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Optimization of VUV characteristics and morphology of $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor particles in spray pyrolysis

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Abstract

The VUV characteristics of $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor particles prepared by an ultrasonic spray pyrolysis were compared with those of commercial product. The precursor effect on the morphology and brightness of phosphor particles was investigated in spray pyrolysis. The phosphor particles were prepared from 24 combinations of barium, magnesium, and aluminum component precursors composing host material. The precursor types strongly affected the morphology and luminescence characteristics of BAM phosphor particles. The BAM phosphor particles posttreated at above 1250 °C had higher brightness than that of commercial product. The maximum brightness of particles obtained at 1350 °C from nitrate precursors was 109% that of commercial product. This optimum posttreatment temperature in spray pyrolysis is lower than that of conventional solid-state reaction method.

Keywords: A. Powders: gas phase reaction; A. Precursors; C. Optical properties

1. Introduction

The remarkable development in display industries requires phosphor particles with improved brightness and morphology [1–5]. But the conventional preparation methods of phosphor particles cannot satisfy this requirement of display industries. Thus, spray pyrolysis is recommended as a promising process for preparing rare-earth-doped oxide phosphor particles. The characteristics of phosphor particles prepared by spray pyrolysis are spherical morphology, fine size, narrow size distribution, and non-aggregation [6–8].

However, despite these advantages, phosphor particles prepared by spray pyrolysis suffer from fatal problems, such as hollowness and high porosity. In the spray pyrolysis, hollow particles can be formed when the solute concentration gradient is created during evaporation. The solute precipitates first at the more highly supersaturated surface if sufficient time is not available for solute diffusion in the droplet. When the formed crust is impermeable to evolving gases, the pressure builds within the particle upon further heating and exploded particles fragments can result. Thus, the choice of precursor with the high solubility and desired physical properties is an important parameter for solid particles formation [9].

$BaMgAl_{10}O_{17}:Eu^{2+}$(BAM) phosphor, which has a plate-like morphology in conventional preparation methods, is an important blue-emitting phosphor for plasma display panel (PDP) and fluorescent lamps. Many new techniques have been applied to preparing this phosphor material and controlling its plate-like morphology [10–15]. Oshio et al. prepared BAM:Eu phosphor particles with spherical shape by conventional solid-state reaction method at high temperature using spherical Al_2O_3 particles as a law material [13].

In the present work, $BaMgAl_{10}O_{17}:Eu^{2+}$(BAM) phosphor particles with high brightness and spherical and filled morphology were prepared by spray pyrolysis. The luminescence characteristics of BAM phosphor particles under vacuum ultraviolet (VUV) were compared with that of commercial product. To control the morphology and luminescence intensity of BAM phosphor particles, the combination of precursor materials used as barium, magnesium, and aluminum sources was attempted.

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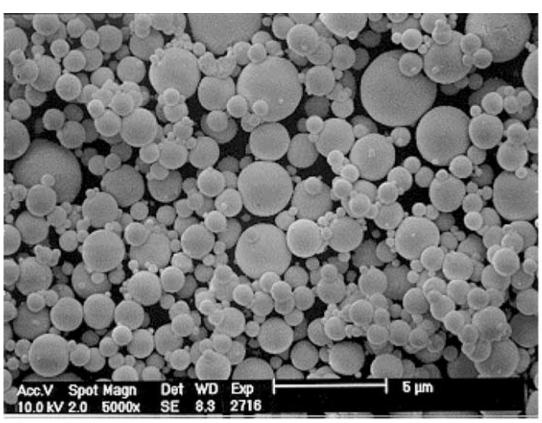
2. Experimental procedure

The precursor solutions for preparing $BaMgAl_{10}O_{17}$:Eu^{2+} phosphor particles were obtained by combining various salts of barium, magnesium, and aluminum components. Hydrate forms of barium nitrate, acetate, chloride, and hydroxide salts were used as a barium source. Hydrate forms of magnesium nitrate, acetate, and chloride salts were used as a magnesium source. The sources of aluminum were nitrate and chloride salts having high solubility. In the present work, the effect of precursor type on the morphologies and luminescence characteristics of BAM were investigated. Twenty-four combinations of the above precursors were applied. Europium nitrate was used as a europium source. The overall solution concentration was 0.5 M, and the doping concentration of the europium was 10 at.% of the barium component.

