Thermal Phenomenon of $BaMgAl_{10}O_{17}$:Eu^{2+} Blue Phosphor by XANES and Rietveld Method

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Abstract

The blue phosphor, $BaMgAl_{10}O_{17}$:Eu^{2+}, showing a blue emission band at about 450 nm were prepared by solid state reaction of $BaCO_3$, Al_2O_3, MgO and Eu_2O_3 with AlF_3 as a flux. The thermal quenching of $BaMgAl_{10}O_{17}$:Eu^{2+} phosphor significantly reduces the intensity of the blue emission. It is reduced by an amount of 50% after heating at around 800℃ for 1 hr. The red emission in the 580~720 nm region of $^5D_0\rightarrow^7F_1$ and $^5D_0\rightarrow^7F_2$ transition of Eu^{3+} is produced from the phosphor heated above 1,100℃. The EPR spectrum also reveals that some part of Eu^{2+} ions are oxidized to trivalent ions above 1,100℃ at around 90 and 140mT. This oxidation evidence is also detected from XANES absorption spectra for L_{III} shell of Eu ions: an absorption peak is at 6,977eV of Eu^{2+} and 6,984eV of Eu^{3+}. The combined X-ray and neutron data suggests that the new phase of $EuMgAl_{11}O_{19}$ magnetoplumbite structure may be formed by heat treatment.

Key Words : $BaMgAl_{10}O_{17}$:Eu^{2+} blue phosphor, plasma display panel, EPR, XANES, Rietveld method, magnetoplumbite(M/P)

1. Introduction

$BaMgAl_{10}O_{17}$:Eu^{2+}(BAM) blue phosphor has been applied to plasma dispaly panel (PDP) in flat panel display (FPD) because it has a good efficiency under vacuum ultraviolet excitation [1,2]. However, it is well known that the luminescence degradation of BAM results from the oxidation of luminescence centers Eu^{2+}. This phenomenon is a serious and critical problem which is raised to about 500~700℃ during the manufacturing of PDP on the barrier rib [3]. This ambient atmosphere oxidize BAM blue phosphor and results in the luminescence degradation among red, green and blue phosphors. Eventually, the oxidation of doped Eu^{2+} ions in BAM phosphor shows the variation of chromaticity and quantum efficiency. However, these problems of luminescence degradation due to oxidation still remain unsolved. Nevertheless, there have been few efforts not only to make clear the mechanism of luminescence decrease but also understand the phenomenon [4-5]. In this present paper, we have investigated that the environmental behavior of Eu^{2+} and Eu^{3+} ions in $BaMgAl_{10}O_{17}$:Eu^{2+} due to the oxidation by means of the photoluminescence spectra and a combined crystal structure analysis.

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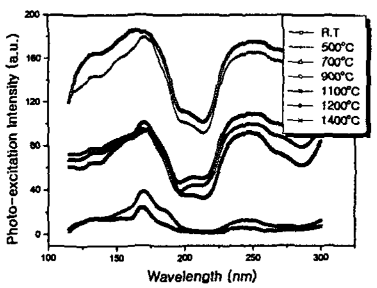
2. Experiments

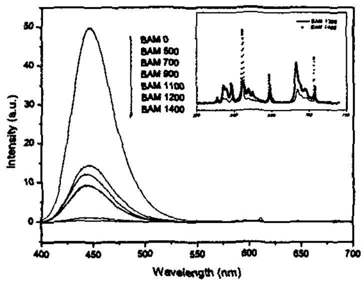
The phosphor samples were prepared by solid-state reaction with $BaCO_3$, MgO, -Al_2O_3, and Eu_2O_3 at a specific weight ratio in a mixing gas of 94% nitrogen and 6% hydrogen at a muffle furnace. BAM blue phosphor, which has a composition of xBaO, Al_2O_3, MgO, (1-x)Eu, was synthesized by firing mixtures at 1400~1450℃ (1st and 2nd firing). Thermal degradation was carried out by firing at each temperature for 1hr in air and slowly cooled down to room temperature at the furnace. The X-ray diffraction data were measured at room temperature in the scattering range of 15 ~ 140 with a 0.04 interval in 2 using CuK_α radiation with graphite monochromator. Furthermore, neutron powder diffraction data were collected up to 2 = 140 with a 0.05 step per 10 sec and the neutron wavelength was 1.8348Å on the High Resolution Powder Diffractometer (HRPD) at the Hanaro Center, KAERI. The structure refinement was carried out by the Rietveld method, using the RIETAN profile refinement program [6]. The photoluminescence (PL) of the excitation, electron paramagnetic resonance (EPR) and X-ray absorption near edge structure (XANES) were measured.

