

Synthesis of rod shaped BAM nano-phosphors by a liquid phase precursor method and their luminescence properties

A. Duld^a, M. K. Jung^b, W. J. Park^b, T. Masaki^b and D. H. Yoon^{a,b,*}

^aSungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Korea

^bSchool of Advanced Material Science and Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Blue emitting Eu^{2+} doped barium-magnesium aluminate (BAM) nano-phosphors were synthesized using liquid phase precursor (LPP) method corresponding to $\text{Ba}_{0.87-0.90}\text{Mg}_{0.91-1.0}\text{Al}_{10}\text{O}_{17-17.05}:\text{Eu}_{0.05}$. The phosphor particle size, morphology and crystallinity were characterized by FESEM and X-Ray diffraction analysis. The effects of composition and particle size on the luminescence efficiency were investigated by employing photoluminescence spectroscopy. The rod shaped phosphor particles ~60 nm in diameter and 400-700 nm in length were obtained. The phosphor particles emission peaks shifted towards a longer wavelength with 80% luminescence intensity compared with the commercial BAM.

Key words: Luminescence, Hexagonal aluminate, Nano-phosphor, Rod shape.

Introduction

Blue emitting Eu^{2+} doped BAM phosphors have been widely used in fluorescent lights (FL) and plasma display panels (PDPs) [1-5]. Despite recent efforts to fabricate PDPs with a large screen, low energy consumption and wide viewing angle, some problems still exist to provide optimum brightness, color purity and resolution. Small-sized phosphor particles with good dispersibility have advantages for patterning small pixels. Small pixels with a high packing density contribute to obtain is high resolution and luminescence efficiency. All of these factors are influenced by the phosphor material itself or by the morphology of the phosphor layer. The porosity of the layer determines whether vacuum ultraviolet (VUV) photons can be transmitted through the phosphor layer. For instance, the existence of pinholes results in the absorption of VUV photons at the back plate leading to a reduction of the pixel efficiency. Therefore, the phosphor layer should be optically dense. This is optimally achieved with small (2-4 μm) and spherical particles [1].

Apart from the morphology, further improvement on the luminescence efficiency can be achieved by studying the defect mechanism. The earlier studies reported that a profound influence on the luminescence efficiency of Eu^{2+} doped BAM was obtained by a compositional variation or by introducing defects [6, 12]. The ternary phase diagram for the $\text{BaO-MgO-Al}_2\text{O}_3$ system was reported by Goebbels et al. [6] and solid solutions between BAM and $\text{Ba}_{0.75}\text{Al}_{11}\text{O}_{17.25}:\text{Eu}^{2+}$ (BAL) were prepared to provide some important insight into the relationships

between the structure and the compositional change. BAL has been known as a highly Ba^{2+} deficient aluminate which forms at the end of the solid solution of Ba-poor hexagonal aluminates. The hexagonal aluminates are classified as the β -alumina and magnetoplumbite type structures. Both types consist of spinel blocks and conduction layers. The difference in the atomic arrangement of the conduction layer defines the type of structure. Generally, the emission peaks of hexagonal aluminates shifts in the longer wavelength as the type of structure alters from magnetoplumbite to β -alumina. In addition, by changing the composition from BAM to BAL, emission peaks shift towards the same direction [7, 15].

So far, commercialized BAM has been prepared by a solid state reaction method with high luminescence intensity. However, this method has some disadvantages, such as inhomogeneous dispersibility of the dopant ions, the formation of polyhedral shaped large size particles [6]. Our aim in this paper is to develop BAM phosphors with high luminescence efficiency of nanosize, and also to control the particle morphology.

Experiments

The preparation of the phosphor particles by is the LPP method consists of a three step process. The first step, the so-called impregnation process, is shown in fig. 1; a cellulose pulp was used as a template, and the mixed water solutions containing the metal salts were prepared. The metal salts consisted of barium chloride ($\text{BaCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$) and europium chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$). The BAM solutions were prepared by mixing these metal salt solutions corresponding to the mol ratio of $\text{Ba}_{0.87-0.90}\text{Mg}_{0.95-0.91}\text{Al}_{10}\text{O}_{17-17.05}:\text{Eu}_{0.05}$. The

*Corresponding author:
Tel : +82 31 290 7361
Fax: +82 31 290 7371
E-mail: dhyoon@skku.edu

