Oxidation of Europium-ion in the $BaMgAl_{10}O_{17}$: Eu^{2+} Phosphor During the Annealing

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***Abstract*— $BaMgAl_{10}O_{17}$: Eu^{2+} blue emitting phosphors have been prepared by urea-nitrate solution combustion synthesis at 590^0C for 5 minutes. After combustion process, the phosphor was annealed at different temperatures in reducing atmosphere and in air. This material had hexagonal single phase crystal structure that was confirmed by X-ray diffraction (XRD). The experimental results of photoluminescence showed that the emission spectra was a broad band with maximum intensity at the wavelength λmax = 450 nm due to transitions from the $4f^65d^1$ to the $4f^7$ electronic configuration of Eu^{2+}. After the annealing process, emission spectra were shown the emission lines corresponding to the $^5D_0 - ^7F_J$ electronic transition of Eu^{2+}, which were the typical emission of Eu^{3+}. When annealed temperature raises, luminescent intensity of Eu^{2+} decreases and luminescent intensity of Eu^{3+} increases. Many research have indicated that oxidation of $Eu^{2+} \rightarrow Eu^{3+}$ occurs in the lattice during thermal treatment process.**

Keywords—$BaMgAl_{10}O_{17}$, nanoparticle, combustion, degradation.

I. INTRODUCTION

$BaMgAl_{10}O_{17}$: Eu^{2+} (BAM: Eu^{2+}) blue emitting phosphor is one of the important phosphors utilized in luminescent devices. BAM: Eu^{2+} has been widely used in modern lighting, displays and optical communications fields such as manufacturing tricolor fluorescent lamps (FL), field emission displays (FED), plasma display panels (PDPs) and liquid crystal displays (LCD) [1], [2]. Because of its high luminance efficiency and brightness under vacuum ultraviolet light excitation. Emission spectra of BAM: Eu^{2+} phosphor have a broad band with peak at 450 nm due to transition from the $4f^65d$ excited state to the $4f^7$ ground state of Eu^{2+} ion. However, the thermal stability of BAM: Eu^{2+} is not good. It undergoes determination of luminance intensity and color quality by thermal treatment during the manufacturing process [3]. This low durability is one of the major factors limiting the longevity of optical devices.

BAM has a hexagonal crystal structure and belongs to the $P6_3/mmc$ space group. Al^{3+} ions and O^{2-} ions formed a rigid 3D network structure as AlO_4 tetrahedron and AlO_6 octahedron in spinel layer. Besides, Mg^{2+} ions occupied one Al site in a unit cell while Ba^{2+} ions occupy the conduction layer sites, which connected two spinel layers. The BR site is the substitution site of Ba and the other two sites are interstitial sites.In BAM: Eu^{2+}, Eu^{2+} ion can be located at three sites in the lattice [4], [5].

In this paper, we report luminescent degradation of $BaMgAl_{10}O_{17}$: Eu^{2+} phosphors prepared with urea - nitrate solution combustion method in reducing media and in the air.

The problem of luminescent degradation due to oxidation will be clarified in this paper. The oxidation process $Eu^{2+} \rightarrow Eu^{3+}$ in the BAM: Eu^{2+} phosphor and the change of emission intensity of Eu^{2+} ion in the lattice were investigated to determine how various sites are affected during the oxidation process [6]. The photoluminescent properties of the phosphors will be presented and discussed.

II. EXPERIMENTS

$BaMgAl_{10}O_{17}$: Eu phosphors were prepared by urea - nitrate solution combustion synthesis. This method was detailed in our other papers [7], [8].

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 ^{0}C to 1200 ^{0}C for 15 minutes in the reduced atmosphere and in the air.

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 fluorescence spectrometer. The morphology were taken on by FESEM-Hitachi S-4800.