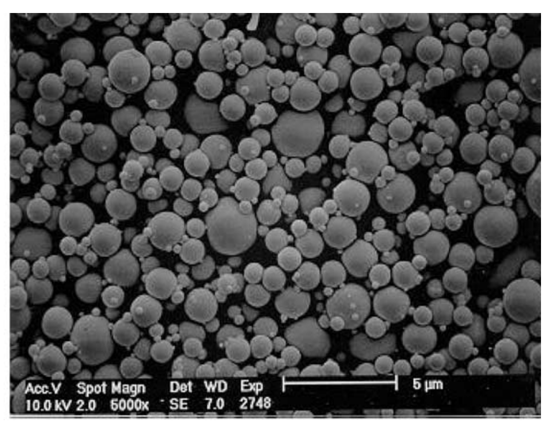
An ultrasonic spray generator having a frequency of 1.7 MHz was used to form droplets with micron size. The particles with amorphous phase were prepared at 900 °C by spray pyrolysis and posttreated at $\geqslant$1200 °C for 3 h. The reduction process of BAM:Eu^{2+} phosphor particles for emitting blue light was also conducted at 1200 °C for 3 h using 10% H_2/N_2 mixture gas. X-ray diffractometry (XRD) was used to confirm the crystal structure and crystallinity. Scanning electron microscopy (SEM) was used to identify the mean sizes and morphologies of the particles. Optical properties of the particles were measured under 147 nm by vacuum ultraviolet (VUV) photoluminescence (PL) spectroscopy with Kr lamp.

3. Results and discussions

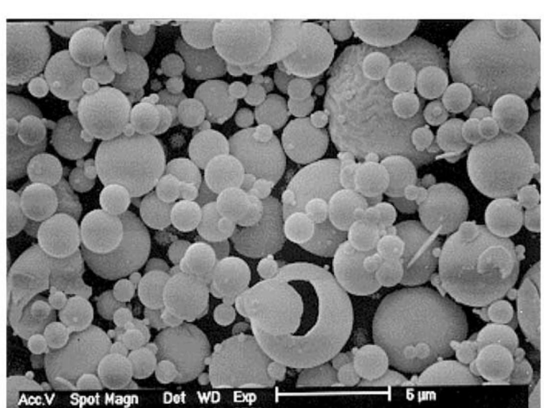
The precursor types strongly affected the morphologies of BAM phosphor particles in spray pyrolysis. The as-prepared particles by spray pyrolysis had spherical shape and non-aggregation characteristics regardless of precursor types. However, the extent of hollowness of particles was strongly influenced by the precursor type. The morphologies of as-prepared BAM:Eu^{2+} phosphor particles from different barium precursors are illustrated in Fig. 1, in which magnesium and aluminum nitrate salts were used as magnesium and aluminum sources. Although the particles were prepared under the same conditions such as reaction concentration and droplet



