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# Photoluminescence Characteristic of $Ce^{3+}$-$Eu^{3+}$ Co-doped $Y_3Al_5O_{12}$ Phosphor Prepared by Combustion Method

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*For this study, Yttrium aluminum garnet (YAG) particles co-doped with $Eu^{3+}$ and $Ce^{3+}$ were prepared by combustion process using the 1:1 ratio of metal ions as reagents. The characteristics of the synthesized nano powder were investigated by means of X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and photoluminescence (PL). The various YAG peaks, with the (420) main peak, appeared at all Ce concentration in XRD patterns. The YAG phase crystallized with results that are in good agreement with the JCPDS diffraction file 33-0040. The SEM image showed that the resulting YAG:Ce,Eu powders had uniform sizes and good homogeneity. The grain size was about 50 nm. The photoluminescence spectra of the YAG:Ce,Eu nanoparticles were investigated to determine the energy level of electron transition related to luminescence processes. It was composed of a broad band of $Ce^{3+}$ activator, inclusive of the line peaks of $Eu^{3+}$. The PL intensity of $Ce^{3+}$ has the wavelengths of 480–650 nm and the PL intensity of $Eu^{3+}$ has main peak at 590 nm.*

**Keywords:** $Ce^{3+}$ ion; co-doping; combustion method; $Eu^{3+}$ ion; YAG

## INTRODUCTION

White light emitting diodes (LEDs) have been extensively used in lighting devices such as required for room illumination, and car

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headlights and in display devices such as liquid crystal display (LCD) TVs, monitors, cellular phones, digital cameras, and camcorders, because of their various advantages such as low applied voltage, power efficiency, high brightness and long lifetime. Study of white LEDs has thus been very active. Recently, a new type of LED based on gallium nitride (GaN) that emits blue light (at 450∼480 nm) efficiently has been developed. Research into phosphors emitting yellow light as a result of the absorption of blue or ultra violet (UV) light is also active because phosphors have been found to be suitable for converting blue LED radiation into a very broad yellow emission band. This yellow emission is intense enough to complement the residual blue light that escapes through the phosphor; white LED results because blue and yellow are complementary [1–3]. But, white light that used YAG:$Ce^{3+}$ has a weak point. Because of white light made up blue light and yellow light, that is unnatural about expression of red light.

The other side, YAG:$Eu^{3+}$ is red phosphor widely used in optical display and lighting applications. Furthermore YAG:$Eu^{3+}$ can be used as fluorescence properties varing with temperature [4]. It seems that the merit of $Eu^{3+}$ ions make up the weak point of YAG:Ce phosphor.

In this study, $Ce^{3+}$, $Eu^{3+}$ co-doped YAG phosphor precursors were synthesized using the combustion method. We fixed $Eu^{3+}$ metal ion at 3 mol%. And through various concentration of $Ce^{3+}$ metal ion, we evaluated the luminescence, formation process, and structure of phosphor powders.

## EXPERIMENTAL

### Synthesis

$Y(NO_3)_3 \cdot 6H_2O$ (99.9%, Aldrich), $Al(NO_3)_3 \cdot 9H_2O$ (99.997%, Aldrich), $Ce(NO_3)_3 \cdot 6H_2O$ (99.9%, Aldrich), $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%, Aldrich) and citric acid ($C_6H_8O_7 \cdot H_2O$, Aldrich) were used as starting materials in this study, citric acid was the source of citrate anion that was used both gelating agent to metal cations and fuel for the combustion. Yttrium nitrate, aluminum nitrate, cerium nitrate and europium nitrate were combined to yield a composition with the general formula $(Y_{1-x-y}Ce_xEu_y)_3Al_5O_{12}$, with $y = 0.03$. And concentration of $Ce^{3+}$ changed to 0.002, 0.01, 0.018, 0.026. The ratio of all the metal ions to the citric acid used in this study was 1:1.

