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Origin of PL intensity increase of $CaMgSi_2O_6:Eu^{2+}$ phosphor after baking process for PDPs application

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Abstract

We have synthesized blue-emitting $CaMgSi_2O_6:Eu^{2+}$ (CMS) and evaluated its thermal stability after baking process. To evaluate its thermal stability, CMS was baked in air at 500 and 600 °C for 20 min, respectively, and compared with $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) treated in the same condition. After baking process, CMS showed somewhat increased photoluminescence (PL) intensity with baking temperature. To investigate the reasons behind the increase of PL intensity after baking process, vacuum ultraviolet (VUV)/PL, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) techniques were applied. From the ESR and the XPS analyses, it is noted that spectral intensity of Eu^{2+} ion somewhat increased. It was believed that due to charge balance Eu^{3+} ions reduced to Eu^{2+} ions during the baking process in air. It is clear that the concentration of Eu^{2+} increased after the baking process in air and it leads to slight increase of the VUV/PL intensity of CMS phosphor.

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Keywords: A. Phosphor; A. $CaMgSi_2O_6:Eu^{2+}$; D. Optical properties; E. Luminescence

1. Introduction

Recently, plasma display panels (PDPs) have been used for large flat panel display (FPD) devices. Among the various type of FPD, PDP is the most promising technology for large size flat television applications because it has a wide view angle and good image quality. However, there are some issues to be improved in terms of luminous efficiency and life time which are directly related to the performance of phosphors used in PDPs. Among used phosphors for PDPs applications, $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) is an important blue phosphor. However, the luminance decrease and color shift of this phosphor during baking process are the well-known problems. Many researchers have tried to improve the stability of BAM. It has been found that the degradation process is caused by several paths such as thermal treatment during PDP manufacturing, irradiation by vacuum ultraviolet (VUV) photons (<200 nm), and ion sputtering, etc. The thermal degradation during the manufacturing process is a particularly serious problem. It has been reported that the thermal degradation is probably related with both change of valance of Eu^{2+} to Eu^{3+} and crystal structure of BAM (β-alumina) which has an open layer in the crystal [1–3].

Kunimoto et al. [4] reported that the $CaMgSi_2O_6:Eu^{2+}$ (CMS) had a good thermal stability during baking process. Because the CMS has a one-dimensional like structure and its Ca site is tightly enclosed by eight oxide ions. Thus, the

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CMS structure has a stable structure in comparison with that of BAM. It is expected that the CMS can be applied to PDPs due to its resistance to luminance degradation induced by baking process. However, the photoluminescence (PL) intensity of CMS excited by 147 nm sources is lower than that of BAM. In order to increase the PL intensity of CMS, it is necessary to understand physical and chemical properties of CMS very well. In addition, studies on PL intensity increase of CMS after baking have not been sufficiently performed even though its PL increase was reported.

In this study, we have synthesized blue-emitting CMS and evaluated its thermal stability after baking process. And we investigated the reason why the PL intensity of CMS increased slightly after baking process as a function of Eu^{2+} concentration.

2. Experimental section

Powder samples of CMS were prepared by conventional solid-state reaction method. To synthesize CMS, $CaCO_3$ (Kojundo 99.99%), MgO (Aldrich 99.99%), SiO_2 (Kojundo 99.99%) and EuF_3 (Aldrich 99.99%) were used as raw materials. Small quantities of NH_4F were added as a flux. The raw materials were mixed in a ball mill mixer for 12 h and heated subsequently at 1150 and 1200 °C in a reducing atmosphere of mixture between H_2 (5%) and N_2 (95%) for 3 h, respectively. In this study, the optimum concentration of Eu^{2+} ions was 0.01 mol for CMS. To investigate the effect of baking process on the luminescence property of CMS, it was baked from 500 to 1000 °C in air for 20 min and compared with BAM treated in the same condition.

