Effects of Annealing on the Luminescence Properties of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ Blue Emitting Phosphor

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Abstract—BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ blue emitting phosphors have been prepared by urea-nitrate solution combustion synthesis at 590°C for 5 minutes. After combustion process, the phosphor was annealed at different temperatures in reducing atmosphere. The experimental results of XRD, SEM, and photoluminescence and thermo luminescence showed that the phosphor had hexagonal single phase, the increase of average particle size and the decrease of photo luminescent and thermoluminescent intensity when annealed temperature increases. The emission spectra was a broad band with maximum intensity at the wavelength $\lambda_{max} = 450$ nm due to transitions from the 4f$^3$5d$^1$ to the 4f$^2$ electronic configuration of Eu$^{2+}$ ion that was according to emission of Eu$^{2+}$ ions located at different positions in the lattice.

Key words: BaMgAl$_{10}$O$_{17}$, nanoparticle, combustion, degradation.

I. INTRODUCTION

BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ blue emitting phosphor has been used extensively in manufacturing tricolor fluorescent lamps (FL), field emission displays (FED), plasma display panels (PDPs) and liquid crystal displays (LCD) [1, 2]. This phosphor has high luminous efficiency and brightness. Emission spectra of BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ (BAM) phosphor have a broad band with peak at 450 nm due to transition from the 4f$^3$5d$^1$ excited state to the 4f$^2$ ground state of ion Eu$^{2+}$. However, the stability of BAM is not good. Its luminous efficiency decreases during the panel manufacture and also during the operation of the panel [3].

II. EXPERIMENTAL

Starting materials for the preparation of BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ phosphors by urea - nitrate solution combustion synthesis are Ba(NO$_3$)$_2$, Mg(NO$_3$)$_2$6H$_2$O, Al(NO$_3$)$_3$9H$_2$O and Eu$_2$O$_3$ oxide. Urea was used to supply fuel and reducing agent. Eu$_2$O$_3$ oxide has been nitrified by nitric acid. The reaction for the formation of BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$, assuming complete combustion, may be written as:

\[(1 - x)\text{Ba(NO}_3\text{)}_2 + \text{Eu(NO}_3\text{)}_3 + \text{Mg(NO}_3\text{)}_2 + 10 \text{Al(NO}_3\text{)}_3 + 28.34 \text{CH}_3\text{N}_2\text{O} \rightarrow \text{Ba}_{10-x}\text{Eu}_x\text{MgAl}_{10}\text{O}_{17} + \text{by products.}\]

Aqueous solution containing stoichiometric amounts of nitrate metal and urea was mixed by magnetic stirrer and heated at 60°C for 2 hours to gel. Next, the gel was dried at 80°C to dehydrate and combusted at temperature 590°C within 5 minutes. Urea concentration was 60 times of product mole (theory 28.34). The product was BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ with white powder. The samples were prepared with invariable concentration of Eu$^{2+}$ (3 %mol). After the combustion process, the phosphors were annealed at different temperature from 200°C to 1200°C for 15 minutes or at temperature 600°C for different times in the reduced atmosphere. The synthesized products were characterized by X-ray diffraction (XRD) using a Bruker D8-Advance X-ray diffractometer. Excitation and emission spectra were measured by FL3-22 fluorescent spectrometer. The morphology was taken on by
FESEM-Hitachi S-4800. The glow curves were analyzed by Harshaw TLD-3500 equipment.

III. EXPERIMENTAL RESULTS

A. X-ray diffraction and morphology

![XRD diagrams of the BAM: Eu²⁺ (3 %mol)](image)

(a) non-annealing, (b) annealed at 300 °C, (c) annealed at 500 °C, (d) annealed at 900 °C

The crystalline structure of BaMgAl₁₀O₁₇: Eu²⁺ phosphor was confirmed by X-ray diffraction diagram (XRD), the results showed in the Fig. 2. BaMgAl₁₀O₁₇ phosphors have hexagonal single phase structure that is classified into β-alumina structure with a space group P6₃/mmc [5]. No change of the structure of BaMgAl₁₀O₁₇: Eu²⁺ phosphors annealed at different temperature. Fig. 3 shows SEM images of the samples annealed at different temperatures. From the result of Fig. 3, crystalline particle formed hexagonal disks with average thickness of disk about 70 nm. The thickness increases insignificantly when annealed temperature increases and diameter of disk is bigger.