III. RESULTS AND DISCUSSION

3.1. X-ray diffraction of BAM: Eu

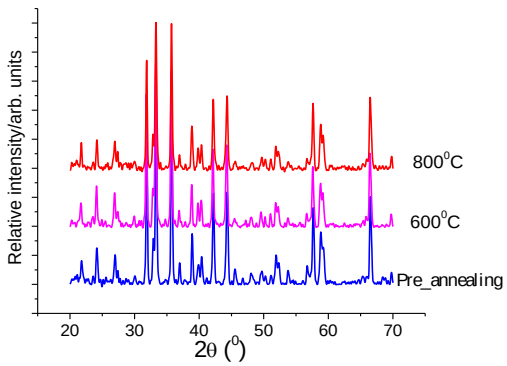

Fig.1. XRD diagrams of the BAM: Eu annealed at different temperature in air

The crystalline structure of $BaMgAl_{10}O_{17}$: Eu phosphor was confirmed by X-ray diffraction diagram (XRD), the result of samples annealed at different temperature in reduced media were presented in our other paper [8]. Figure 1 illustrates the XRD patterns for BAM: Eu phosphors annealed at different temperature in air. These results have hexagonal single phase structure that is classified into β-alumina structure with a space group $P6_3/mmc$ [5]. On the other hand, there were no detectable changes in the structure of BAM: Eu phosphors by annealing at different temperature in both environment.

3.2. Influence of annealing on luminescent properties of BAM: Eu

Figure 2 presents emission spectra of BAM: Eu annealed at 800 ^{0}C in the reducing atmosphere and in air, excited by radiation 365 nm. The result indicate that the spectra have a same broad band with maximum peak at about 450 nm, corresponding to the $4f^65d$ - $4f^7$ electronic transition of Eu^{2+} ion.

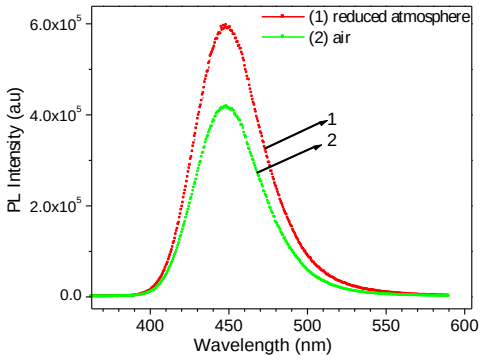

Fig.2. Emission spectra of BAM: Eu annealed at 800^{0}C in the reducing atmosphere and in air with emission wavelength λ_{ex} = 365 nm

When annealed temperature raises from 200 ^{0}C to 800 ^{0}C, maximum luminescent intensity of the phosphors decreases insignificantly. But as annealed temperature is above 800 ^{0}C, maximum emission intensity decreases fast as showed in figure 3.

On another hand, the results in figure 2 and figure 3 show when phosphors are annealed in air, the degradation speed of luminescent intensity is faster than in reduced media. In addition, oxygen vacancies in BAM: Eu phosphor in the reducing media exist more than these in air. This degradation could due to activator centers Eu^{2+} were oxidized to Eu^{3+} in the lattice [7] and this process occurred fast at temperature above 800 ^{0}C.

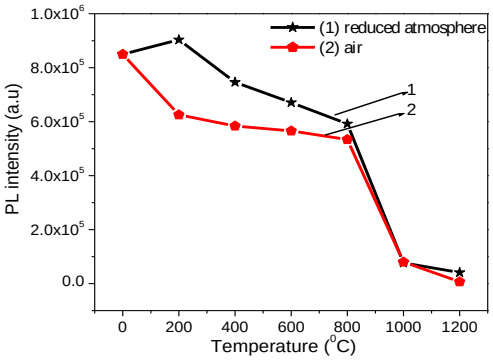

Fig.3. Dependency of maximum intensity PL on annealin temperatures in the reducing atmosphere and in air

These oxygen vacancies which are close enough to Eu^{2+} centers can capture electrons from Eu^{2+} centers and then the Eu^{3+} centers are created. Therefore, when annealing in air, the emission intensity of Eu^{2+} center decreases faster than in the reduced media [9], [10].

