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Co-precipitation Synthesis and Photoluminescence of YAG:Ce Phosphors

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Ce-doped YAG ($Y_{3-x}Al_5O_{12}$:xCe, YAG:Ce) phosphor were prepared by co-precipitation method using ammonium hydrogen carbonate as a precipitant. The influence of precipitation condition such as pH on the powder properties and the optimum Ce content in YAG:Ce were investigated. Throughout the experiment, phase pure YAG:Ce powders with 50 ~ 70 nm particle sizes were obtained. The luminescence intensity and particle size increased as calcination temperature increased in the range of 900 ~ 1300°C. The maximum luminescent intensity was observed at 2 mol % of Ce concentration in the YAG:Ce phosphor. The luminescent intensity the YAG:Ce particles was significantly affected by the pH of the precipitation condition. Within the scope of this study (pH 5–8), the lower pH was favored for the higher emission intensity. The phosphors prepared had maximum excitation band at 467 nm and a maximum emission band at 525 ~ 530 nm.

Keywords: Ce doping; phosphor; photoluminescence; precipitatpitation; YAG

INTRODUCTION

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) materials doped with various rare-earth-metals have been widely used as phosphors in lighting devices and optical displays due to their stable chemical and physical properties [1,2]. For instance, trivalent cerium doped YAG ($Y_{3-x}Al_5O_{12}$:xCe, YAG:Ce) can be used as a phosphor for white light

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generation based on excitation by UV-blue emitting diodes. By far, YAG:Ce has been considered as the most efficient phosphor in white light emitting diodes (LEDs) [3–5]. The phosphor powders are typically prepared by solid state reactions [6–8]. The conventional techniques require prolonged heat treatments at high temperatures (>1500°C) and repeated mechanical grinding and milling to obtain small particles of pure garnet structures. Several types of wet-chemical methods, such as sol-gel process [9–11], hydrothermal treatment [12], glycothermal synthesis [13], spray pyrolysis [14], combustion [15], and co-precipitation have been reported for the synthesis of phosphor powders [16–18]. The wet chemistry-derived powders were reported to show better reactivity than those prepared by solid-state reaction. Recently, a carbonate co-precipitation method, which is a common process for producing oxide salts in large scale because of its simple and ease of operation, was applied in the preparation of rare-earth-doped YAG. It was reported that pure YAG structures was obtained at temperatures as low as 900°C.

In this study, a carbonate co-precipitation method was used to prepare YAG:Ce precursors and optimum precipitation conditions were investigated. The influence of precipitant type and precipitation condition such as pH on the powder properties and luminescence intensity of the phosphor were evaluated. The optimum cerium content in YAG:Ce was also investigated.

EXPERIMENTAL

YAG:Ce powders were synthesized by co-precipitation using ammonium hydrogen carbonate $(NH_4)HCO_3$ as a precipitant. The starting salts were $Y(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$. These salts were dissolved distilled water with molar ratio of 2.88Y:5.0Al. An aqueous solution of ammonium hydrogen carbonate with a concentration of 3 M was used as the precipitant. The precipitant solution of was slowly added at into the mixed salt solution at 40°C with mild stirring. After the addition of reactant, the resulting solution was aged for 2 h. It was then filtered using a suction filter. The precipitate was washed three times with distilled water and one time with ethanol. The precipitate was dried at 60°C for 24 h. The dried powder was calcined at various temperatures.

The crystal structures of the calcined samples were identified using X-ray diffraction (D/MAX-2200, Rigaku) analysis. Thermogravimetric properties of the dried powder were analyzed using a TG-DTA analyzer (SDT Q600). Particle morphology of YAG:Ce powders was observed through a field emission scanning electron microscopy (FESEM)

(Model S-4700, Hitachi). The luminescent properties were analyzed using a spectrofluorometer (FP-6200. JASCO).

RESULTS AND DISCUSSION

The XRD patterns of YAG:Ce powders calcined at different temperatures from 800 to 1300°C are shown in Figure 1. YAG:Ce powders calcined at 800°C found to be amorphous. The phase-pure YAG:Ce powders, as compared with JCPDS diffraction file 33–0040, were formed after calcinations at above 900°C. This level of calcination temperature is significantly lower than that of heat treatment required in a conventional solid-state reaction [8]. A gradual increase of the relative intensity of the diffraction peaks was observed with increasing calcination temperatures, indicating the improvement of crystallinity and particle growth.

