

## PHOTOLUMINESCENCE OF BARIUM BASED ALUMINATE PHOSPHORS

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### Abstract

In plasma display panel, the  $\text{Eu}^{2+}$ -activated barium magnesium aluminate (BAM) phosphor has been conventionally adopted as a blue-emitting component due to its availability and high quantum efficiency. Attempt had done to prepare BAM in addition with gallium. In this paper, we used combustion synthesis for preparation for barium based phosphor. Combustion synthesis furnishes a quick method for preparing these phosphors. Photoluminescence (PL)

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characteristics of all these compounds were studied by using a Hitachi F-4000 spectrofluorimeter, at room temperature, using 1.5nm spectral slit width in the range of 200-700nm.

## 1. Introduction

### 1.1. $\text{BaMgAl}_{10}\text{O}_{17}$

$\text{Eu}^{2+}$  activated barium magnesium hexa-aluminate phosphor,  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  (BAM) has been widely utilized in fluorescent lights (FLs), high resolution (HR), field emission displays (FEDs), and projection TVs (PTVs). At present, increasing attention is being paid to BAM owing to their application in plasma display panels (PDPs) as a component of the blue-emission phosphor showing a high emission efficiency and ideal chromaticity on vacuum ultraviolet (VUV) irradiation [1-4]. Thus far, commercialized BAM phosphors have been prepared by conventional solid-state synthesis route. Recently, combustion synthesis (CS) has emerged as an attractive technique for the production of homogeneous, high-purity, and crystalline oxide powders at significantly lower temperatures than the conventional synthesis methods, because the starting raw materials are homogeneously mixed, and the high temperature generated instantly by exothermic reaction can volatilize low boiling point impurities [5-7]. Several aluminate compositions were investigated and used as photoluminescence, cathodoluminescence, and plasma display panel phosphors for their high quantum efficiency in the visible region. The persistence time for aluminate based phosphor materials is about 10 times longer than that of conventional sulphide based phosphors [8, 9]. Emission of  $\text{Eu}^{2+}$  is very strongly dependent on the host lattice and can occur from ultraviolet to red region of the electromagnetic spectrum. This is because the  $5d \rightarrow 4f$  transition is associated with the change in electric dipole and the  $5d$  excited state is affected by crystal field effects. Notably barium and strontium aluminates have been reported as good host materials. Ying-Liang Liu et al. [10] studied luminescent centers of  $\text{Eu}^{2+}$  in  $\text{BaMgAl}_{10}\text{O}_{17}$  phosphor by influence of  $\text{BaF}_2$  as a flux. Ha-Kyun Jung et al. [11] studied the fabrication of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  particles by spray-pyrolysis method.

### 1.2. BaAl<sub>12</sub>O<sub>19</sub>

Among the oxide catalysts, hexa-aluminate (BaAl<sub>12</sub>O<sub>19</sub>) was described as a good candidate for reactions at high temperatures [12]. Further, BaAl<sub>12</sub>O<sub>19</sub> is one of the commonly used phosphor host materials [13, 14]. For example, BaAl<sub>12</sub>O<sub>19</sub>:Mn [15] and BaAl<sub>12</sub>O<sub>19</sub>:Eu [16] are green and blue phosphors, respectively. Jeon et al. [17] reported two independent energy transfer mechanisms in BaAl<sub>12</sub>O<sub>19</sub>:Ce<sup>3+</sup>, Eu<sup>2+</sup> phosphor. Recently, Wang and Li [18] reported that BaAl<sub>12</sub>O<sub>19</sub>:Mn<sup>2+</sup> phosphor would be favourable for application in plasma display panels (PDPs) and Hg-free lamps. It is well known that green-emitting phosphors play an important role in improving the luminescence efficiency and luminous flux of luminescence materials. According to the host category, the green-emitting phosphors used currently in plasma display and fluorescent lamps are mainly included in four groups: Mn<sup>2+</sup>-activated silicate, Tb<sup>3+</sup> or Tb<sup>3+</sup>–Ce<sup>3+</sup>-activated phosphate, Tb<sup>3+</sup>-activated borate, and Mn<sup>2+</sup>-or Tb<sup>3+</sup>–Ce<sup>3+</sup>-activated aluminates. Xiao et al. [19] prepared a series of BaAl<sub>12</sub>O<sub>19</sub>:Tb<sup>3+</sup> phosphors by using the sol-gel method, their preparation conditions, structures, and luminescence properties were investigated. He found the excitation band of BaAl<sub>12</sub>O<sub>19</sub>:Tb at approximately 240nm, originating from the <sup>4</sup>f<sub>8</sub> – <sup>4</sup>f<sub>7</sub><sup>5</sup>d<sub>1</sub> transition of Tb<sup>3+</sup>. The emission spectrum consisted of eight emission peaks, originating from the <sup>5</sup>D<sub>3</sub> – <sup>7</sup>F<sub>i</sub> and <sup>5</sup>D<sub>4</sub> – <sup>7</sup>F<sub>j</sub> transitions of Tb<sup>3+</sup>. The emission of BaAl<sub>12</sub>O<sub>19</sub>:Tb phosphors at 543nm.