PL spectra were obtained at room temperature by scanning wavelength region from 390 to 600 nm under an excitation of 147 nm radiation from a deuterium lamp. The Eu^{2+} concentration in CMS and BAM were evaluated by electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS). The ESR measurements were carried out at X-band frequency and at room temperature using an ESR spectrometer (ESP-300E). And the XPS spectra of the phosphors were obtained using an XPS spectrometer (ESCALAB 250) equipped with an Al K_α X-ray sources ($h\nu = 1486.6$ eV).

3. Results and discussion

To investigate thermal stability, both CMS and BAM were baked in air at 500 and 600 °C for 20 min, respectively. VUV/PL, ESR, XPS were measured for the phosphors before and after baking process. Fig. 1 shows relative PL intensity of CMS and BAM before and after baking. In the case of BAM, the luminance was significantly reduced after baking at 500 and 600 °C, corresponding to reduction of 22 and 31%, respectively. However, in the case of CMS, its PL intensity slightly increased by about 6 and 8%, respectively.

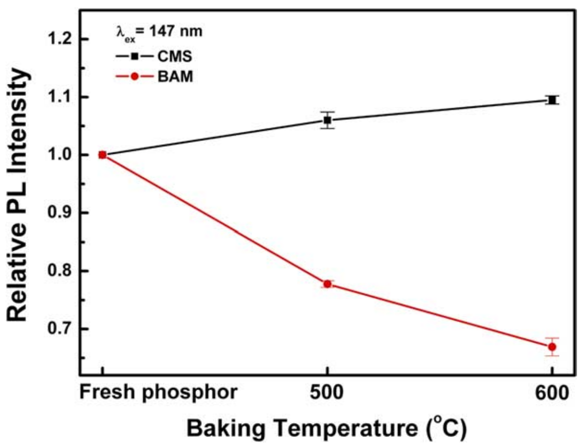

Fig. 1. Relative PL intensity after baking process depending upon baking temperature.

In general, when Eu^{2+} activated phosphors were baked in air, the PL intensity decreased seriously since Eu^{2+} ions changed to non-luminescence Eu^{3+} ions easily [1].

To investigate the reason for the increase of PL intensity of CMS after baking process, we measured ESR spectra of these phosphors. Because Eu^{2+} ion has an uncoupled electron ($4f^7$, $S=7/2$, $L=0$, $J=7/2$), while Eu^{3+} does not have it ($4f^6$, S, $L=3$, $J=0$) [1]. The ESR spectra of BAM with baking temperature are shown in Fig. 2(a). As baking temperature was increased, the signal of Eu^{2+} at 985.3 and 1346.2 G decreased significantly. This results show that the concentration of Eu^{2+} decreases, while that of Eu^{3+} increases with baking temperature [1,5]. Because the ESR results of CMS have not been reported before and the *g*-values are different depending upon kinds of host lattice, we need to determine Eu^{2+} peak position in the ESR spectra. The ESR peaks of Eu^{2+} for a fluoride phosphate (FP) glass were reported in *g*-values of 2.0, 2.8 and 6.0 [6]. Fig. 2(b) shows the ESR spectra of CMS. All the samples show the similar peak positions and shapes to reference ones. In the ESR spectra of CMS, the signal of Eu^{2+} at 2034.9 and 1056.5 G increased, which corresponds to *g*-values of 2.8012 and 6.0084, respectively. These results suggest that the concentration of Eu^{2+} increases with increasing baking temperature.