3. Results and discussion

The excitation and emission spectra of $BaMgAl_{10}O_{17}$:Eu^{2+} blue phosphor depending on the annealing temperature are shown in Fig. 1. Compared to unannealed phosphor, the annealed phosphor has the remarkable reduction of excitation efficiency in the shorter wavelength region of 140~200nm.



(a) excitation spectra



(b) emission spectra

Fig. 1. (a) excitation and (b) emission spectra of $BaMgAl_{10}O_{17}$:Eu^{2+} blue phosphor with annealing temperature for 1hr in air.

As increasing the annealing temperature, the main features are observed at 590 and 615nm emission lines, corresponding to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} appeared from the phosphor annealed at 1,100℃, while the blue Eu^{2+} emission band peaking at 450nm decreased by annealing and disappeared for the phosphor around 1,200~1,300℃ [7].

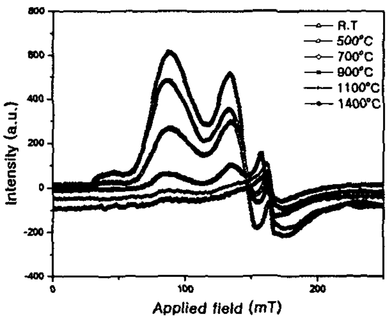


Fig. 2. EPR spectra of $BaMgAl_{10}O_{17}$:Eu^{2+} blue phosphors with various annealing temperature.

In Fig. 2, EPR spectra of BAM showed that signal observed at around 90 and 140mT are thought to be due to Eu^{2+} ions and 160mT for $BaMgAl_{10}O_{17}$ host lattice. The signal started to decrease at 500℃ annealing and disappeared by annealing at round 1,100℃. This result also suggests that Eu^{2+} concentration decreases with increasing annealing temperature.

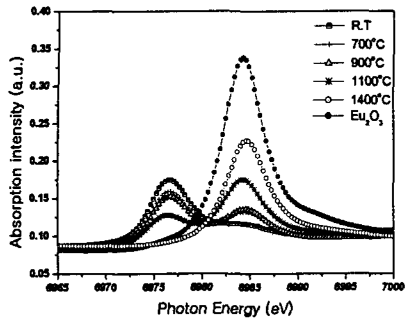


Fig. 3. XANES spectra of $BaMgAl_{10}O_{17}:Eu^{2+}$ (L_{III} shell of europium) phosphor after annealing at various temperature for 1hr.

XANES spectra of the L_{III} shell of Eu ions in $BaMgAl_{10}O_{17}:Eu^{2+}$ is shown in Fig. 3. By the annealing temperature of 700℃, the 6,977eV absorption peak began to decrease small, while weak absorption at 6,984eV became observable. For the annealing of 1,200℃, a 6,977eV absorption peak almost disappeared, while 6,984eV absorption peak, which coincides with that observed in the Eu_2O_3 spectrum, became predominant. For the phosphor annealed over 1,400℃, the 6,977eV absorption peak was barely observed.

The combined Rietveld refinement patterns using X-ray and neutron powder diffraction data at annealed sample of 700℃ and 1,500℃ are shown in Fig. 4. The mass fraction of $Ba_{1-x}Eu_xMgAl_{10}O_{17}$ and $EuMgAl_{11}O_{19}$ phase based on the refined scale factors for two phases were 2.5% and 11.5% for 700 and 1,500℃ annealed, respectively. Through the X-ray and neutron powder diffraction data, it was not be able find that a very small amount of $EuMgAl_{11}O_{19}$ exists even in $BaMgAl_{10}O_{17}:Eu^{2+}$ annealed below 700℃.

