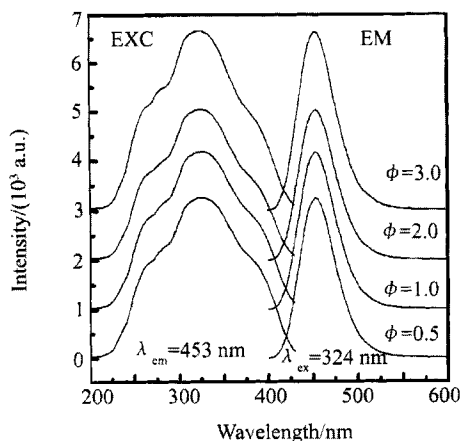


Fig. 9 Excitation (EXC) and emission (EM) spectra of $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ precursors heated at 1400 °C for 4 h in air followed by heating at 1400 °C for 4 h in reducing atmospheres

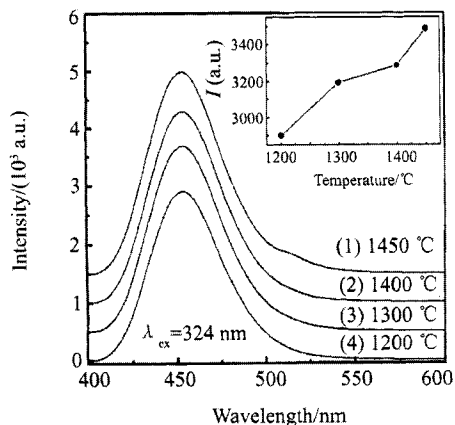


Fig. 10 Emission spectra of $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ precursors heated at various temperatures

excitation bands at about 265 and 324 nm. The excitation band at 265 nm was less intense than the second band at 324 nm. Consequently, the first absorption band (255 ~ 265 nm) was less efficient for energy transfer than the second absorption band (321 ~ 324 nm). Further the undoped BAM showed less absorption than the Eu-doped BAM (Fig. 11). Therefore, the optimum excitation band of this sample was 311 ~ 324 nm.

The emission spectrum of BAM can be deconvoluted into two Gaussians. As shown in Fig. 12, the peaks occurring at 22175 cm^{-1} (451 nm) and 21327 cm^{-1} (469 nm) may be assigned to Eu^{2+} on a normal Ba site (Beever-Ross) and Eu^{2+} displaced on an anti-Beever-Ross site in the BAM lattice respectively^[23].

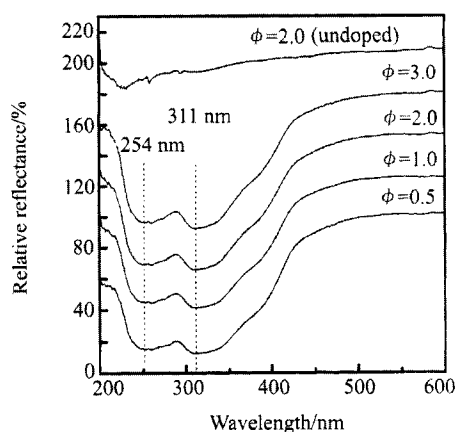


Fig. 11 Reflection spectra of $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ prepared by the sol-gel process with various Φ values via heating at 1400 °C

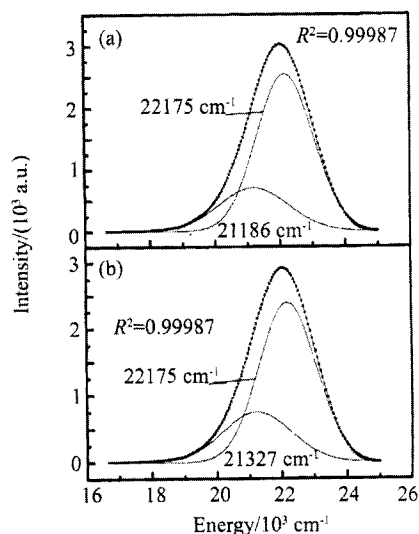


Fig. 12 Emission spectra of $(\text{Ba}_{0.9}\text{Eu}_{0.1})\text{MgAl}_{10}\text{O}_{17}$ prepared by the sol-gel process ($\Phi = 2.0$) fit to two Gaussian peaks (excitation at 324 nm)
(a) 1400 °C; (b) 1200 °C

3 Conclusion

The effects of the molar ratio of ethylene glycol to citric acid (Φ value) with respect to phase formation and luminescence properties of BAM:Eu²⁺ were investigated. An increase in Φ value leads to an increase in the rate of the phase formation of BAM:Eu²⁺. The photoluminescent intensity of the prepared phosphors increases with a rise in the heating temperature because of the enhanced crystallization. On the basis of the results obtained in this study, the optimum Φ value in the sol-gel process should be well controlled for obtaining BAM phosphors with desired microstructures and luminescent properties.

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