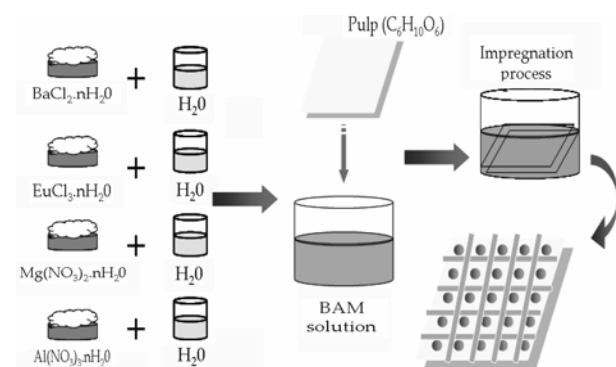


Fig. 1. A schematic representation of the impregnation process.

pulp and BAM solution were used in the proportion of 1:1. The pulp was impregnated by inserting it into the mixed water solution and then dried at 80 °C in a dry oven to evaporate the water. The second step was conducted at 800 °C. The conditions were as follows: heating from room temperature to 800 °C a heating rate of 333 K/h⁻¹, maintaining the temperature at 800 °C for 1h and cooling to room temperature. At the last step, the calcined powder was heated from room temperature to 1400 °C at a heating rate of 333 K/h⁻¹ under 5% of H₂ containing N₂ atmosphere.

The emission spectrum was measured at room temperature using a Kr-excimer lamp as a source of PL spectrophotometer in the ranges of 350-700 nm for 200 msec. under 2.664×10^{-3} Pa. The excitation spectrum was measured using a deuterium lamp and a VUV monochromator in the ranges of 120-340 nm with 2 nm scanning step. A powder X-ray diffractometer (XRD, Cu K, 30 kV, 100 mA, Rigaku) was used to determine the crystalline phases of synthesized specimens. The morphologies of the phosphor particles were observed using a scanning electron microscope (FESEM, JEOL JSM6700F).

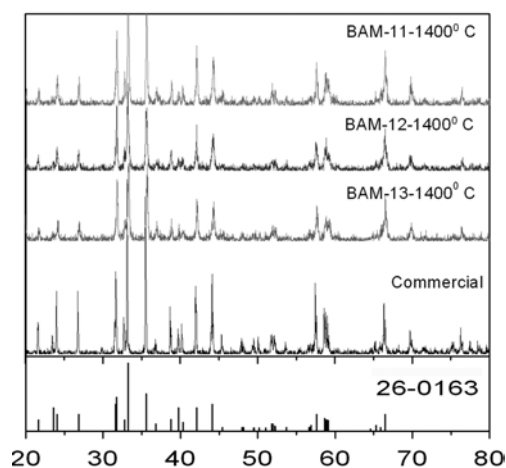


Fig. 2. The XRD patterns of commercial BaMgAl₁₀O₁₇:Eu⁺² phosphor and BAM specimens prepared at 1,400 °C with different composition (BAM11, BAM12, BAM13) and spectral lines of BaMgAl₁₀O₁₇ registered in JCPDS card no: 260163 .

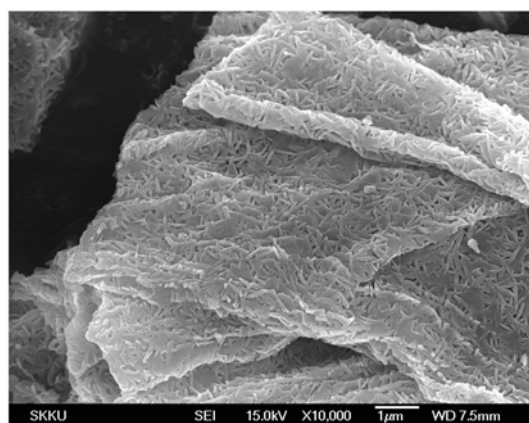


Fig. 3. FESEM image of the rod shaped BAM particles.

Results and Discussion

Fig. 2 shows the XRD pattern of the BAM specimens. The diffraction peaks are in agreement with the XRD pattern of barium magnesium aluminum oxide registered in JCPDS card No: 26-0163 with a hexagonal crystal structure in the space group *P6₃/mmc*. These peaks are less intense and broader due to their crystallite sizes compared with the commercial product.

Fig. 3 shows a FESEM image of the rod shaped BAM particles contained within thin layers. The rod shaped phosphor particles were crystallized in a particular direction; in this case, horizontally along the thin layer. It can be assumed that this type of morphology is developed due to the micro fibrous structure of the pulp. The pulp was used as a template to alleviate the agglomeration of the particles and to restrict the crystal growth direction. By inserting the pulp into the BAM solution, liquid nano-droplets that will be the seeds of the nano-sized particles are impregnated into the pulp, owing to the pulp's micro fibrous structure [16]. The impregnated liquid nano-droplets are surrounded by the fiber walls. Therefore, the nano-droplets tend to crystallize along the direction of the fiber until another fiber intersects it. During the initial step of the calcination process, the growth speed is fast and, therefore, the growth is suppressed by the pulp until it vaporizes at around 600 °C [16], then growth continues in the free space.

