

Thermal Stability Study of Eu^{2+} -doped $\text{BaAl}_2\text{Si}_2\text{O}_8$ Phosphor using Polymorphism for Plasma Display Panel applications

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Abstract

We have evaluated thermal stability of a $\text{BaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ (BAS: Eu^{2+}), which have polymorph property such as hexagonal, monoclinic structure depending upon firing temperature. When both polymorph BAS: Eu^{2+} were baked in air at 500 °C for 30 min, the photoluminescence (PL) intensity of monoclinic-BAS: Eu^{2+} was maintained of the initial intensity. However, the PL intensity of hexagonal-BAS: Eu^{2+} decreased significantly, corresponding to about 34 %. From analyses of Rietveld refinement, the difference of thermal stability of both BAS: Eu^{2+} can be ascribed to both crystal structure of host materials and the average inter-atomic distances between Eu^{2+} ion and oxygen their crystal structure which plays a key role of shield for Eu^{2+} ions against oxidation atmosphere.

1. Introduction

Recently, plasma display panels (PDPs) have been widely used as large flat panel display (FPD) devices since they have a wide view angle and good image quality among the various FPD devices. However, there are some issues to be related to the performance of phosphors in PDPs manufacturing process. For manufacturing process of panels, all phosphors have to be heat-treated up to 500 °C for binder burn-out.

Unfortunately, the baking process is unavoidable to seal panels, and is also critical for good adhesion between phosphor and substrate. The blue phosphor, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM), has been widely studied because it is significantly less stable than the red and green phosphor components during panel manufacturing process. It has been reported that the thermal degradation of the BAM is probably related with change of either valance of Eu^{2+} to Eu^{3+} or its crystal structure (β -alumina) which has an open layer in the crystal [1-3].

As mentioned above, thermal stability of phosphors during the burn-out of binder after applying phosphor paste in manufacturing of PDPs has been the most important factor demanded by color emitting phosphors. Recently, it is reported that $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ (CMS: Eu^{2+}) which is expected to be a promising material as a new blue PDP phosphor shows no degradation under baking process and plasma discharge environment [4, 5]. Although its thermal stability reported, we do not know which structures have a thermal stability during the baking process. In particular, to determine stable crystal structure for Eu^{2+} ions is very important if we would design blue phosphor for PDP application or demanded thermal stability. However detailed information on its property is insufficient compared with degradation mechanism of BAM in the baking process. In addition, it is difficult to compare BAM with CMS: Eu^{2+} in terms of thermal stability during the baking process since each phosphor has different chemical composition. Therefore, to investigate thermal stability as a function of crystal structure for

the baking process, we have selected $\text{BaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ ($\text{BAS}:\text{Eu}^{2+}$) phosphor, which have a polymorph property such as monoclinic, hexagonal structure depending upon firing temperatures. Due to use of polymorph property of $\text{BAS}:\text{Eu}^{2+}$, we can successively exclude contributions of differences in chemical compositions for thermal stability evaluation.

In this study, we have synthesized of single phase monoclinic and hexagonal $\text{BAS}:\text{Eu}^{2+}$ phosphor and evaluated their thermal stability depending upon its crystal structures. Furthermore, this letter suggests a criterion of selection of host lattices for a PDP blue-emitting phosphor from a point of view of thermal stability during the baking process.

2. Experimental

Powder samples of polymorph $\text{BAS}:\text{Eu}^{2+}$ were prepared by conventional solid-state reaction method. To synthesize phosphors, BaCO_3 , Al_2O_3 , SiO_2 and EuF_3 were used as raw materials. Small quantities of NH_4F were added as a flux. The raw materials of $\text{BAS}:\text{Eu}^{2+}$ were mixed in a ball mill mixer for 12 hours and firing temperatures between 1300 and 1400 were employed in a reducing atmosphere of mixture between H_2 (5%) and N_2 (95%) for 3 hours, respectively. To investigate the effect of baking process, the samples were baked at 500 in air for 30 min. PL spectra were obtained at room temperature by scanning wavelength region from 300 nm to 700 nm under an excitation of 147 nm radiation from a deuterium lamp. The X-ray diffraction data were obtained over the scattering angle range $10^\circ \leq 2\theta \leq 130^\circ$ at a 2θ step of 0.02 using $\text{CuK}\alpha$ radiation with a graphite monochromator at room temperature (Rigaku Dmax2200V). The structural refinement was made with the general structure analysis system (GSAS) program [6]. A pseudo-Voigt function was chosen as a profile function among the profile functions in GSAS.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of polymorph $\text{BAS}:\text{Eu}^{2+}$ for firing at 1300 and 1400, respectively. Lin and Forster, during an investigation of BAS polymorphism, concluded that there are four polymorphs of BAS (viz. paracelsian form, orthorhombic form, hexagonal form, and monoclinic form) [7]. Among existed polymorphs of BAS, we