The XRD patterns of YAG:Ce samples with different Ce contents calcined at 1200°C were shown in Figure 2. The concentration of Ce in YAG:Ce was represented as x in the $Y_{3-x}Al_5O_{12}:Ce_x$. The XRD patterns of YAG:Ce with a low concentration of Ce (up to $x = 0.06$) corresponded to that of a well crystallized pure YAG phase, indicating that the YAG:Ce samples obtained were fully crystallized monophasic YAG:Ce oxides with homogeneously distributed cerium dopant.

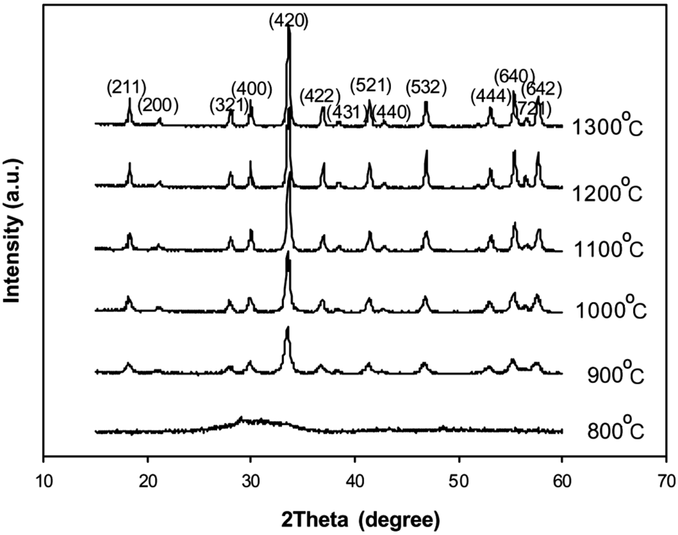

FIGURE 1 XRD patterns of YAG:Ce powders calcined at different temperatures.

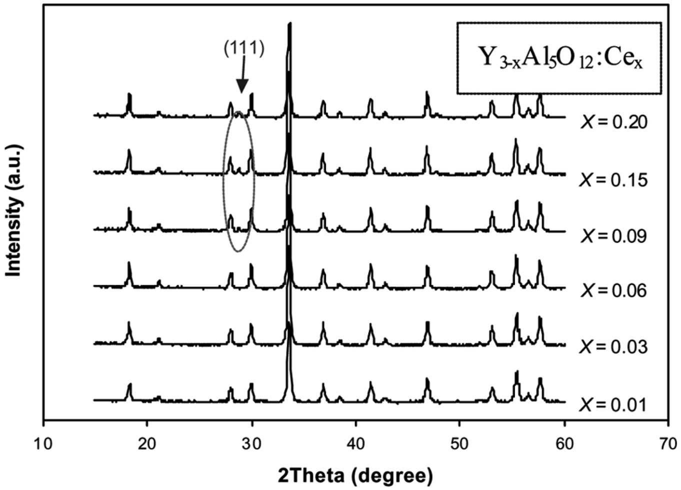

FIGURE 2 XRD patterns of YAG:Ce powders prepared at different Ce concentrations. (The concentration of Ce in YAG:Ce is denoted as x in the $Y_{3-x}Al_5O_{12}:Ce_x$).

However, the addition of a high concentration of Ce (above $x = 0.06$) resulted in a phase separation of CeO_2 and YAG:Ce. As shown in Figure 2, a low intensity peak at $2\theta = 28.6$ corresponding (111) peak of the CeO_2 appeared in the XRD patterns of the YAG:Ce powder with a high concentration of Ce. The intensity of the diffraction peak attributable to the CeO_2 increased slightly with increasing Ce content above $x = 0.06$ (2 mol%). This result indicates that a high doping concentration of Ce resulted in incomplete activation of Ce in the matrix of the YAG host material.

The thermal behavior of precursors obtained using the ammonium co-precipitation method was investigated by DSC/TG analysis. Figure 3 shows DSC/TG curves of YAG:Ce precursors. The curve indicates that the thermal decomposition occurred in two steps. Weight loss below 100°C was contributed to absorbed moisture. Weight loss between 100°C and 300°C could be attributed to the partial decomposition of the ammonium lanthanide carbonates into oxycarbonates and the weight loss between 300°C and 850°C could be attributed to the decomposition of oxycarbonates into oxide. From the TGA results, the calcinations temperatures for the precursors were determined at about 900°C.