To measure the concentration of Eu^{2+} in these phosphors precisely, we performed XPS analysis on $Eu3d_{5/2}$ core level. Since, the shape and the energy position of the $Eu3d_{5/2}$ core level in the XPS spectra for Eu^{2+} and Eu^{3+} states of Eu compounds are clearly distinguished from each other, we could directly determine the chemical state of Eu by measuring XPS on its core level [7,8]. The XPS spectra of the $Eu3d_{5/2}$ core level of CMS and BAM are shown in Fig. 3 along with the spectra of typical Eu^{2+} and Eu^{3+}. In order to compare the area of Eu^{2+} ions with that of Eu^{3+} ions after baking process, we performed peak de-convolution since the areas of Eu^{2+} and Eu^{3+} in XPS

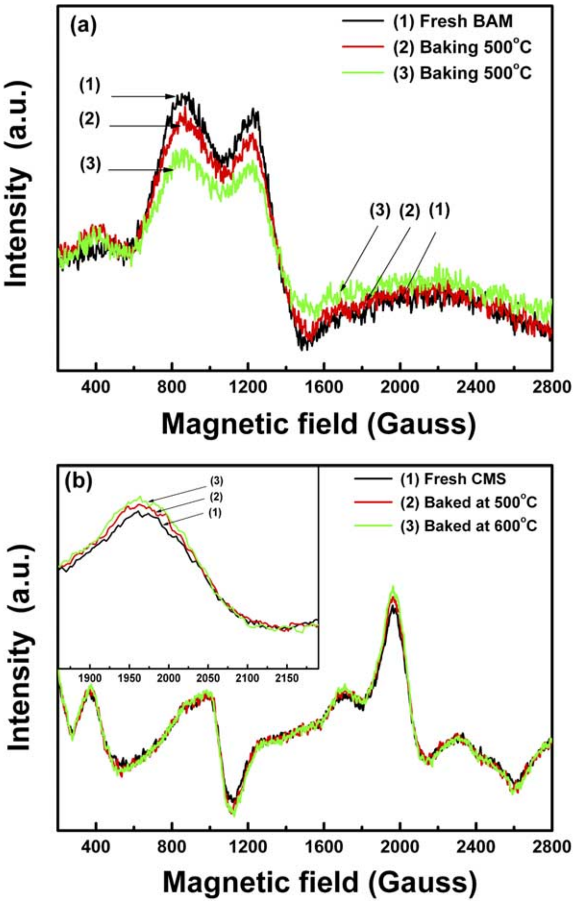

Fig. 2. ESR spectra of (a) BAM and (b) CMS after baking process at various temperature.

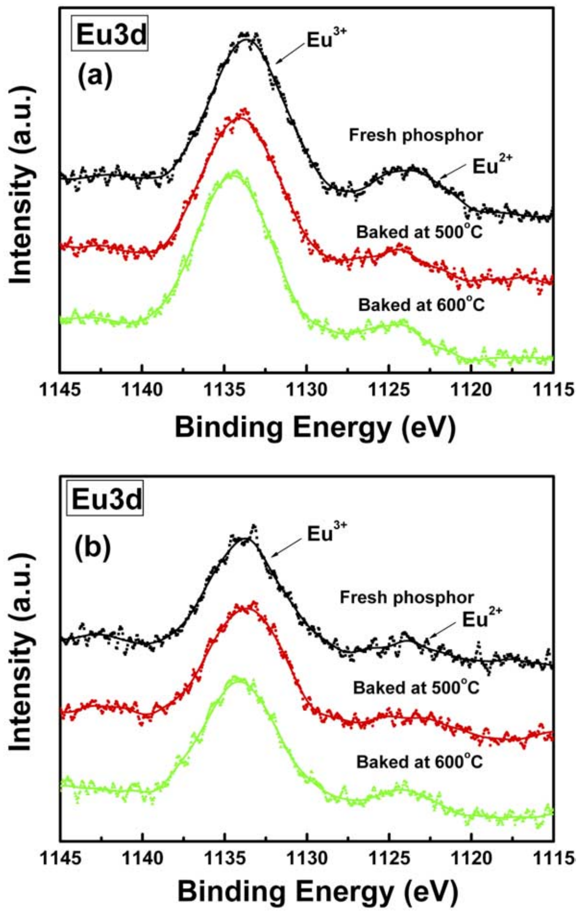

Fig. 3. XPS spectra of the $Eu3d_{5/2}$ core level: (a) BAM, (b) CMS.