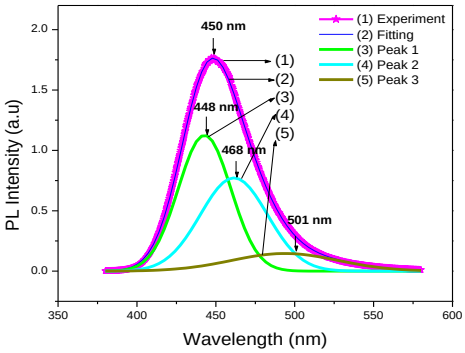

Fig.4. The emission spectra of BAM: Eu^{2+} was fitted with three Gaussian peaks

In order to clarify the assignment of the emission centers in the lattice, these emission spectra were fitted with combination of three Gaussian peaks.

Figure 4 gives the results of peak-fitting for the emission spectra of BAM: Eu annealed at 800 ^{0}C. The emission band was separated into three peaks which had maximum wavelength at 448 nm (peak 1), 468 nm (peak 2) and 501 nm (peak 3), corresponsively. These 3 peaks are ascribed to 3 sites of Eu^{2+} (BR, aBR, mO) in the BAM lattice [4],[5].

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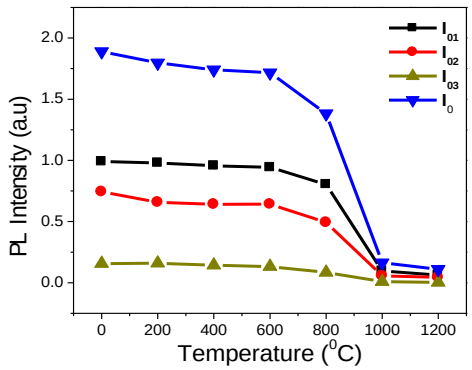

Fig.5. Maximum intensity of Gaussian peaks and total maximum intensity as function of annealed temperture

It is clearly indicated that the three Gaussian peaks do not have the same intensity. Besides, the figure 5 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 slightly shorter wavelength. These results is similar to that when samples were annealed in air.

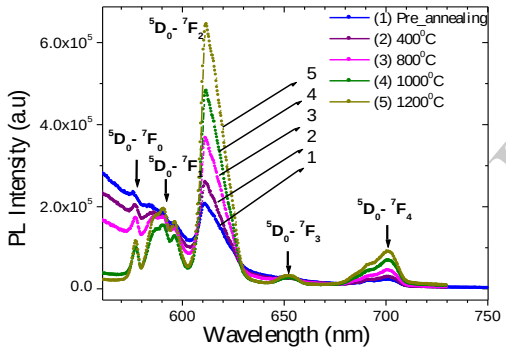

Fig.6. Emission spectra of Eu^{3+} ion in lattice BAM annealed at different temperatures in reducing atmosphere, λ_{ex}=394 nm

The oxidation from Eu^{2+} ion to Eu^{3+} ion in lattice BAM was demonstrated by luminescence of Eu^{3+} ion at different annealed temperatures in the reducing atmosphere and in air.

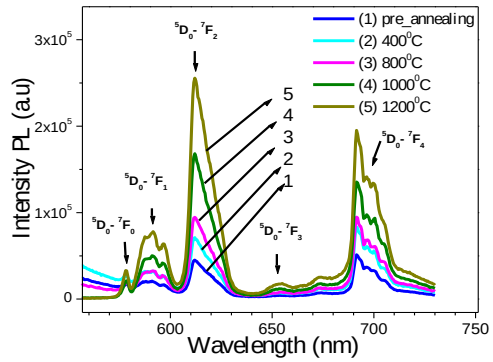

Fig.7. Emission spectra of Eu^{3+} ion in lattice BAM annealed at different temperatures in air, λ_{ex}=394 nm

Emission spestra of BAM: Eu phosphor annealed at different temperatures with excitation wavelength λ_{ex} = 394 nm present in the figure 6 and figure 7.

According to the above results, emission spectra of BAM: Eu with excitation wavelength λ_{ex} = 394 nm are narrow lines at the range of 550-720 nm that is corresponding to $^5D_0$ - ^7F_J (J=0,1,2,3,4) transitions of Eu^{3+} ion. These results indicated, when the annealing temperature increases then the luminescent intensity of Eu^{3+} ion increases. Thus, Eu ions in the BAM lattice can exist simultaneously divalent and trivalent states.