Figure 4 shows the SEM photographs YAG:Ce powders calcined at different temperatures. It is clearly shown that coarsening of particles occurred after calcinations at 1100°C and was more remarkable at

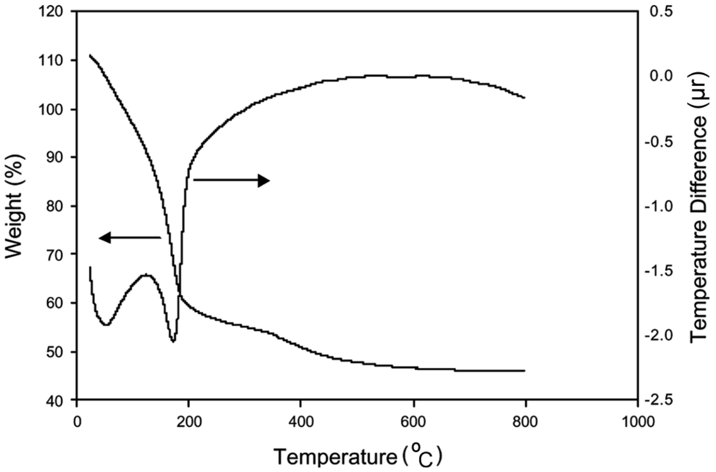

FIGURE 3 DTA/TGA analysis of YAG:Ce precursor prepared by ammonium hydrogen carbonate co-precipitation.

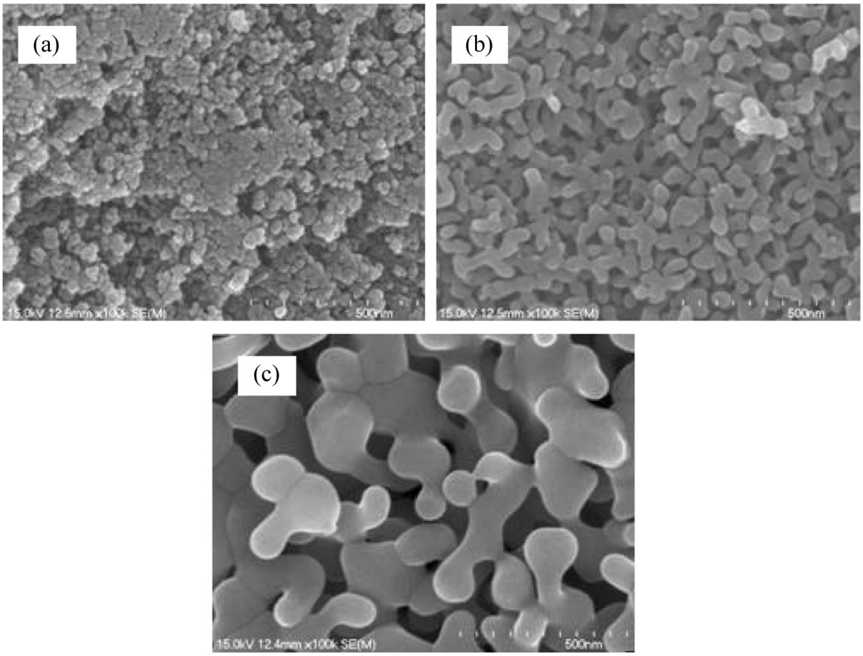

FIGURE 4 SEM photographs of YAG:Ce powders calcined at different temperatures: (a) 900℃, (b) 1100℃, and (c) 1300℃.

1300°C. The mean particle sizes of the samples calcined at 900, 1100, and 1300°C were 50, 100, and 250 nm, respectively, as measured from SEM images.

Figure 5 shows the emission spectra of the YAG:Ce phosphor prepared at different calcinations temperatures. The emission intensity of the YAG:Ce phosphor increased with increasing calcinations temperature due to the improvement of crystallinity of particles and homogeneous distribution of Ce^{3+} ions in YAG lattice, as also indicated in the XRD patterns.

Figure 6 represents the photoluminescence intensity the YAG:Ce phosphors as a function of the doping concentration of Ce. The precursor powders of YAG:Ce were calcined at 1200°C for 5 h. As shown in Figure 6, the emission intensity was not a monotonous function of Ce concentration due to incomplete activation of Ce at a high doping concentration. The maximum emission intensity appeared at Ce concentration of $x = 0.06$ (2 mol%).