Fig. 4 shows the FESEM images of the rod shaped phosphor particles having the compositions of (a) BAM-11, (b) BAM-12 and (c) BAM-13 as shown in table 1. They have a similar morphology, but their particle size slightly differs. The diameter of individual rod shaped nano-phosphor particles varies in the range of 60-100 nm and 400-700 nm in length.

Fig. 5 shows the PL emission spectrum of BAM specimens and the commercial BAM phosphor excited at (a) 147 and (b) 254 nm. The commercial BAM phosphor has a broad emission band with a maximum of around 450 nm corresponding to the blue emission in visible region of the

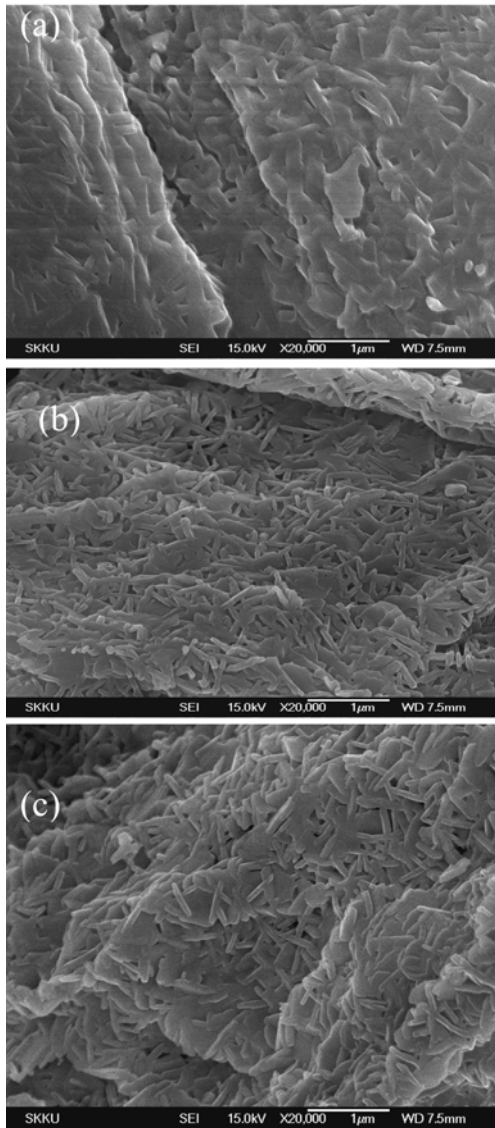


Fig. 4. FESEM images of the rod shaped phosphor particles having the compositions of (a) BAM-11, (b) BAM-12 and (c) BAM-13.

electromagnetic spectrum. This broad band originates due to the transitions of Eu^{2+} ions from the $4f^65d^1$ excitation state to the $4f^7$ ground state. However, our specimens have a peak shift towards the longer wavelength direction at around 465 nm in both emission spectra. Our specimens, labeled BAM-11 ($\text{Ba}_{0.90}\text{Mg}_{0.95}\text{Al}_{10}\text{O}_{17.05}:\text{Eu}_{0.05}$), BAM-12 ($\text{Ba}_{0.88}\text{Mg}_{0.93}\text{Al}_{10}\text{O}_{16.96}:\text{Eu}_{0.05}$), and BAM-13 ($\text{Ba}_{0.87}\text{Mg}_{0.91}\text{Al}_{10}\text{O}_{16.93}:\text{Eu}_{0.05}$) each have a non-stoichiometric composition. A shift in the emission band towards a longer wavelength direction was obtained as the concentration of Ba and Mg

Table 1. BAM compositions of specimen's in mol percent

Specimen compositions (mol %)	Code
0.90 BaO + 0.95MgO + 5 Al ₂ O ₃ + 0.05 Eu ₂ O ₃	BAM-11
0.88 BaO + 0.93MgO + 5 Al ₂ O ₃ + 0.05 Eu ₂ O ₃	BAM-12
0.87 BaO + 0.91MgO + 5 Al ₂ O ₃ + 0.05 Eu ₂ O ₃	BAM-13