(a) Barium nitrate



(b) Bariumhydroxide

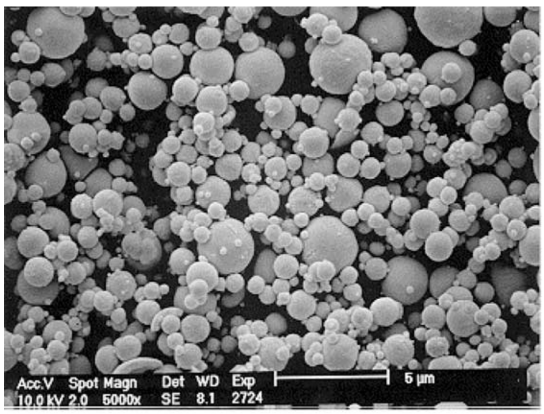


(c) Bariumchloride

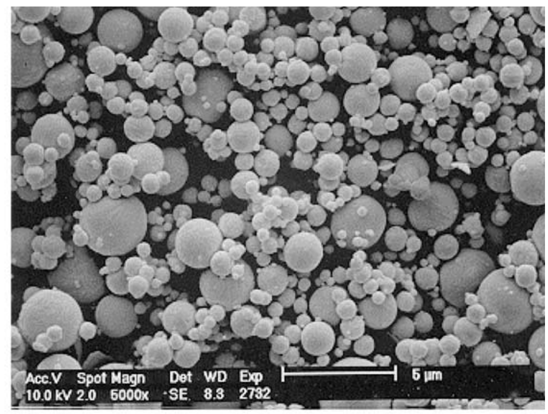
Fig. 1. SEM photographs of BAM:Eu^{2+} particles prepared from different barium precursors.

size, the particles prepared from barium chloride had some fragments and two times higher mean particle size than the particles from barium nitrate and barium hydroxide salts. This indicates that barium nitrate and hydroxide salts resulted in the formation of solid phosphor particles, while the barium chloride salt formed hollow particles. This morphological difference is assumed to be due to the different drying and decomposition characteristics of the metal salts.

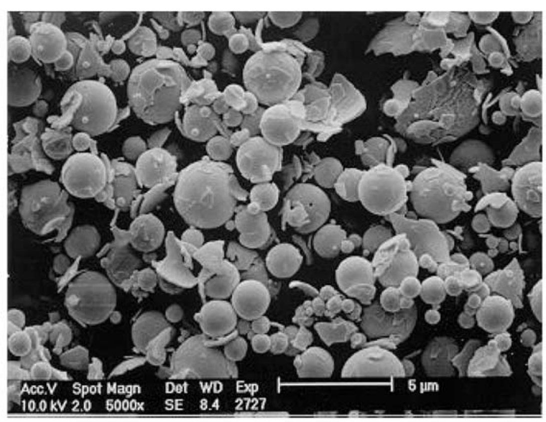
Fig. 2 shows the morphologies of posttreated BAM particles prepared from different barium precursors. The effect of barium precursor type on the morphology in posttreated particles became clearer than that in as-prepared particles. The BAM particles prepared from



(a) Barium nitrate

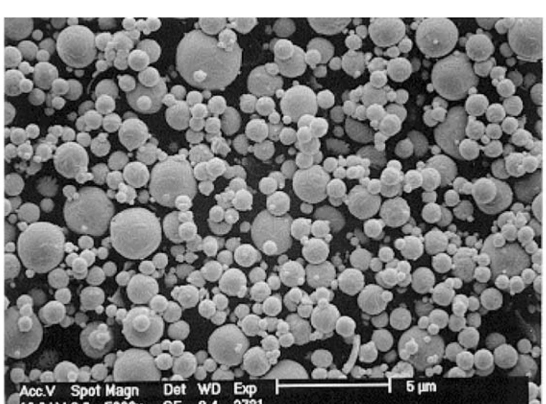


(b) Barium hydroxide

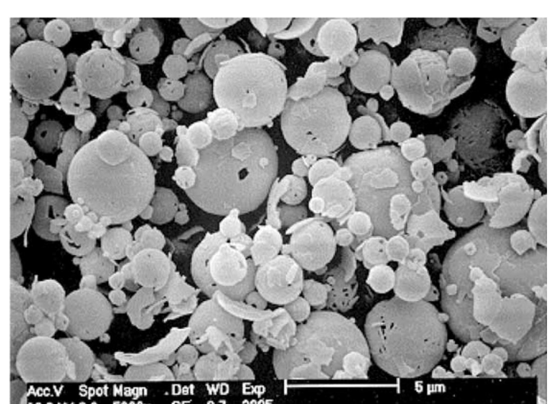


(c) Barium chloride

Fig. 2. SEM photographs of posttreated BAM:Eu^{2+} particles from different barium precursors, (a) Barium nitrate, (b) Barium hydroxide, (c) Barium chloride.