![SEM photography of BAM: (3 %mol)Eu²⁺ annealed at different temperature](image)

(b) annealed at 300 °C, (c) annealed at 500 °C, (d) annealed at 900 °C

B. Influence of annealing on luminescent properties of BAM: Eu²⁺

B.1. Influence of annealing to photo luminescent properties

![Emission spectra of BAM: Eu²⁺ annealed at different temperatures](image)

The emission spectra of BAM: Eu²⁺ phosphors annealed at different temperature after combustion process, excited by radiation 365 nm, show in the Fig. 4. The spectra consist of a same broad band with maximum peak at about 450 nm, corresponding to the 4f⁵5d - 4f⁷ electronic transition of Eu²⁺ ion. When annealed temperature raises from 200 °C to 600 °C, maximum luminescent intensity of the phosphors decreases insignificantly. But as annealed temperature is above 600 °C, maximum emission intensity decreases fast. At once, maximum of emission peak lightly shifted to shorter wavelength with increasing of the annealed temperature. It could due to activator centers Eu²⁺ were oxidized to Eu³⁺ in the lattice [6] and this process occurred fast at temperature above 600 °C. In order to clarify the assignment of the emission centers in the lattice, luminescent spectra of the phosphor BAM: Eu³⁺ annealed at 200 °C that have been fitted with combination of three Gaussian peaks as present in Fig. 5.
Fig. 5: The emission spectra of BAM: Eu$^{2+}$ was fitted with three Gaussian peaks

The Fig. 5 shows that emission spectra of BAM: Eu$^{2+}$ consist of three peaks which had maximum wavelength at 442 nm (peak 1), 461 nm (peak 2) and 493 nm (peak 2), correspondingly. These 3 peaks coincide with 3 sites of ion Eu$^{2+}$ (BR, aBR and mO) in the BAM lattice. Besides, the Fig. 6 also shows that maximum emission intensity ($I_0$) of the phosphors and these of 3 Gaussian peaks ($I_{01}$: peak 1, $I_{02}$: peak 2, $I_{03}$: peak 3) decrease when the annealed temperature increase and faster degradation of intensity of peak 2 and 3 compare with the peak 1 leads to shift blue of the phosphor.

Fig. 6: Maximum intensity of Gaussian peaks and total maximum intensity as function of annealed temperature

Luminescent spectra of the BAM: Eu$^{2+}$ phosphors annealed at temperature 600 °C in different intervals and the change of maximum emission intensity of ion Eu$^{2+}$ depends on annealed time were shown in Fig. 7 and Fig. 8. The emission of the Eu$^{3+}$ ion was insignificantly observed in the emission spectra of these phosphors. It could due to quenching of Eu$^{3+}$ ion emission by immediate environment or energy transfer to other centers [7].

Fig. 7: Emission spectra of BAM: Eu$^{2+}$ annealed at temperature 600 °C with different annealed time

Excitation spectra of BAM: Eu$^{2+}$ annealed at different temperature with emission wavelength $\lambda_{em} = 450$ nm present in the Fig. 9. The spectra consist of some overlapped broad bands from 280 nm to 420 nm. These bands correspond with excitation transitions of Eu$^{2+}$ ions that located different positions in the lattice.

Fig. 8: Maximum emission intensity of Eu$^{2+}$ ion as function of different annealed time

When annealed temperature of sample increases, maximum position of excitation bands do not change but relative intensity of peak decreases significantly. This is could explain due to concentration of Eu$^{2+}$ ion decreases.

Fig. 9: Excitation spectra of BAM: Eu$^{2+}$ annealed at different temperatures with emission wavelength $\lambda_{em} = 450$ nm
B.2. Influence of annealing to thermoluminescent properties

Glow curves of BAM: Eu$^{2+}$ phosphors annealed at different temperatures, irradiated with dose of β-ray 1.5 Gy that were recorded with heating rate 1 °C/s, showed in the Fig. 10. They consist a main peak at temperature 173 °C and an other peak at 334 °C. Glow curves of the annealed phosphors have the same shape but their thermoluminescent intensity decrease when annealed temperature increases. The change of thermoluminescent intensity of these peaks depends on the annealed temperature in the Fig. 11.

![Glow curve of BAM: Eu$^{2+}$ annealed at different temperature when irradiation with β ray, dose 1.5 Gy](image)

These results showed that no change of trap depth of the phosphors and the decrease of thermoluminescent intensity coincide with these of photo luminescent intensity when annealed temperature increases.

![Dependence of PL and TL intensity of BAM:Eu$^{2+}$ on annealed temperature, TL peak 1 (173 °C), TL peak 2 (334 °C)](image)

It could be confirm that degradation of photo luminescent and thermo luminescent intensity of the phosphors when annealing could due to the decrease of the activator centers Eu$^{2+}$. It supported a conversion of Eu$^{2+}$ ions to Eu$^{3+}$ ions by oxidation process when annealing. Hence, the luminous efficiency of the phosphor was decreased during the manufacture and the operation of FL and PDPs.

IV. CONCLUSION

BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ blue emitting phosphors were prepared by nitrate-urea solution combustion technology. Nanosized phosphor has hexagonal single phase structure. Emission of the phosphor due to the contribution of ion Eu$^{2+}$ that could be located at 3 different sites in the lattice. The oxidation of activator ions is the main cause of the degradation photo luminescent and thermo luminescent intensity and the blue-shift of emission spectra of the phosphor was observed when annealed temperature or annealed time increases.

REFERENCES