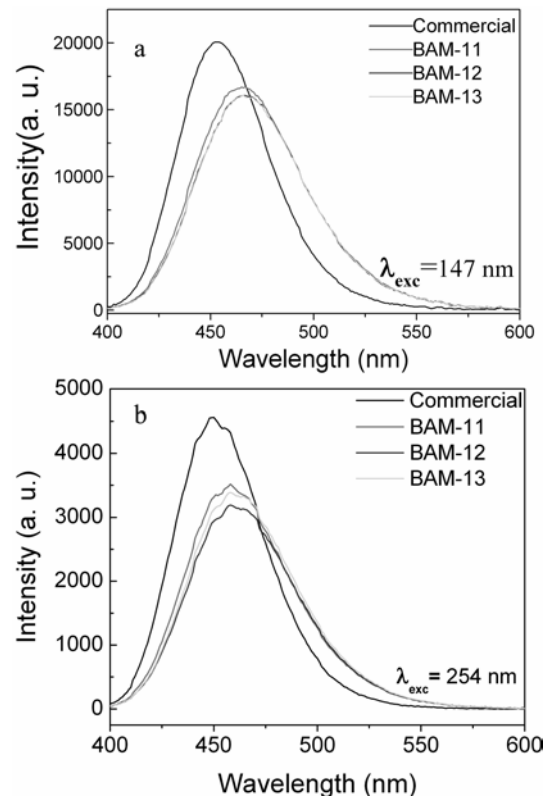


Fig. 5. Emission spectrum of BAM specimens excited at (a) 147 nm and (b) 254 nm.

ions decreased. This type of shift can be called a red shift because the red wavelength is the end of the visible electromagnetic spectrum. In our specimens, the red shift increased due to Eu-O associations. As the concentration of Ba^{2+} or Mg^{2+} ions decreases in the composition, O^{2-} ions replace the Ba sites. This results in a variation in the crystal field of Eu^{2+} ions. The red shift was obtained on the both emission spectra because the interactions of Eu-O complexes in such short distances suppress the position of the excited 5d levels to the lower energy position [12, 13]. Apart from the red shift, another notable feature is the decrease of the maximum emission intensities of our specimens on the PL spectra excited at 147 and 254 nm compared with the commercial BAM. It is suggested that the presence of Ba^{2+} vacancies made the emission intensity drop in our specimens as shown in fig. 5. Stevels [10] reported that the deficiency of Ba^{2+} ions in the conduction layer may cause a decrease in the emission intensity because the deficiency of Ba^{2+} ions may lead to formation of traps. The absorption of UV photons from these traps causes the decrease in the luminescence intensity. This explains why the luminescent intensity is very low when the Ba^{2+} is highly deficient in BAM phosphors. On the other hand, the substitution of O^{2-} ions for Ba^{2+} sites leads to the migration of Al^{3+} ions next to the conduction layer to compensate the charge neutrality. This may cause a formation of the Al-O-Al bridges, the so-called Reidinger defects. The formation of Reidinger defects leads to a decrease of intensity due to

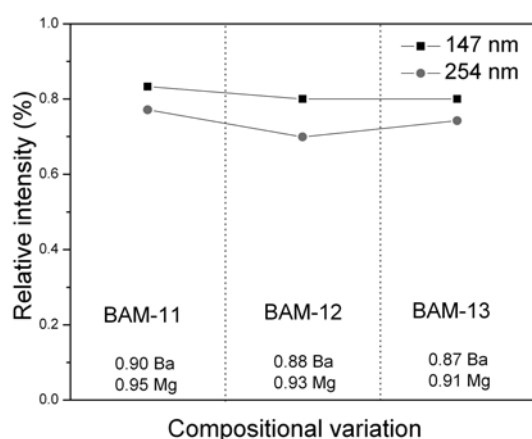


Fig. 6. Relative emission intensity of BAM specimens excited at 147 nm and 254 nm wavelength..

the non-radiative transitions [15]. The particle size also primarily affects the luminescence efficiency. As the particle size decreases the defects on the surface will increase due to the larger surface area of the smaller particles. In our experimental results, 80% of PL intensity was obtained as shown in fig. 5. It is expected that this lower intensity originates from the defects on the surface of the smaller particles.

Fig. 6 shows the relative emission intensities of BAM specimens under 147 and 254 nm wavelength excitations. It was found that there was essentially no big difference in the emission spectra between that excited at 147 and 254 nm. It is expected that the energy transfer takes place via exciton emission because there is no big difference in the relative intensities of the emission centers in both emission spectra, if the transfer mechanism was dependent on the local Eu^{2+} environments [14].