(a) Magnesium acetate



(b) Magnesium chloride

Fig. 3. SEM photographs of posttreated BAM:Eu^{2+} particles from different magnesium precursors.

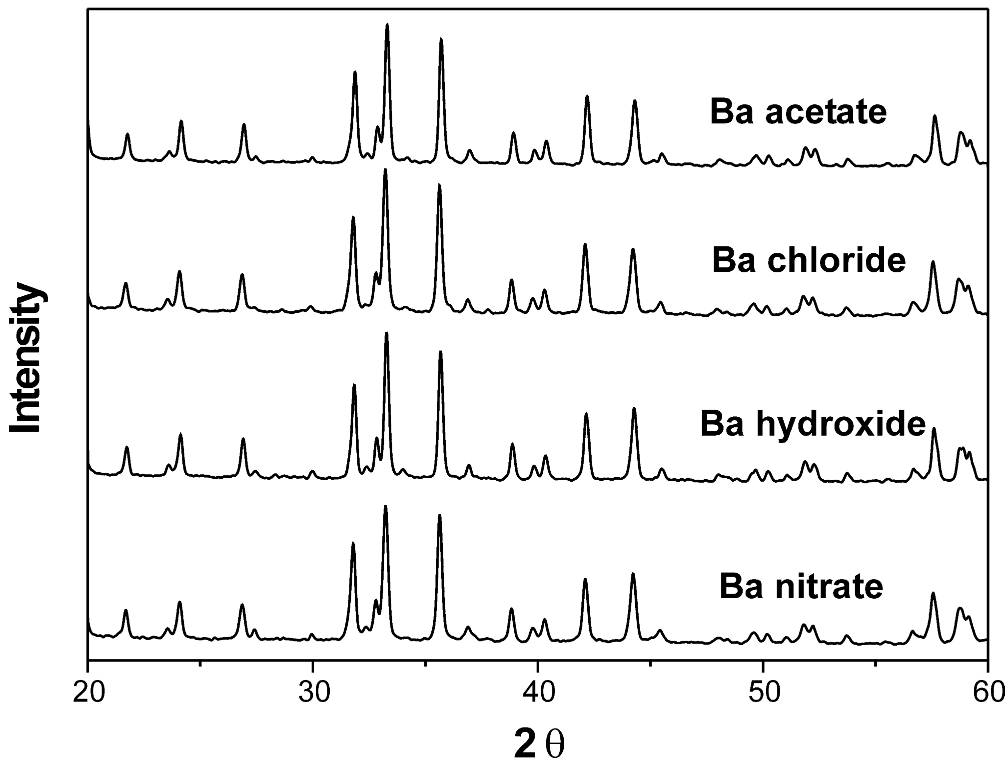


Fig. 4. XRD spectra of BAM:Eu^{2+} particles prepared from different barium precursors.

barium chloride solution had non-spherical shape and fractured structure because of low thermal stability of the as-prepared particles with hollow structure [Fig. 1(c)], while those prepared from barium nitrate and hydroxide precursors maintained their sphericity.

Fig. 3 shows the SEM photographs of posttreated particles prepared from magnesium acetate and chloride precursors, in which nitrate precursors were used as the sources of barium and aluminum precursors. The BAM particles prepared from magnesium nitrate [Fig. 2(a)] and acetate precursors had more filled morphology than those prepared from magnesium chloride precursor. The aluminum precursor type also affected the morphology of BAM:Eu phosphor particles and aluminum nitrate precursor was favored for the formation of particles with filled and spherical morphology.