### 1.3. Ba<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>

The engineering of next-generation long-persistence phosphors (LPPs) continues to receive a great deal of attention. Such phosphors may find practical application in self powered emergency lighting systems and traffic signs, information displays, luminous fabric, directional, and other

glow-in-the-dark signs, etc. They also can be used in optical memory units. The first generation of LPPs were sulphides, such as CaS:Bi and ZnS:Cu. These materials offer high rates of trap filling and many colours, but their phosphorescence time does not meet modern technological requirements. Long persistent afterglow phosphor,  $\text{Ba}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  was prepared by Emen et al. [20] at high temperature by a solid-state reaction in a weak reductive atmosphere. The crystal structure of  $\text{Ba}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  has been determined as an orthorhombic Pmmm space group with  $a = 18.200(6) \text{ \AA}$ ,  $b = 16.923(6) \text{ \AA}$ ,  $c = 5.131(21) \text{ \AA}$ ,  $V = 1580.3(9) \text{ \AA}^3$ , and  $Z = 8$ .

In this paper, we report Eu ions-doped BAM in addition with gallium oxide, Tl-doped BAM, Eu-doped  $\text{Ba}_4\text{Al}_{14}\text{O}_{25}$ , and Tb-doped  $\text{BaAl}_{12}\text{O}_{19}$  prepared with combustion synthesis.

## 2. Experimental

The preparation process involved the combustion of redox mixtures, in which metal nitrate acted as an oxidizing reactant and urea as a reducing reactant. The starting composition of the barium nitrate, aluminum nitrate, and urea was based on the total oxidizing and reducing valencies of the oxidizer and the fuel using the concepts of propellant chemistry [21]. Barium nitrate  $[\text{Ba}(\text{NO}_3)_2]$ , aluminum nitrate  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , europium oxide ( $\text{Eu}_2\text{O}_3$ ), terbium oxide ( $\text{Tb}_4\text{O}_7$ ), thallium nitrate ( $\text{TlNO}_3$ ), gallium oxide ( $\text{Ga}_2\text{O}_3$ ), and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) were taken in suitable stoichiometric ratios to get a product of chemical formulae  $\text{Ba}_{0.95}\text{Eu}_{0.05}\text{MgAl}_9\text{GaO}_{17}$ ,  $\text{Ba}_{0.99}\text{Al}_{12}\text{O}_{19}\text{Tb}_{0.01}$ ,  $\text{Ba}_{3.99}\text{Al}_{14}\text{O}_{25}\text{Eu}_{0.01}$ , and  $\text{Ba}_{0.999}\text{MgAl}_{10}\text{O}_{17}\text{Tl}_{0.001}$ . All these compounds were separately prepared by combustion synthesis. Each of these compounds was thoroughly mixed in an agate mortar. The mixing resulted in a thick paste due to large crystallization of water in

aluminum nitrate. The resulting paste was transferred into a China dish and the dish was introduced into a muffle furnace maintained at 500°C. Initially, the paste melts and undergoes dehydration followed by decomposition with evolution of large amounts of gases. Then, spontaneous ignition occurred and underwent smoldering combustion with enormous swelling, producing white foamy and voluminous  $\text{Ba}_{0.95}\text{Eu}_{0.05}\text{MgAl}_9\text{GaO}_{17}$ ,  $\text{Ba}_{0.99}\text{Al}_{12}\text{O}_{19}\text{Tb}_{0.01}$ ,  $\text{Ba}_{3.99}\text{Al}_{14}\text{O}_{25}\text{Eu}_{0.01}$ , and  $\text{Ba}_{0.999}\text{MgAl}_{10}\text{O}_{17}\text{Tl}_{0.001}$  compounds. The whole process is over within less than 5 min. The China dish was immediately removed from the furnace. The foamy and voluminous combustion ash easily crushed into powder using pestle and mortar.