In addition, the change of maximum emission intensity of Eu^{2+} and Eu^{3+} ions depend on annealed temperatures was shown in figure 8. When annealed temperature of sample increases, maximum luminescent intensity of Eu^{2+} ion decreases and maximum luminescent intensity of Eu^{3+} ion increases. It obviously indicates that the oxidation from $Eu^{2+} \rightarrow Eu^{3+}$ occurred.

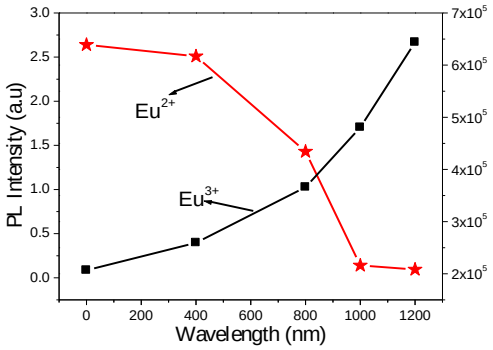

Fig.8. Maximum emission intensity of Eu^{2+} ion and Eu^{3+} ion as function of different annealed temperatures

Excitation spectra of pre-annealed and annealed BAM: Eu at different temperature with emission wavelength λ_{em} = 450 nm present in the figure 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.

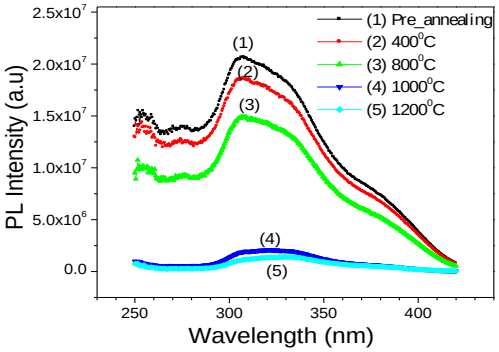

Fig.9. Excitation spectra of samples BAM: Eu annealed at different temperatures with emission wavelength λ_{em} = 450 nm

When annealed temperature of sample increases, maximum positions of excitation bands of ion Eu^{2+} do not change but maximum intensity decreases significantly.

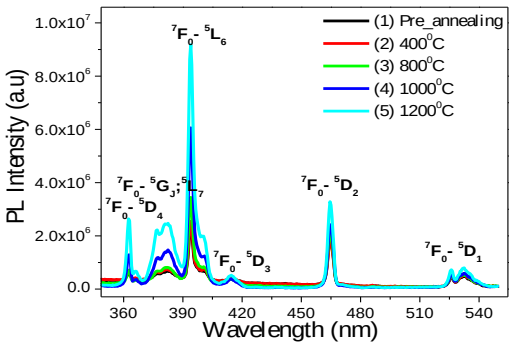

Fig.10. Excitation spectra of BAM: Eu annealed at different temperatures with emission wavelength λ_{em} = 612 nm

Simultaneously, maximum intensity of excitation peaks of Eu^{3+} ion increases as exhibits in figure 10. This could be confirm due to concentration of activator Eu^{2+} ion decreases and concentration of Eu^{3+} ion increases when annealed temperature of sample increases.

IV. CONCLUSION

$BaMgAl_{10}O_{17}$: Eu phosphors were prepared by urea - nitrate solution combustion method, after samples annealed in reducing atmosphere and in the air. These phosphors have hexagonal single phase structure. The emission spectra was a broad band with maximum intensity at the wavelength λ_{max} = 450 nm due to transitions from the $4f^6 5d^1$ to the $4f^7$ electronic configuration of Eu^{2+} ions that occupy three different sites (BR, aBR, mO) in the BAM lattice. When annealing temperature increases, emission spectra of BAM : Eu^{2+} shift to short wavelength. Degradation of luminescent intensity of Eu^{2+} ion is due to the oxidation of $Eu^{2+} \rightarrow Eu^{3+}$ in the lattice when annealed temperature raises. At the same time, when phosphors are annealed in air, the degradation speed of luminescent intensity is faster than in reduced media. This degradation occurred fast at temperature above 800 ^{0}C.

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