The effect of precursor type on the crystal structure and crystallinity of BAM phosphor particles was investigated in Figs. 4 and 5. The as-prepared particles were posttreated at 1300 °C for 3 h. All the particles had pure BAM phase and similar crystallinities regardless of barium and magnesium precursor types. The aluminum precursor type also did not change the crystallinity and phase purity of BAM particles. In this work, pure phase BAM particles were obtained at lower posttreatment temperature than that of conventional solid-state reaction method. The pure phase BAM was obtained at $\geqslant$1200 °C and the crystallinity of particles was fully developed at 1250 °C. In spray pyrolysis, good mixing of each component as nanometer scale in the droplet decreased the formation temperature of multi-component BAM phase even with no flux material.

The photoluminescence characteristics of BAM:Eu^{2+} particles were measured under vacuum UV (147 nm) excitation. Fig. 6 shows the photoluminescence spectra of particles prepared from nitrate precursors at different posttreatment temperatures. The particles had the same photoluminescence spectrum as commercial product prepared by solid-state reaction method. The particles posttreated at $\geqslant$1250 °C had adequate peak intensities and had the maximum intensity at 1350 °C. This optimum posttreatment temperature in the spray pyrolysis is lower than that of conventional solid-state reaction method, in which high temperature above 1500 °C is required for preparing pure BAM particles without flux. The maximum peak intensity of BAM:Eu^{2+} particles prepared by spry pyrolysis was 109% that of commercial product, in which nitrate salts were used as precursor.

The precursor type affected the photoluminescence intensities of BAM phosphor particles. Fig. 7 shows the photoluminescence spectra of particles prepared from different barium precursors, in which nitrate precursors were used as magnesium and aluminum sources. The as-prepared particles at 900 °C were posttreated at 1350 °C for 3 h and reduction process was followed at 1200 °C. The BAM phosphor particles prepared from barium nitrate and hydroxide precursors with superior morphological characteristics had higher brightness than those prepared from barium chloride and acetate precursors. The BAM phosphor particles prepared from

