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Enhanced photoluminescence property of Dy^{3+} co-doped $BaAl_2O_4:Eu^{2+}$ green phosphors

Hee-Suk Roh [a], In-Sun Cho [b], Jae-Sul An [c], Chin Moo Cho [a], Tae Hoon Noh [a], Dong Kyun Yim [a], Dong-Wan Kim [d,*], Kug Sun Hong [a,**]

[a] Department of Materials Science & Engineering, Seoul National University, Shillim-dong, San 56-1, Gwanak-gu, Seoul 151-744, Republic of Korea
[b] Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA
[c] LCD Division, Samsung Electronics Co., Maetan 3-dong, Yeongtong-gu, Suwon 443-742, Republic of Korea
[d] Department of Materials Science & Engineering, Ajou University, Woncheon-dong, San 5, Yeongtong-gu, Suwon 443-749, Republic of Korea

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Abstract

Eu^{2+}-doped $BaAl_2O_4$ green phosphors were prepared by a conventional solid-state reaction and the effects of Dy^{3+} co-doping on the photoluminescence property were investigated. The phosphors were characterized by X-ray powder diffraction (XRD), fluorescence spectroscopy, field-emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). XRD showed that all prepared samples exhibited a hexagonal $BaAl_2O_4$ phase. Fluorescence spectroscopy showed that the photoluminescence efficiency increased with increasing Eu^{2+} concentration until 3 mol% then decreased at higher concentrations due to concentration quenching effect. Moreover, Dy^{3+} co-doping increased the photoluminescence efficiency of the Eu^{2+}-doped $BaAl_2O_4$ phosphor.

Keywords: $BaAl_2O_4:Eu^{2+}$; Phosphor; Optimum concentration; Dy^{3+} co-doping effects; Photoluminescence

1. Introduction

The photoluminescence of Eu^{2+}-doped alkaline earth aluminates, $MAl_2O_4:Eu^{2+}$ (M = Ca, Sr, Ba) phosphor in the visible region has attracted considerable attention in recent years owing to their chemically stable and very strong photoluminescence properties [1–3]. Moreover, there have been extensive investigations on their applications to the next generation of displays and lighting devices [4–6]. In particular, $BaAl_2O_4:Eu^{2+}$ had attracted interest on account of its good photoluminescence characteristics, such as high initial luminescent intensity, long lasting time, suitable emitting color and chemical stability [1,7–11].

Generally, it is well known that co-doped rare earth ions, such as Ce^{3+} and Dy^{3+}, in Eu^{2+} doped aluminate phosphors allow the formation of electron traps [12,13]. For example, in the $SrAl_2O_4:Eu^{2+}$ green phosphor, co-doped Dy^{3+} produces electron traps and increases the phosphorescence properties via a "holes trapped–transported–detrapped process" [14]. Many studies have examined the effect of Dy^{3+} co-doping on the phosphorescence of $BaAl_2O_4:Eu^{2+}$ phosphors [7,8,15]. However, to the best of our knowledge, there are no reports on the optimum concentration of Eu^{2+} and the effect of Dy^{3+} co-doping on the photoluminescence property in $BaAl_2O_4:Eu^{2+}$ phosphors.

Herein, we prepared the Eu^{2+}-doped and Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors with different doping concentrations. The phase stability and microstructural homogeneity were presented based on the analysis of the XRD and FESEM. Furthermore, the optimum concentration of Eu^{2+} and the effect of Dy^{3+} co-doping on the photoluminescence property were suggested and discussed.

2. Experimental procedure

All Eu^{2+}-doped and Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors were prepared by a solid-state reaction. Stoichiometric

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* Corresponding author. Tel.: +82 31 219 2468; fax: +82 31 219 1612.
** Corresponding author. Tel.: +82 2 880 8024; fax: +82 2 886 4156.
E-mail addresses: dwkim@ajou.ac.kr (D.-W. Kim), kshongss@plaza.snu.ac.kr (K.S. Hong).