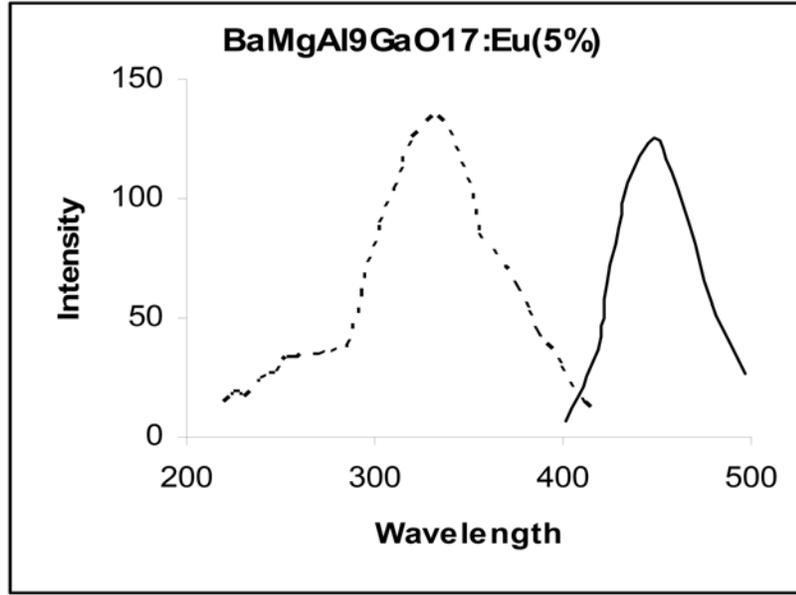
Photoluminescence (PL) characteristics of all these compounds were studied by using a Hitachi F-4000 spectrofluorimeter, at room temperature, using 1.5nm spectral slit width in the range of 200-700nm.

### 3. Result and Discussion

#### 3.1. $\text{BaMgAl}_9\text{GaO}_{17}:\text{Eu}$

Uptil now most of the research worker prepared BAM doped with europium with various synthesis and studied luminescent centers of  $\text{Eu}^{2+}$  in BAM, the surface-coated BAM phosphors with  $\text{MgF}_2$  and its microstructure and luminescent property are also investigated etc. In this paper, we tried to prepare BAM in addition with Ga so that Ga replaces one of the aluminium molecule. Figure 1 shows the photoluminescence spectra for  $\text{BaMgAl}_9\text{GaO}_{17}:\text{Eu}(5\%)$ . We found no change in the result on adding gallium oxide. A strong emission is observed around 449.2nm. The excitation maximum is located around 333nm and has a shoulder at around 381nm. Europium can act as an activator in two forms  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ .  $\text{Eu}^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  $^8S_{7/2}$  state of  $4f_7$  configuration.

The excitation arises from the transition from  $^8S_{7/2}$  state of  $4f_7$  configuration to the states belonging to the  $4f^65d^1$  configuration.  $\text{Eu}^{3+}$  emission usually occurs from  $^5D_0 \rightarrow ^7F_J$  transitions.



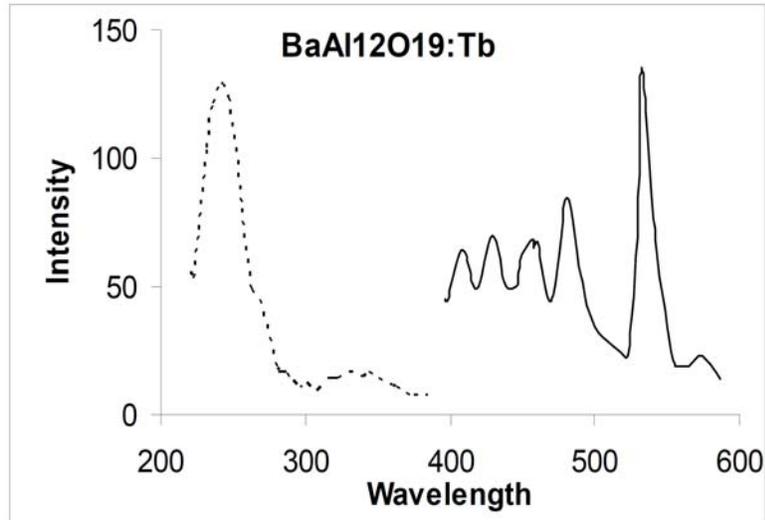
**Figure 1.** Photoluminescence of  $\text{BaMgAl}_9\text{GaO}_{17}:\text{Eu}(5\%)$ .

(a)  $\text{Eu}^{2+}$  emission for 333nm & 381nm excitation.

(b)  $\text{Eu}^{2+}$  excitation for 449.2nm emission.