In order to find an optimum precipitation condition, photoluminescence property of each precursor powders of YAG:Ce prepared under different pH condition was compared. The pH was controlled with the amount of precipitant added. Figure 7 shows the emission spectra of YAG:Ce particles prepared under precipitation conditions of pH 5, 7, and 8. All the samples were calcined at 1200°C for 5 h. Within the scope of this study, the lower pH was favored for the higher emission

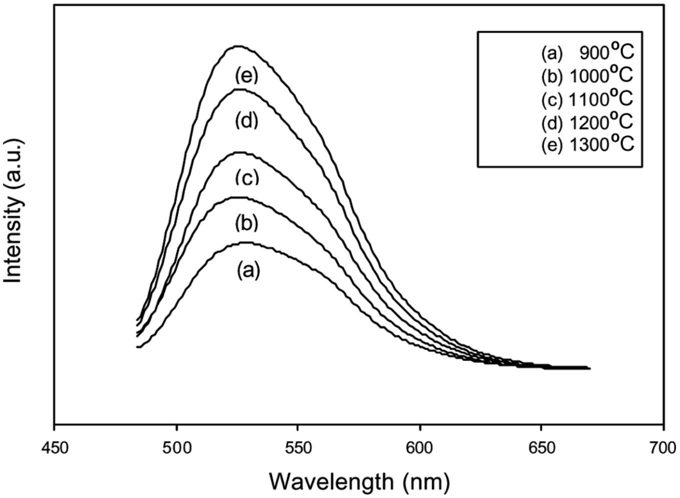

FIGURE 5 Emission spectra of YAG:Ce powders calcined at different temperatures.

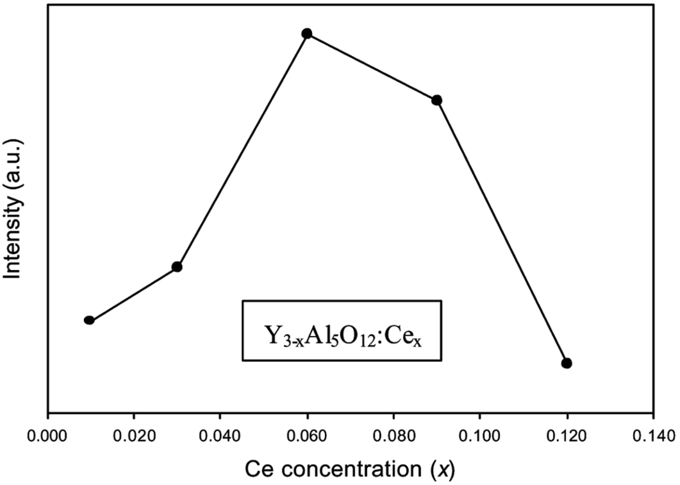

FIGURE 6 The luminescence intensity of YAG:Ce powders as a function of Ce concentrations. (The concentration of Ce in YAG:Ce is denoted as *x* in the $Y_{3-x}Al_5O_{12}:Ce_x$).

intensity. This result indicated that the excess amount of alkaline precipitant was required for the preparation of YAG:Ce particles with high emission intensity.

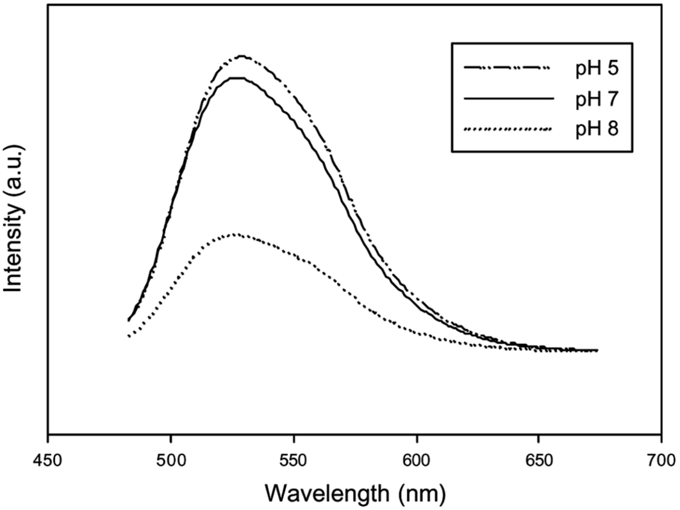

FIGURE 7 Emission spectra of YAG:Ce powders prepared under different pH conditions.

CONCLUSIONS

Phosphor YAG:Ce nanoparticles were successfully synthesized using a co-precipitation method. Phase pure YAG:Ce powders with 50 ~ 70 nm particle sizes were obtained after the calcination of precursors at above 900°C. The luminescence intensity increased with the calcination temperature in the range of 900 ~ 1300°C. The phosphors prepared showed maximum excitation band at 467 nm and a maximum emission band at 525 ~ 530 nm. The optimum Ce concentration in the YAG:Ce phosphor was found to be 2 mol % for the maximum emission intensity. The precipitation conditions such as pH affected the luminescent intensity of the YAG:Ce particles. The higher emission intensity was observed at the lower pH in the range of pH 5 to pH 8. The result of this study could be used in the optimization of Ce-doped YAG phosphor production process.

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