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amounts of the raw materials, $BaCO_3$ (Cerac, 99.9%), Al_2O_3 (High Purity Chemicals, 99.9%), Eu_2O_3 (High Purity Chemicals, 99.9%) and Dy_2O_3 (Cerac, 99.9%), were mixed by ball milling for 24 h and then dried rapidly in an oven. The as-prepared powders were calcined in air at 1300 °C for 4 h. After calcination, all samples were grinded very well by a mortar and re-heated in a forming gas (95% Ar + 5% H_2) at 1600 °C for 12 h to reduce Eu^{3+} to Eu^{2+}.

Powder X-ray diffraction (XRD, D8-Advance, Bruker Miller Co.) was used for crystal phase identification. The photoluminescence (PL) spectra were taken on a LS-55 (PerkinElmer) fluorescence spectrometer equipped with a Xenon lamp light source. The morphology and the phosphor size were observed by field-emission scanning electron microscopy (FESEM, JSM-6330F, JEOL). X-ray photoelectron spectroscopy (XPS) was performed using a Sigma Probe (Thermo VG) X-ray photoelectron spectrometer equipped with monochromatic Al-Kα X-ray radiation source (15 kV). The binding energy scale of the XPS data was calibrated at the C 1s peak position, ideally at 284.6 eV.

3. Results and discussion

3.1. *Optimum concentration of Eu^{2+} in $BaAl_2O_4$ phosphor*

A series of samples were initially prepared to examine the optimum doping concentration of Eu^{2+} on the photoluminescence efficiency of $BaAl_2O_4$ phosphors. Fig. 1 shows XRD patterns of the as-prepared $BaAl_2O_4:Eu^{2+}$ phosphors with different Eu^{2+} concentrations. The XRD patterns of all samples exhibited a phase-pure hexagonal $BaAl_2O_4$ phase (JCPDS Card #17-0306) without $BaAl_{12}O_{19}$ which was often observed as a major second phase.

Fig. 2 shows the PL spectra of the as-prepared $BaAl_2O_4:Eu^{2+}$ phosphors with different Eu^{2+} concentrations at room temperature. The excitation and emission spectra of all samples were similar to those reported in the literature [16], *i.e.*, the maximum wavelengths of the excitation and emission were approximately 355 nm and 499 nm, respectively. The single and symmetric emission peak was observed for each sample, which corresponds to only one Ba^{2+} site preferentially occupied by Eu^{2+} ions in the $BaAl_2O_4$ structure and the straightforward $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion [17]. The PL intensity increased with increasing Eu^{2+} concentration until the optimum Eu^{2+} concentration was reached with a decrease at higher concentrations due to concentration quenching [18,19]. The optimum Eu^{2+} concentration was 3 mol%.

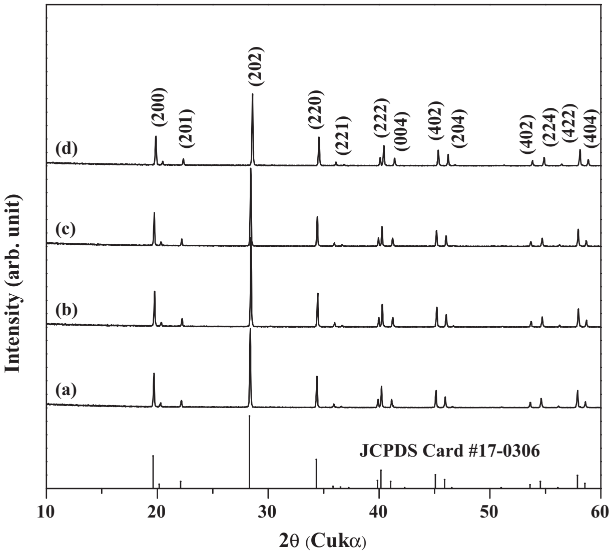

Fig. 1. XRD patterns of the $BaAl_2O_4$ phosphors with different Eu^{2+} concentrations. (a) 1 mol%, (b) 3 mol%, (c) 5 mol% and (d) 7 mol%.