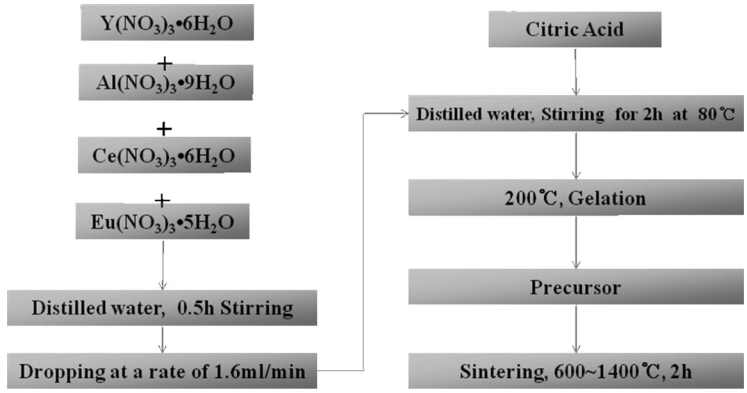


**FIGURE 1** The flowchart for the preparation of phosphors powders.

A flowchart for the preparation of phosphors powders is described in Figure 1. $Y(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 5H_2O$ were dissolved in deionized water. Afterwards, the solution was stirred using a magnetic bar in air for 20 minutes. Also, the citric acid was dissolved in deionized water. Then the citric acid solution was heated at 80°C and continuously stirred using a magnetic bar. Next, the metal solution was dropped into the citric acid solution at a rate of 1.6 ml/min, after which the solution was heated for 2 hours at 80°C. The solution was then rapidly heated to 200°C for combustion. The color of the solution changed to bright yellow. After a few minutes, the solution started combusting into brown gas. Finally, the precursor was produced. The precursor was dried in air and then sintered at 1000°C for 2 hours using an alumina crucible on a box furnace.

## MEASUREMENTS

A Q100 System thermal analyzer was used for recording TGA curves of the nano-crystalline $Y_3Al_5O_{12}$ powder. The crystalline development of the product was identified by x-ray diffraction analysis (XRD, model D/MAX-2200) with CuK$\alpha$-radiation in the range of $2\theta =$ 20$\sim$80°. The particle size and shape of the powders were observed with a Hitachi SEM (scanning electron microscope, S4700). The emission spectra were obtained with a QM 3 PH QuantaMaster Luminescence of PTI.

## RESULTS AND DISCUSSION

Figure 2 shows TGA result of the $Y_3Al_5O_{12}$ precursor. It is indicated that there are three stages of weight loss in the TG curve. The first weight loss stage from 80°C to 150°C corresponds to the evaporation of water. The second weight loss stage from 150°C to 440°C results from the burning out of organic compounds. The little weight loss stage from 440°C to 600°C is due to the crystallization of $Y_3Al_5O_{12}$.

The crystal chemical purity of the materials was checked via XRD. The XRD patterns of the YAG:Ce,Eu phosphor by various Ce concentration are shown in Figure 3. The various YAG peaks, with the (420) main peak, appeared at all Ce concentration. The YAG phase crystallized with results that are in good agreement with the JCPDS diffraction file 33-0040.

Figure 4 shows the SEM images of the YAG:Ce,Eu phosphor. The surface morphologies of the sintered powders had spherical shape at all Ce concentration. The mean size of the particles measured from the SEM image was less than the 50 nm. It was known that the use of spherical phosphor particles would increase the screen brightness and improve resolution because of the lower scattering of the evolved light and the higher packing density compared with the irregularly shaped particles obtained using conventional methods [5–7].