spectra are proportion to the concentration of Eu, respectively. The plot of PL intensity vs. $Eu^{2+}/(Eu^{2+}+Eu^{3+})$ ratio is given in Fig. 4. In the case of BAM, the concentration of Eu^{2+} decreased with increasing temperature. However, in the case of CMS, the concentration of Eu^{2+} increased. The VUV/PL intensity was increased after the baking process and spectra of Eu^{2+} ion related with both ESR and XPS analyses also slightly increased. The results of VUV/PL intensity, ESR and XPS measurements are consistent with each other. These results suggest that the cause of luminance increase and decrease be related with the concentration of Eu^{2+} precisely.

As the ESR and XPS results mentioned above, it is found that the Eu^{2+} concentration of CMS increases after baking process. The structure of CMS has only one kind of Ca^{2+} site in the lattice having six-fold oxygen coordination [9]. When Eu^{3+} ions are doped into CMS host lattice, they will replace the Ca^{2+} sites. Since, the radius of Eu^{2+} is 0.112 nm and similar to that of Ca^{2+} for six-fold oxygen coordination ($r=0.1$ nm). However, as Eu^{3+} ions replaced Ca^{2+} sites, it did not satisfy charge balance. From the XPS results, it is cleared that Eu^{2+} and Eu^{3+} ions exist together non-equivalently in host material. When thermal energy were introduced to host material during baking process, Eu^{3+} ions would need to be reduced to Eu^{2+} ions for charge balance. Consequently, Eu^{3+} ions were reduced to Eu^{2+} ions and the Eu^{2+} concentration increased slightly. These phenomena can be represented as a Kröger–Vink notation

$$(1/2)\mathrm{Eu_2O_3} + \mathrm{MgO} + 2\mathrm{SiO_2} \rightarrow \mathrm{Eu}^{\bullet}_{\mathrm{Ca}} + \mathrm{Mg}^{\mathrm{X}}_{\mathrm{Mg}} + 2\mathrm{Si}^{\mathrm{X}}_{\mathrm{Si}} + 6\mathrm{O}^{\mathrm{X}}_{\mathrm{O}} + \mathrm{e} + (1/2)\mathrm{O_2(g)}$$

$$\mathrm{Eu^{3+}} + \mathrm{e} \rightarrow \mathrm{Eu^{2+}}$$

These phenomena are related to crystal structure of CMS since its structure is very rigid. Because the rigid structure acts as a shield from oxidation environment, the Eu^{2+} ions maintain the divalent states in air even at high temperature. Therefore, in CMS the reduction of Eu was preferable to the oxidation of Eu during baking process. On the other hand, the BAM has an open structure, which is called a conduction