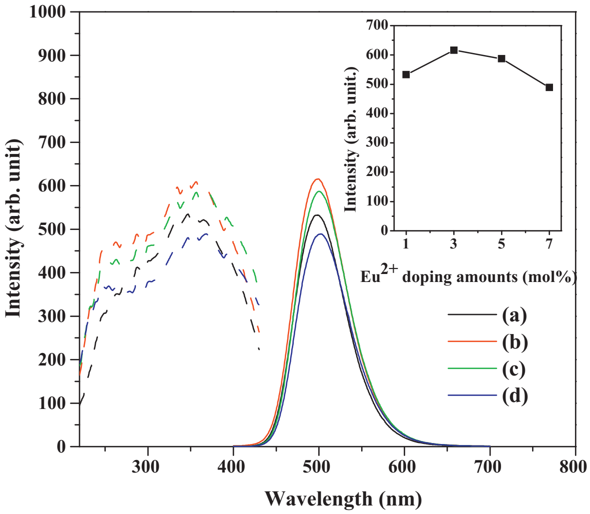

Fig. 2. Photoluminescence (PL) spectra of the $BaAl_2O_4:Eu^{2+}$ phosphors with different Eu^{2+} concentrations. (a) 1 mol%, (b) 3 mol%, (c) 5 mol% and (d) 7 mol%.

3.2. *The effect of Dy^{3+} co-doping on the photoluminescence property*

Using the above optimum Eu^{2+} ion concentration, additional Dy^{3+} ions were co-doped in the $BaAl_2O_4:Eu^{2+}$ phosphors in order to examine the effect of Dy^{3+} ion co-doping on the photoluminescence property. Fig. 3 shows XRD patterns of Eu^{2+}, Dy^{3+}-co-doped samples. As shown in the figure, all the diffraction peaks index well to the hexagonal $BaAl_2O_4$ phase. No significant differences in the peak position or broadening of the reflections were observed for all samples, which indicate structural stability irrespective of co-doping.

Fig. 4 shows the PL spectra of the as-prepared Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors. The PL emission intensities initially increased with increasing Dy^{3+} concentration, reaching a maximum value at 1 mol% of Dy^{3+} content. However, the PL intensity decreased by further increase in Dy^{3+} concentration due to the concentration quenching effect [18,19].

Generally, the emission intensity (photoluminescence efficiency) of a phosphor is affected mainly by two factors: intrinsic factors (doping concentration, crystallization degree and crystal structure, etc.) and extrinsic factors (morphology, size and surface property, etc.) [20–25]. The differences in the extrinsic factors in Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors

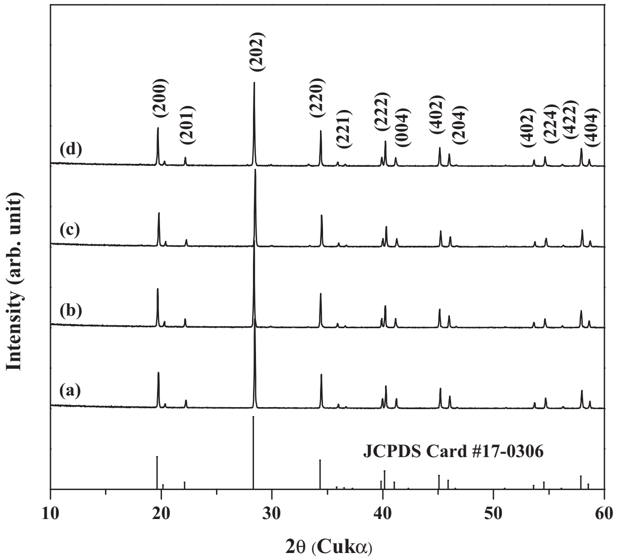

Fig. 3. XRD patterns of $BaAl_2O_4:Eu^{2+}$ phosphors with different Dy^{3+} concentrations (the concentration of Eu^{2+} was fixed at 3 mol%). (a) 0 mol%, (b) 1 mol%, (c) 2 mol% and (d) 2.5 mol%.