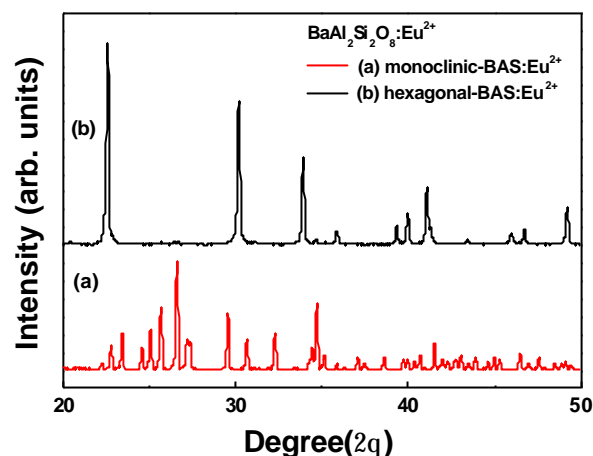


Figure 1. XRD spectra $\text{BaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$: (a) monoclinic- $\text{BAS}:\text{Eu}^{2+}$, (b) hexagonal- $\text{BAS}:\text{Eu}^{2+}$.

could make a hexagonal-, monoclinic-BAS of single phase by changing of firing temperatures as shown Fig.1.

The emission spectra of polymorph $\text{BAS}:\text{Eu}^{2+}$ under VUV excitation source are shown in Fig.2. In the PL spectra, the emission peak of $\text{BAS}:\text{Eu}^{2+}$ were centered at 373, 434 nm, respectively. Their emission bands correspond to the transition from the $4f^65d$ excited state to the $4f^7$ ground state of a Eu^{2+} ion. However, due to difference of its crystal structure such as hexagonal, monoclinic, the 5d electrons are affected by the crystal field significantly depending upon their crystal structure. The emission wavelength Eu^{2+} -activated phosphor was determined relationship between ${}^6P_{7/2}$ as well as 5d and lowest ${}^8S_{7/2}$ level [8]. For hexagonal- $\text{BAS}:\text{Eu}^{2+}$, the emission peak at

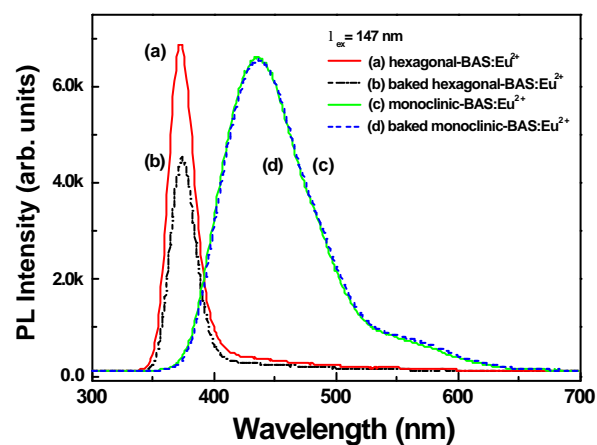


Figure 2. PL spectra of $\text{BaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ before and after baking process.