Fig. 7 shows the excitation spectra of BAM specimens. It was found that the excitation mechanism of each specimen showed a different behavior as the excitation wavelength changed. As shown in fig. 7, there are three regions in the excitation spectrum. The first region extends

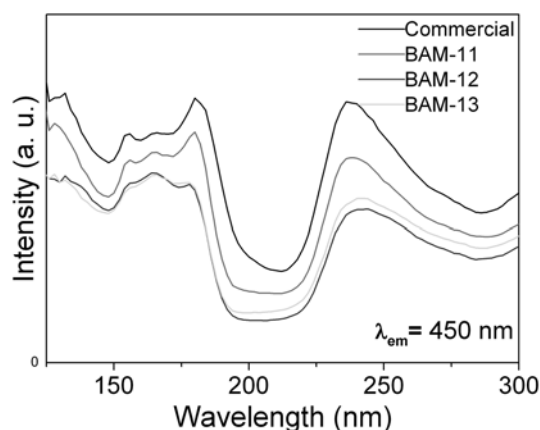


Fig. 7. Excitation spectra of BAM samples at room temperature, with the emission maintained at 450 nm.

from 125 to 147 nm where the excitation takes place through the spinel block. In the second region, the excitation takes place into the Ba^{2+} 5d level and energy transfer comes true over self-trapped exciton (STE) at Ba-O groups in between 147 to 185 nm; beyond 185 nm, excitation takes place directly at Eu^{2+} via $4f^7 \rightarrow 4f^6 5d$ transitions. Beyond 185 nm the samples have similar spectral shapes since all samples have the same Eu^{2+} ion concentrations [14].

Conclusions

Blue emitting Eu^{2+} doped BAM nano-phosphors were synthesized using the LPP method. From FESEM analyses it was formed that the particles have a rod shape morphology and their sizes are about 60-100 nm in diameter and 400-700 nm in length. 80% of PL efficiency has been obtained compared with the larger size commercial product and their peak positions shifted to a longer wavelength (~ 465 nm) direction due to the compositional differences. As the concentration of Ba^{2+} and Mg^{2+} decreases, a shift in the luminescence spectrum towards a longer wavelength was obtained with a lower intensity. The optical properties of our specimens were investigated via the PL emission spectra excited at 147 and 254 nm. It was found that the emission shift was not related to the Eu^{2+} ions location, since there was no big difference in the emission spectra excited at 147 and 254 nm wavelengths.

References

1. T. Justel, H. Nikol, Adv. Mater. 12 (2000) 527-530.
2. C. Feldmann, T. Justel, C.R. Ronda and P.J. Schmith, Adv. Funct. Mater. 13 (2003) 511-514.
3. C. R. Ronda, J. Alloys Comp., 225 (1995) 534-537.
4. C. R. Ronda, J. Lumin. 72 (1997) 49-51.
5. K.Y. Jung and K.H. Han, Electrochem. Solid-State Lett. 8 (2005) 91-94.
6. M. Goebbels, S. Kimura, and E. Woermann J. Solid State Chem. 136 (1998) 253-56.
7. J.P.M.J. Verstegen, A.L.N. Stevels, J. Lumin. 9 (1974) 406-410.
8. N. Iyi, S. Takekawa, and S. Kimura, J. Solid State Chem. 83 (1989) 8-12.
9. A.L.N. Stevels and A.D.M. Schrama-de Pauw, J. Electrochem. Soc. 123 (1976) 691-694.
10. A.L.N. Stevels, J. Lumin. 17 (1978) 121-124.
11. S. Oshio, K. Kitamura, T. Shigeta, S. Horii, T. Matsuoka, S. Tanaka and T. Kanda, J. Electrochem. Soc. 146 (1999) 392-395.
12. B.M.J. Smets and J.G. Verlijndonk, Mater. Res. Bull. 21 (1986) 1305-1308.
13. P. Boolchand, K. C. Mishra, M. Raukas, A. Ellens and P. C. Schmidt, Phys. Rev. B. 66 (2002) 134429.
14. V. Pike, S. Patraw, A. L. Diaz, and B. G. DeBoer, J. Solid State Chem. 173 (2003) 359-362.
15. B. Dawson, M. Ferguson, G. Marking, and A. L. Diaz, J. Lumin. 106 (2004) 39-42.
16. T.S. Yue, A. Kai, Kenjii, K. Okazima, A. Ishizu, A. Isogai, K. Ishii, Z. Honda, Hajime, T. Shibata, T. Hirato, K. Maeda, S. Makoto and Hazime, *Functional Cellulose*, (CMC Publishing co. ltd., Japan, 2003).