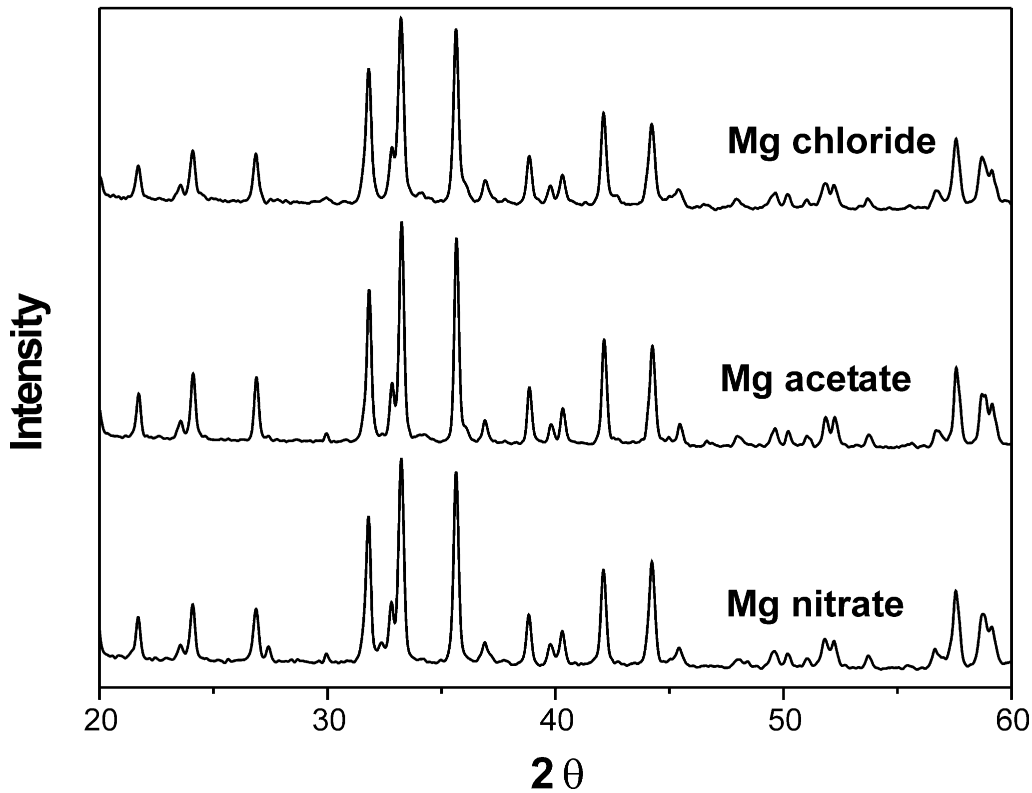


Fig. 5. XRD spectra of BAM:Eu^{2+} particles prepared from different magnesium precursors.

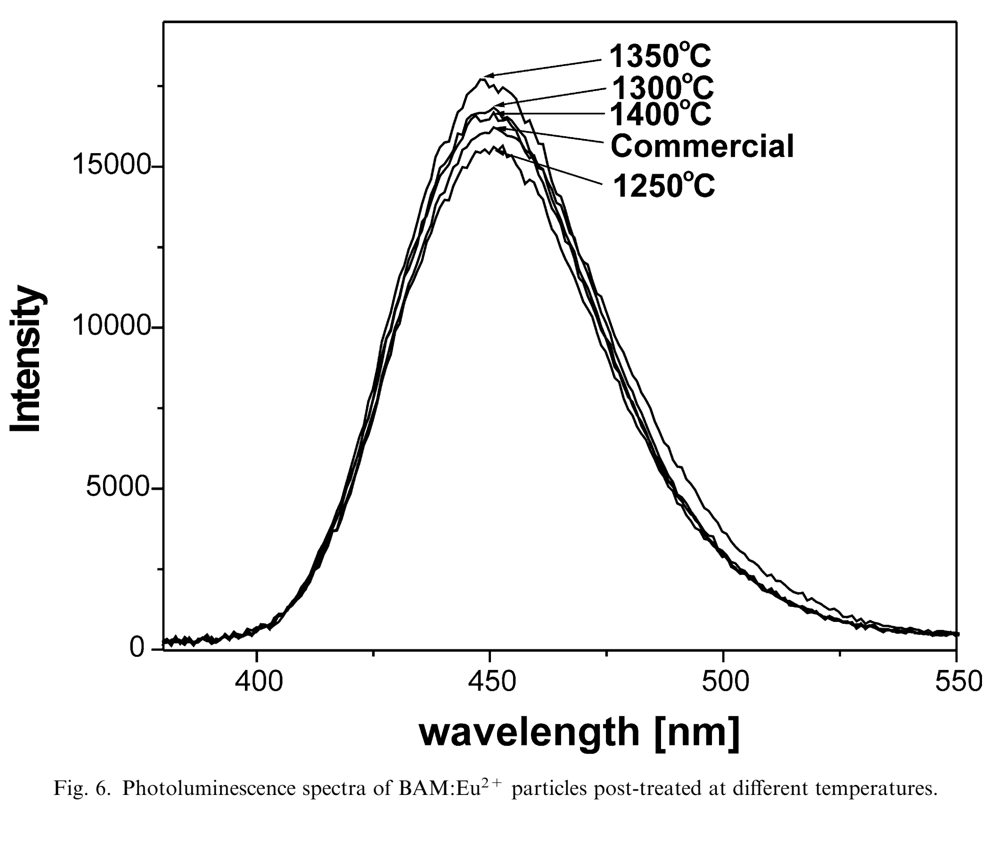


Fig. 6. Photoluminescence spectra of BAM:Eu^{2+} particles post-treated at different temperatures.