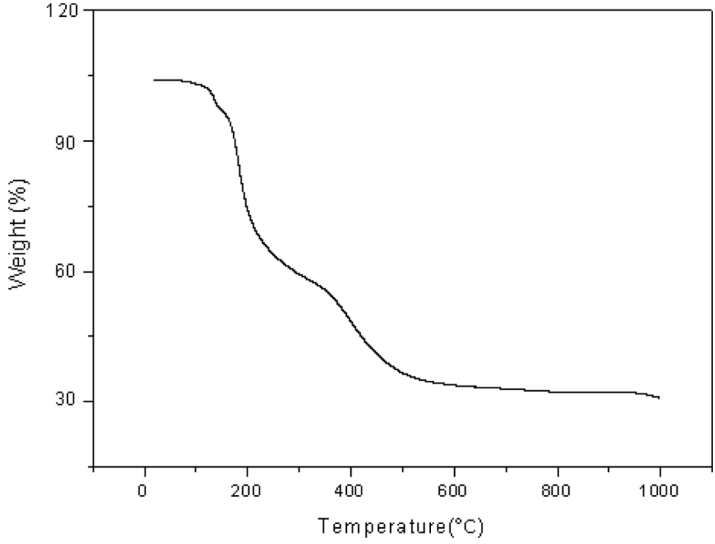


**FIGURE 2** TGA data of $Y_3Al_5O_{12}$: $Ce^{3+}$, $Eu^{3+}$ powders with temperature.

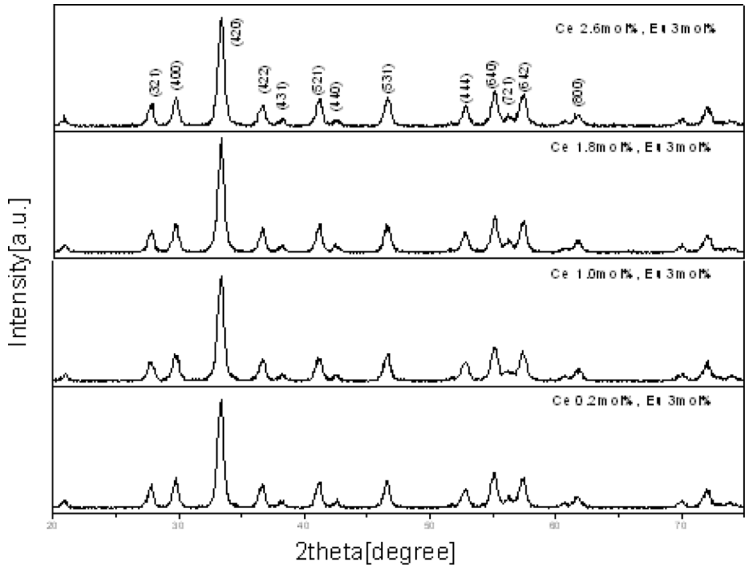


**FIGURE 3** XRD patterns of $Y_3Al_5O_{12}$: $Ce^{3+}$, $Eu^{3+}$ powders at various concentration of $Ce^{3+}$.

Figure 5 shows the emission spectra of the as-prepared YAG:Ce,Eu powder. Eu concentration was fixed at 3 mol% and Ce concentration was changed various concentration. For photoluminescence measurement, YAG:Ce,Eu phosphor was excited with 460 nm wavelength. Emission spectra of YAG:Ce,Eu powder has 528 nm of YAG:Ce phosphor and 590 nm, 620 nm of YAG:Eu phosphor. The emission of $Ce^{3+}$ is ascribed to the electron transitions from the lowest crystal splitting component of 5d level to the ground state $Ce^{3+}$, which is $^2F_{5/2}$ and $^2F_{7/2}$ [8]. At the same time, the energy transfer in the pair

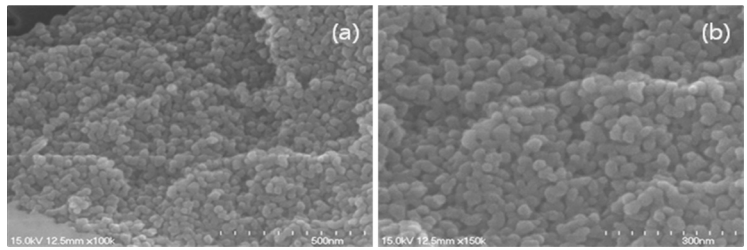


**FIGURE 4** SEM images of $Y_3Al_5O_{12}$: $Ce^{3+}$, $Eu^{3+}$ powders at 1.8 mol% of $Ce^{3+}$. (a) 100 k and (b) 150 k.

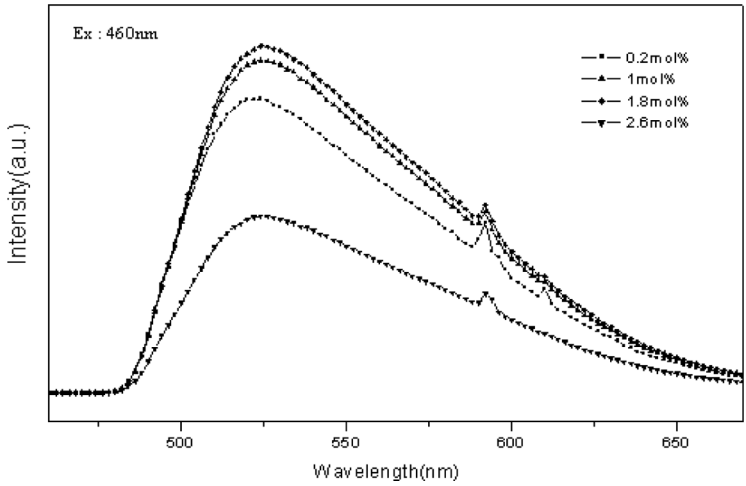


**FIGURE 5** PL spectra of $Y_3Al_5O_{12}$: $Ce^{3+}$, $Eu^{3+}$ powders at various concentration of $Ce^{3+}$.

$Ce^{3+}$-$Eu^{3+}$ takes place both by mean of the dipole-dipole interaction between these two ions [9]. 5d level energy of $Ce^{3+}$ transfer to $^5D_0$ level of $Eu^{3+}$. The emission spectra of 590 nm and 620 nm, which correspond to the transitions from the excited $^5D_0$ level to $^7F_J$ ($J = 1 \sim 4$) [10]. Figure 6 is cascade excitation of $Ce^{3+}$ and $Eu^{3+}$. But, the emission spectra was decreased with $Ce^{3+}$ ion increasing. It seems that