### 3.2. $\text{BaAl}_{12}\text{O}_{19}:\text{Tb}$

Figure 2 shows the PL spectra for  $\text{BaAl}_{12}\text{O}_{19}:\text{Tb}(1\%)$ . The excitation peak of  $\text{BaAl}_{12}\text{O}_{19}:\text{Tb}$  was a wide band at approximately 244nm, originating from the  $^4f_8 - ^4f_7^5d_1$  transition of  $\text{Tb}^{3+}$ . The emission spectrum consisted of eight emission peaks, originating from the  $^5D_3 - ^7F_1$  and  $^5D_4 - ^7F_j$  transitions of  $\text{Tb}^{3+}$ . The emission of  $\text{BaAl}_{12}\text{O}_{19}:\text{Tb}$  phosphors is found at around 542nm.



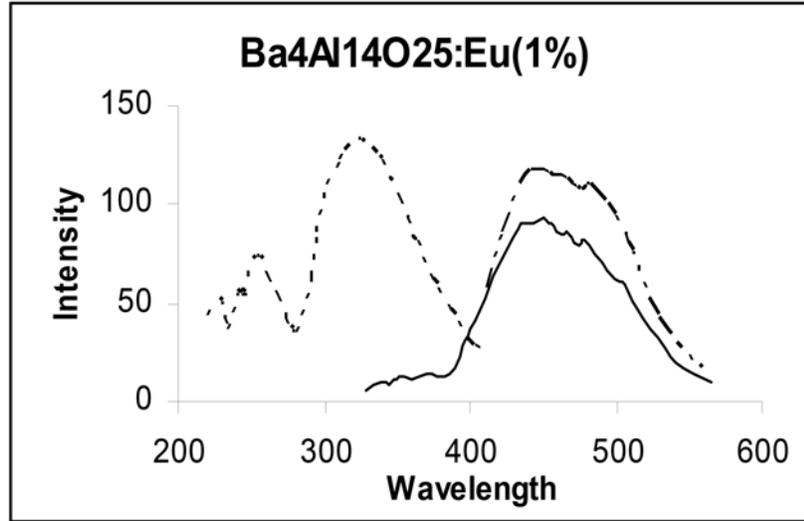
**Figure 2.** Photoluminescence of  $\text{BaAl}_{12}\text{O}_{19}:\text{Tb}^{3+}(1\%)$ .

(a)  $\text{Tb}^{3+}$  emission for 244nm excitation.

(b)  $\text{Tb}^{3+}$  excitation for 542nm emission.

### 3.3. $\text{Ba}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$

Figure 3 shows the PL spectra of  $\text{Ba}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}(1\%)$ . The excitation and emission peaks are broad bands and the emission peak is found at 450nm. The emission is due to the transition of  $\text{Eu}^{3+}$  from  ${}^4f_6 {}^5d_1 \rightarrow {}^4f_7$ , respectively. The excitation band is narrow compare to emission band and the excitation is found at 254nm and 330nm.



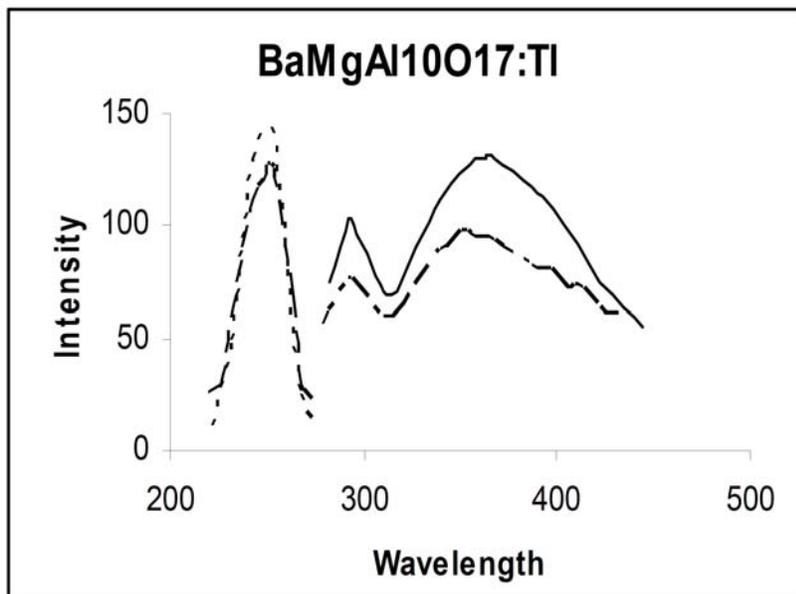
**Figure 3.** Photoluminescence of  $\text{Ba}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{3+}(1\%)$ .