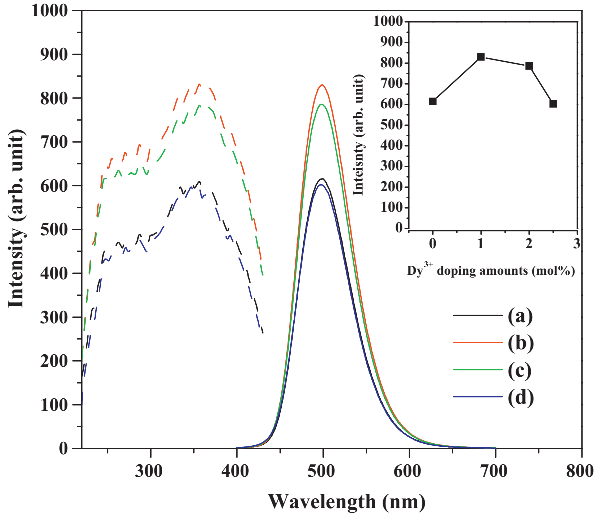

Fig. 4. PL spectra of $BaAl_2O_4:Eu^{2+}$ (3 mol%) phosphors with different Dy^{3+} concentrations. (a) 0 mol%, (b) 1 mol%, (c) 2 mol% and (d) 2.5 mol%.

were examined based on the microstructural analysis. Fig. 5 shows the FESEM images of Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphor samples. As shown in the figure, the morphology and particle size (ca. 3–5 μm) of all phosphors were similar, and the particles showed a smooth surface. Therefore, it is expected that the extrinsic factors in Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphor samples are negligible.

The intrinsic factors such as crystal structure, stress/strain in the $BaAl_2O_4$ lattice, and degree of crystallization were not critical factors between different samples for enhancing the emission intensity of the Dy^{3+} co-doped $BaAl_2O_4$ phosphors, as described in the XRD analyses (Figs. 1 and 3). To further examine the intrinsic factors, the XPS spectra were investigated to determine the chemical and binding state of the surface, which possibly affects the emission intensity of a phosphor, as shown in Fig. 6. The Eu $3d_{5/2}$ core level in the XPS spectra for the Eu^{2+} and Eu^{3+} ions were clearly different from each other [26,27]. As expected, there was only one Eu $3d_{5/2}$ peak at ~1136 eV (unfortunately, Dy $4d_{5/2}$ core level XPS spectra could not be obtained due to the small concentrations in our

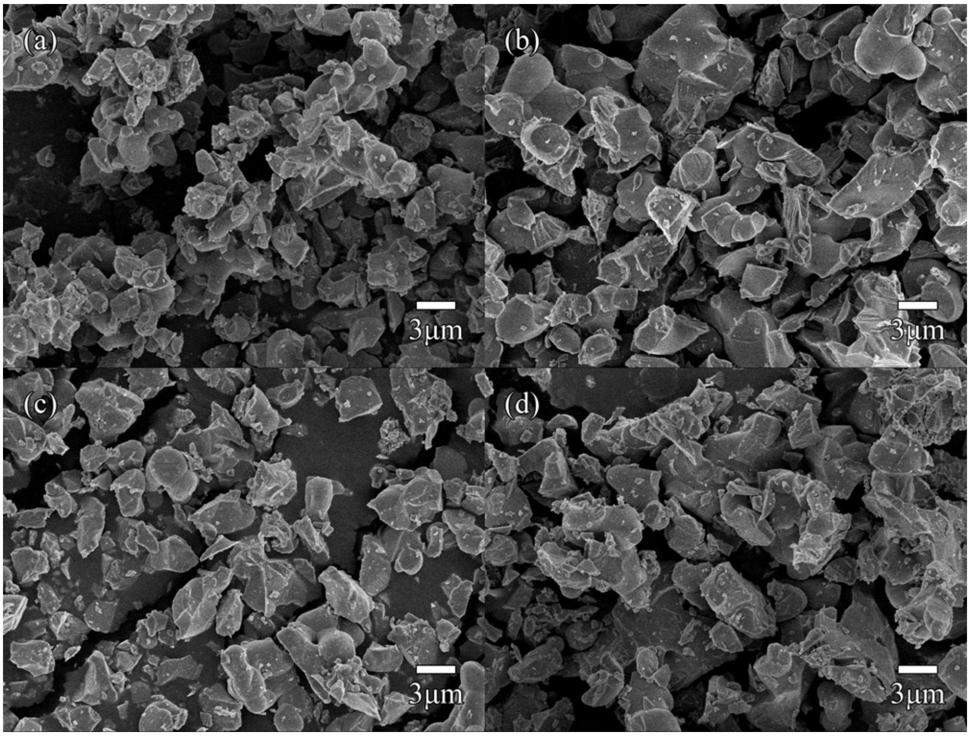

Fig. 5. FESEM images of the $BaAl_2O_4:Eu^{2+}$ (3 mol%) phosphors with different Dy^{3+} concentrations. (a) 0 mol%, (b) 1 mol%, (c) 2 mol% and (d) 2.5 mol%.