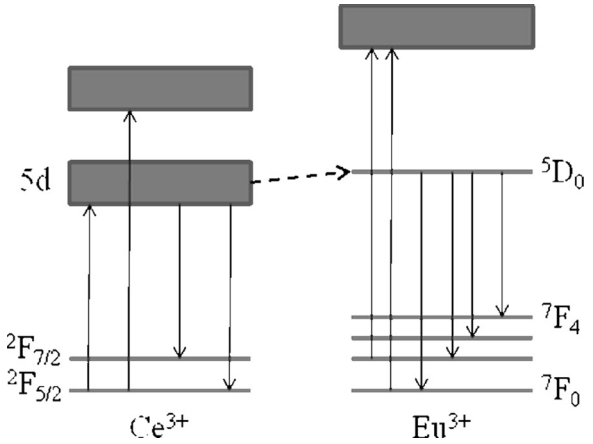


**FIGURE 6** Capitalize excitation of $Ce^{3+}$ and $Eu^{3+}$ about energy transportation.

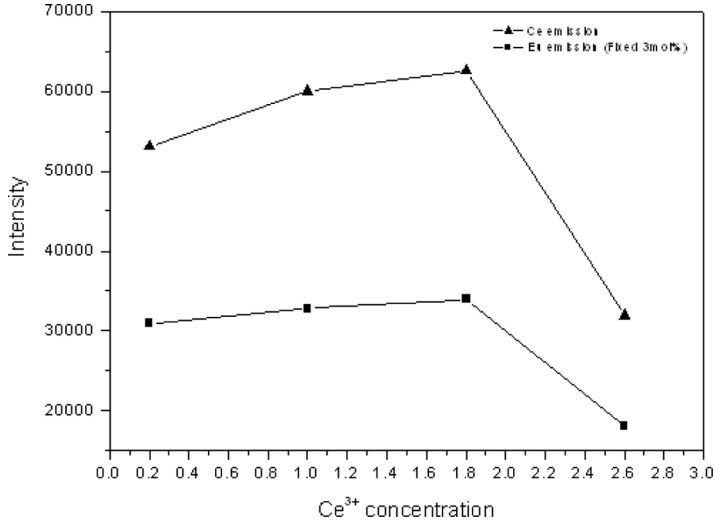


**FIGURE 7** The emission intensity ratio of 524 nm peak of $Ce^{3+}$ and 590 nm peak of $Eu^{3+}$.

excessive addition of $Ce^{3+}$ ions brought concentration quenching as luminescent killer [11].

Figure 7 shows the emission intensity ratio of 524 nm peak of $Ce^{3+}$ and 590 nm peak of $Eu^{3+}$. We can see from this figure that emission spectra of $Eu^{3+}$ strongly depends on the emission spectra of $Ce^{3+}$. Because of concentration quenching, energy transition was not progressed well at 2.6 mol% $Ce^{3+}$ ion. However, this result is in agreement with the energy transfer $Ce^{3+}$ to $Eu^{3+}$, totally.

## CONCLUSIONS

Nanoparticles of YAG:Ce,Eu phosphor were synthesized using a combustion method. The various YAG peaks, with the (420) main peak, appeared at all Ce concentration in XRD patterns. The YAG phase crystallized with results that are in good agreement with the JCPDS diffraction file 33-0040 through SEM images. The surface morphologies of the sintered powders had spherical shape at all Ce concentration. The mean size of the particles measured from the SEM image was less than the 50 nm. Emission spectra of YAG:Ce,Eu powder has 524 nm of YAG:Ce phosphor and 590 nm, 620 nm of YAG:Eu phosphor. We can see from this figure that emission spectra of $Eu^{3+}$ strongly depends on the emission spectra of $Ce^{3+}$.

In this study, we make up for weak point of YAG:Ce phosphor through the addition of $Eu^{3+}$. And we will study to progress the photoluminescence characteristic of $Eu^{3+}$ on YAG:Ce,Eu phosphor.

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