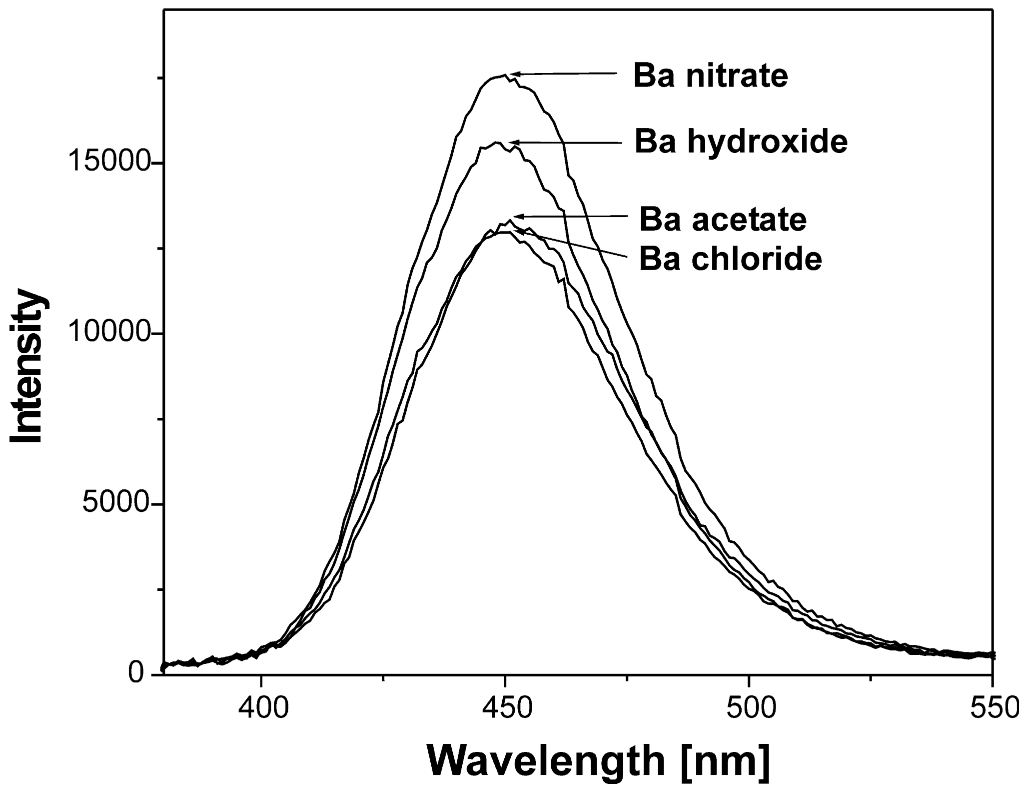


Fig. 7. Photoluminescence spectra of BAM:Eu^{2+} particles prepared from different barium precursors.

magnesium nitrate and acetate precursors with superior morphological advantage also had higher brightness than those from magnesium chloride precursor. Aluminum nitrate precursor was favored for the formation of particles with more filled morphology and high photoluminescence intensity. The difference of morphological and surface characteristics of particles obtained from different precursors affected the photoluminescence intensities of BAM:Eu^{2+} phosphor particles by spray pyrolysis.

In summary, the optimum combinations of barium–magnesium–aluminum precursors for BAM phosphor particles with high brightness and spherical morphology were nitrate–nitrate–nitrate, nitrate–acetate–nitrate, hydroxide–nitrate–nitrate, and hydroxide–acetate–nitrate. On the other hand, the BAM phosphor particles prepared from combinations of nitrate–chloride–nitrate, chloride–nitrate–nitrate, chloride–chloride–nitrate, and chloride–chloride–chloride had non-spherical morphology and poor photoluminescence characteristics.

4. Conclusion

BAM phosphor particles prepared by conventional preparation process have a plate-like morphology because of their crystal growth characteristics. To improve the morphology of BAM phosphor particles, in this work, an ultrasonic spray pyrolysis process was applied. In the spray pyrolysis, the morphology of particles is strongly affected by the types of precursors used as source materials of particles. From this point of view, 24 combinations of barium, magnesium, and aluminum precursors having high solubility in water were investigated to control the morphology and luminescence characteristics of BAM phosphor particles. The optimum combinations of precursors producing BAM phosphor particles with dense morphology and high brightness under VUV were developed.

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