(a)  $\text{Eu}^{3+}$  emission for 254nm and 330nm excitation.

(b)  $\text{Eu}^{3+}$  excitation for 450nm emission.

#### 3.4. $\text{BaMgAl}_{10}\text{O}_{17}:\text{Tl}$

Figure 4 shows the PL spectra of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Tl}(1\%)$ . We tried for 0.1 mol% and for 1 mol% and found slight change in the excitation value but the emission is at the same point. The excitation maximum is located around 253.6nm and 254nm and the broad band emission is around at 264nm, 295nm, and 355nm.  $\text{Eu}^{3+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  ${}^8\text{S}_{7/2}$  state of  ${}^4f_7$  configuration. The excitation arises from the transition from  ${}^8\text{S}_{7/2}$  state of  ${}^4f_7$  configuration to the states belonging to the  $4f^65d^1$  configuration.



**Figure 4.** Photoluminescence of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Tl}^{3+}$  (0.1 & 1%).

- (a)  $\text{Tl}^{3+}$  emission for 254nm excitation.
- (b)  $\text{Tl}^{3+}$  excitation for 264nm, 295nm, and 355nm emission.

#### 4. Conclusion

All the barium based phosphor was prepared by combustion synthesis. Appreciable luminescence has been observed in all the barium based aluminate samples doped with various activators. In  $\text{BaMgAl}_9\text{GaO}_{17}:\text{Eu}$  sample, we got the same emission as in original BAM doped with Eu, it conclude that on addition of gallium, there is no effect on BAM:Eu.

**References**

- [1] C. R. Ronda, *J. Lumin.* 72-74 (1997), 49-54.
- [2] S. Oshio, T. Matsuoka, S. Tanaka and H. Kobayashi, *J. Electrochem. Soc.* 145 (1998), 3898-3903.
- [3] C. R. Ronda, *J. Alloys Compd.* 225 (1995), 234-238.
- [4] Y. Liu and C. Shi, *Mater. Res. Bull.* 36 (2001), 109-115.
- [5] P. Yang, G. Yao and J. Lin, *Inorg. Chem. Commun.* 7 (2004), 389.
- [6] S. Shikao and W. Jiye, *J. Alloys Compd.* 327 (2001), 82.
- [7] F. Gu, S. F. Wang, M. K. Lu, W. G. Zou, G. J. Zhou, D. Xu and D. R. Yuan, *J. Cryst. Growth* 260(3-4) (2004), 507-510.
- [8] D. Jia, J. Zhu and B. Wu, *J. Electrochem. Soc.* 147 (2000), 386.
- [9] W. Jia, H. Yuan, L. Lu, H. Liu and W. M. Yen, *J. Lumin.* 76-77 (1998), 424.
- [10] Ying-Liang Liu and Chun-Shan Shi, *Mater. Res. Bull.* 36(1-2) (2001), 109-115.
- [11] H.-K. Jung, D.-W. Lee, K. Y. Jung and J.-H. Boo, *J. Alloys Compd.* 390 (2005), 189-193.
- [12] M. F. M. Zawrah and N. M. Khalil, *Ceram. Int.* 27 (2001), 309.
- [13] T. R. N. Kutty and W. Nayak, *Mater. Res. Bull.* 30 (1995), 325.
- [14] D. Ravichandran, S. T. Johnson, S. Erdei, R. Roy and William B. White, *Displays* 19 (1999), 197.
- [15] D. Y. Lee, Y. C. Kang, H. D. Park and S. K. Ryu, *J. Alloys Compd.* 353 (2003), 252.
- [16] A. L. N. Stevels and A. D. M. Schrama-dePauw, *J. Electrochem. Soc.: Solid-State Sci. Technol.* 691 (1976), 123.
- [17] H. S. Jeon, S. K. Kim, H. L. Park, G. C. Kim, J. H. Bang and M. Lee, *Solid State Commun.* 120 (2001), 221.
- [18] Yu Hua Wang and Feng Li, *J. Lumin.* 122-123 (2007), 866.
- [19] L. Xiao, M. He, Y. Tian, Y. Chen, T. Karaki, L. Zhang and N. Wang, *Japanese J. Appl. Phys.* 46 (2007), 5871-5873.
- [20] F. M. Emen, N. Külcü and A. N. Yazıcı, *European J. Chem.* 1(1) (2010).
- [21] S. R. Jain, K. C. Adiga and V. R. Pai Vernekar, *Combust. Flame* 40 (1981), 71.