As a Rietveld refinement of phase ratio, the predominant mechanism of the luminance decrease observed by annealing at the lower temperature range from 500 to 600℃ would also be due to formation of $EuMgAl_{11}O_{19}$ in $BaMgAl_{10}O_{17}:Eu^{2+}$ blue phosphor [8].

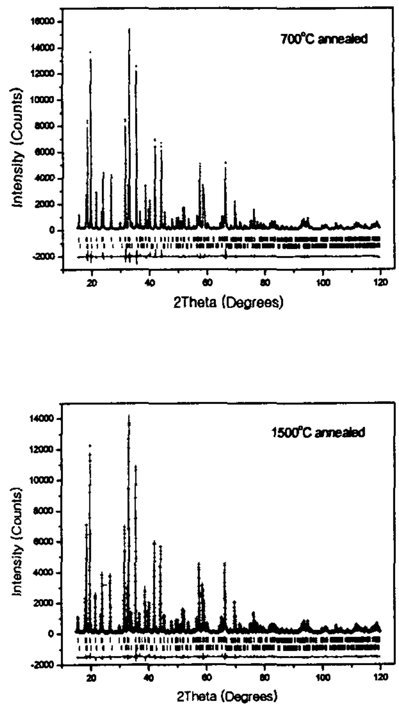


Fig. 4. Rietveld refinement patterns of X-ray data for $BaMgAl_{10}O_{17}:Eu^{2+}$ blue phosphor 700℃ and 1,500℃ annealed.

Table 1. Crystallographic data of $EuMgAl_{11}O_{19}$ magnetoplumbite structure

Atom	Site	x	y	z	$g^{a)}$	U_{iso}*100
Eu	2d	1/3	2/3	3/4	1.0	0.98
Al(1)	12k	0.1894(4)	0.3788(9)	-0.1095(2)	1.0	0.55(2)
Al(2)	4f	1/3	2/3	0.0811(5)	$0.50^{b)}$	$0.91(6)^{c)}$
Mg	4f	1/3	2/3	0.0166(6)	$0.50^{b)}$	0.91(6)
Al(3)	4f	1/3	2/3	0.1853(3)	1.0	0.74(5)
Al(4)	2a	0.0	0.0	0.0	1.0	0.33(6)
Al(5)	2b	0.0	0.0	1/4	1.0	1.76(9)
O(1)	12k	0.1497(6)	0.2995(2)	0.0615(6)	1.0	1.21(1)
O(2)	12k	0.4912(9)	0.9825(9)	0.1591(4)	1.0	0.65(4)
O(3)	4f	1/3	2/3	-0.0987(6)	1.0	0.72(1)
O(4)	4e	0.0	0.0	0.1629(8)	1.0	0.81(3)
O(5)	6h	0.1430(9)	0.2861(9)	1/4	1.0	1.73(9)

a) Occupation factor
b) Constraint on occupancy: $g(Ba)+g(Eu)=1.0$
c) Isotropic temperature factor($/Å^2$): $U_{iso}(Al(2))=U_{iso}(Mg)$

The final magnitudes of the atomic position coordinates and isotropic thermal parameters of magnetoplumbite(M/P) structure are listed in Table. 1. Eu and Al site occupancies, allowed to vary independently, strongly indicate that all Al, Mg and Eu sites are fully occupied in M/P structure. The atomic positions for Al and O in the spinel block were in accordance with those reports for $LaMgAl_{11}O_{19}$ M/P structure [9].

4. Conclusion

According to increasing with the annealing temperature, the mass fraction of the conversion of $BaMgAl_{10}O_{17}$:Eu^{2+} into a mixture of $EuMgAl_{11}O_{19}$ magnetoplumbite structure are considered to increase proceeding from the particle surface to containing amount of Eu ions. It is also assumed that the oxidation processes from the particle surface and deactivates the Eu^{2+} luminescent center, resulting in the decreased photoluminescence efficiency. Consequently, the luminescence decrease due to the electron transfer of Eu oxidation in $BaMgAl_{10}O_{17}$:Eu^{2+} would be a combination of a center having a tendency to become oxidize of $EuMgAl_{11}O_{19}$, such as Eu^{2+}, with a center having a tendency to become reduced like Eu^{3+} showing no good efficient luminescence.

Acknowledgements

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