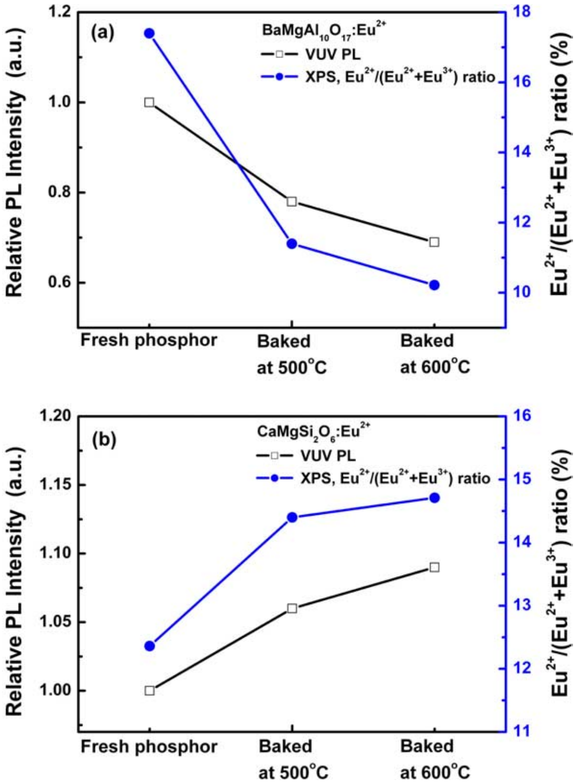

Fig. 4. $Eu^{2+}/(Eu^{2+}+Eu^{3+})$ ratio vs. VUV/PL intensities: (a) BAM, (b) CMS.

plane. Hence, in BAM the oxidation of Eu was preferable to the reduction of Eu.

Furthermore, to investigate Eu reduction in air, we measured relative PL intensity depending upon baking temperature as shown in Fig. 5. Up to about 600 °C, the PL intensity of CMS increased by as much as 8%. However, the

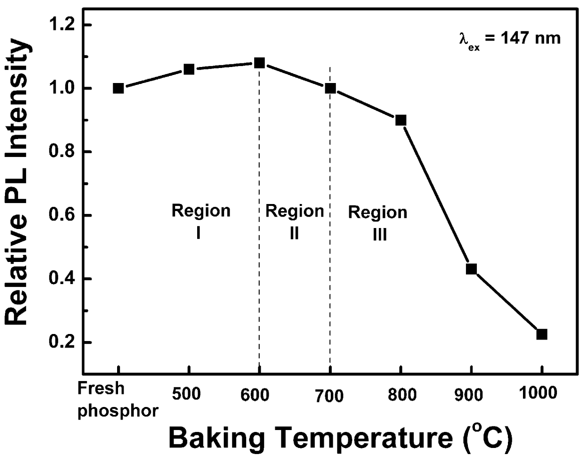

Fig. 5. Relative PL intensity after baking process depending upon baking temperature.

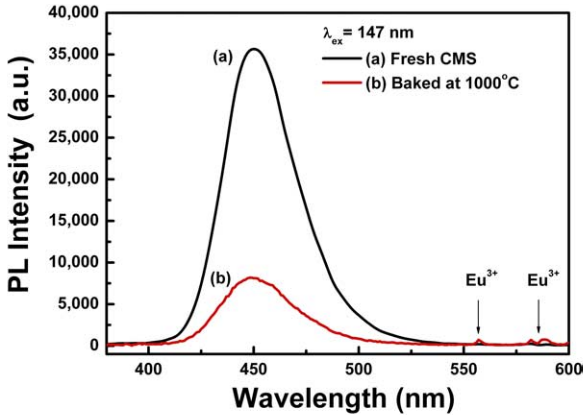

Fig. 6. PL spectra of both fresh phosphor and baked phosphor at 1000 °C.

PL intensity decreased as much as 70% above 800 °C. In region I, the reduction of Eu was dominant with charge balance phenomena. In region II, reduction and oxidation rate of Eu was similar. In region III, the oxidation of Eu was dominant. Fig. 6 shows PL spectra of CMS after baking process at 1000 °C. We observed peak intensity of Eu^{3+} in the spectral region from 550 to 600 nm. Thus, the PL intensity decreased seriously over 800 °C due to oxidation of Eu.

4. Conclusion

To understand the increase of PL intensity of CMS after the baking process, VUV/PL, ESR, XPS techniques were applied. The obtained results suggest that the cause of luminance increase be related with the Eu^{2+} ion concentration. In the case of CMS, the VUV/PL intensity was increased after the baking process and spectra of Eu^{2+} ion obtained by both ESR and XPS techniques also somewhat increased. It was believed that Eu^{3+} ions reduced to Eu^{2+} ions for satisfying charge balance during the baking process in air. It is revealed the reason why CMS has a good stability in comparison with BAM upon going through the baking process for manufacturing PDPs devices.

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