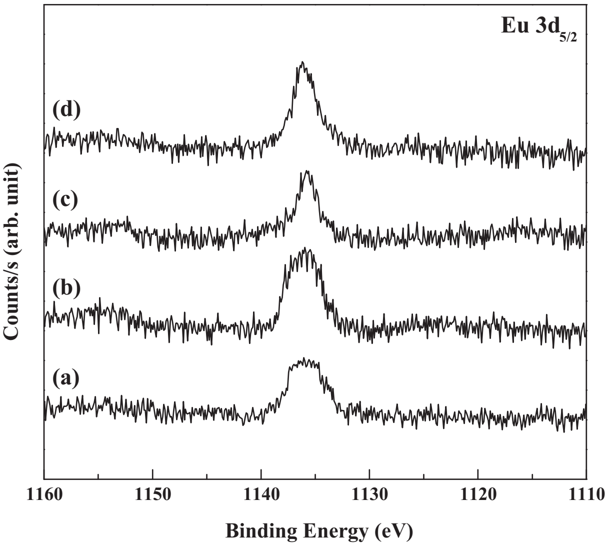

Fig. 6. Eu 3d XPS spectra of the $BaAl_2O_4:Eu^{2+}$ (3 mol%) phosphors with different Dy^{3+} concentrations. (a) 0 mol%, (b) 1 mol%, (c) 2 mol% and (d) 2.5 mol%.

XPS analysis). Although the position of this peak was higher than the reported value for Eu^{2+} ions, this peak was assigned to the Eu^{2+} ions because the characteristic emission peaks of Eu^{3+} ions were not observed in the PL spectra (Fig. 4). Moreover, the intensity of the Eu $3d_{5/2}$ peaks was similar. Thus, it was also confirmed that one of important intrinsic factors, the presence of Eu^{3+} can be excluded [17]. According to previous reports, one possible reason for enhancement of emission intensity of the Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors can be a decrease in the number of traps [28]. In the case of the Eu^{2+}-doped phosphor, the traps are the anion vacancies (oxygen vacancies in $BaAl_2O_4:Eu^{2+}$ phosphor) located near the activator [28]. The luminescence efficiency of the Eu^{2+}-doped phosphor could be increased if the number of oxygen vacancies located near the activator is decreased. Therefore, it is suggested that Dy^{3+} co-doping enables a decrease in the number of oxygen vacancies located near Eu^{2+} during the heat-treatment, which results in a decrease in the number of traps (oxygen vacancies in $BaAl_2O_4:Eu^{2+}$ phosphor), offering a positive effect on enhancing the emission intensity in the Eu^{2+} and Dy^{3+} co-doped $BaAl_2O_4$ phosphors though further detailed analyses are needed [12].

4. Conclusion

Eu^{2+}-doped $BaAl_2O_4$ green phosphors were prepared by a conventional solid-state reaction and the effect of Dy^{3+} co-doping on the photoluminescence property was investigated. The optimum Eu^{2+} concentration was 3 mol%. Moreover, Dy^{3+} co-doping induced an increase in the photoluminescence efficiency of Eu^{2+}-doped $BaAl_2O_4$ phosphor. When the doping concentrations of Eu^{2+} and Dy^{3+} are 3 mol% and 1 mol%, respectively, Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphor has the maximum emission intensity. The phase stability and micro-structural homogeneity were almost identical for Eu^{2+}-doped and Eu^{2+}, Dy^{3+}-co-doped $BaAl_2O_4$ phosphors with different doping concentrations. Further studies on intrinsic factors such as a decrease in the number of traps by co-doping will be needed in detail to obtain possible mechanism for effective enhancement of the emission intensity.

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