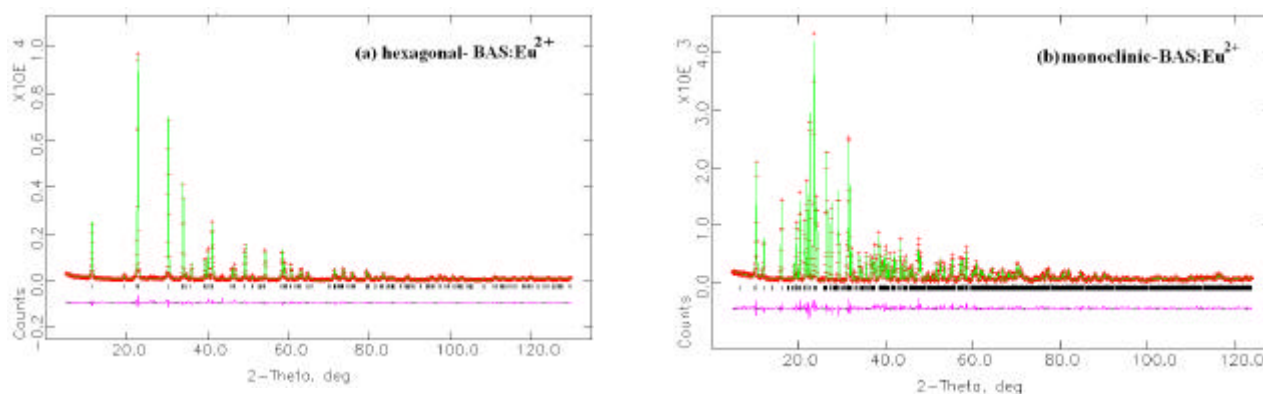


Figure 3. The Rietveld refinement patterns for polymorph BAS:Eu²⁺ x-ray powder diffraction data: (a) hexagonal-BAS:Eu²⁺, (b) monoclinic-BAS:Eu²⁺. Dot marks represent the observed intensities, and the solid line is calculated ones. A difference (obs. - cal.) plot is shown beneath. Tick marks above the difference data indicate the reflection position.

374 nm can be ascribed to the transition of ${}^6P_{7/2} - {}^8S_{7/2}$ of Eu²⁺ ions. On the other hand, for monoclinic-BAS:Eu²⁺, due to the strong crystal field around Eu²⁺ ions, the lowest 5d level would become lower than the ${}^6P_{7/2}$ level. Therefore, its emission peak was observed at 434 nm.

The Rietveld refinement against XRD data was carried out to quantitatively confirm the sensitiveness of Eu²⁺ ions to the outer oxidation atmosphere. Figure 3 shows the Rietveld refinement results of polymorph BAS:Eu²⁺, respectively. The structural parameters for polymorph BAS:Eu²⁺ were successfully determined by the Rietveld refinement using X-ray powder diffraction data. For hexagonal-BAS:Eu²⁺, the final weighted *R*-factor, *R*_{wp}, was 11.77% and the goodness-of-fit indicator, *S* ($= R_{wp}/R_e$), was 1.515. For monoclinic-BAS:Eu²⁺, *R*_{wp} was 11.36% and *S* was 1.355. The initial structural model, which has approximations for the actual structure for polymorph BAS:Eu²⁺, was constructed with crystallographic data based on hexagonal, monoclinic space group $P\bar{3}$, $I/2c$. The initial structural refinement cycles included the zero-point shift, the lattice parameters, the scale factor and background parameters as variables. Following satisfactory matching of peak positions, the atomic positions, the thermal parameters and the peak profile parameters including the peak asymmetry were refined. Si (NIST 640c) powder was used as an external standard to correct the zero-point shift for the measured diffraction data.

Monoclinic-BAS:Eu²⁺ has a space group $I/2c$, and Eu²⁺ ions share the same site as Ba²⁺ ions, surrounded tightly with each set of tetrahedral SiO₄ and AlO₄ units, the one above and below. On the other hand, Eu²⁺ ions substituting for Ba sites in hexagonal-BAS:Eu²⁺ with a space group $P\bar{3}$, occupy the sites sandwiched by the double layers. The site corresponds to the position of the open layer structure. Considering their crystal structures, Eu²⁺ ions in hexagonal-BAS:Eu²⁺ may be more susceptible to the outer oxidation atmosphere than that of monoclinic-BAS:Eu²⁺ because the substitutional sites of Eu²⁺ ions in hexagonal-BAS:Eu²⁺ are placed in an open layer.

From the Rietveld refinement results, the average interatomic length between Eu²⁺ and oxygen (*d*_{Eu-O}) in monoclinic-BAS:Eu²⁺ was 2.98805(4) Å, while *d*_{Eu-O} of hexagonal-BAS:Eu²⁺ was 3.31805(4) Å. The difference of *d*_{Eu-O} in the two crystal structures supports that Eu²⁺ ions substituting for the Ba²⁺ ions in hexagonal-BAS:Eu²⁺ may be more sensitive than those of the monoclinic-BAS:Eu²⁺ to the external environmental conditions such as temperature and oxidation atmosphere because *d*_{Eu-O} of hexagonal-BAS:Eu²⁺ is longer than that of monoclinic-BAS:Eu²⁺, and also Eu²⁺ ions of hexagonal-BAS:Eu²⁺ occupy the position.

4. Conclusion

In conclusion, the difference in the thermal stability of monoclinic- and hexagonal-BAS:Eu²⁺ can be ascribed to both crystal structures and the average interatomic

length between Eu^{2+} ion and oxygen. This study suggests that the host lattice having a non opened-structure and the substitutional site to make $d_{\text{Eu-O}}$ to be short in the host lattice should be considered as an important criterion of selection of host lattice for thermal stability during the baking process.

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6. References

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