



Preparation and characterization of blue-light-excited nanophosphors using an economically low-energy process



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ABSTRACT

Spherical and red nanophosphors of $Y_2O_3:Eu^{3+}$ are prepared using urea hydrolysis that needs a long coprecipitation time (>4 h) and post-annealing at 800 °C for 2 h. Three microwave (MW) processing routes of MW-urea hydrolysis, MW-urea-EG solvolysis, and MW-urea-EG + KOH solvolysis were used to achieve short processing time and low energy consumption, thus obtaining high photoluminescence (PL) efficiency. The organic ethylene glycol (EG) solvent could prevent the nanoparticle surface from developing defects and provide a high-temperature bath for homogeneous nucleation and activator homogenization through rapid microwave volume heating. The 611 nm red emission of MW-urea-EG + KOH-derived phosphors excited by 466 nm was higher than that of the MW-urea-EG-derived phosphors after post-heat treatment at 600 °C. The pre-crystallized structure may have formed during microwave heating in EG + KOH system, but the amorphous structure formed in the EG system. The low power (100 W for 3.5 min) of the MW-urea-EG + KOH process economically reduced the post-heating temperature to 600 °C, and maintained the nano-size of phosphors with a high PL intensity. The residual hydroxyl and carbonyl groups on the obtained nanophosphors may be beneficial to be as chemical grafting in subsequent paste/slurry regulation for various LED and FPD applications.

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1. Introduction

Europium (III)-activated Y_2O_3 is a red emitting phosphor that is frequently used in several applications in optoelectronic devices, fluorescent lamps, and flat-panel displays (FPDs), because of the excellent luminescent characteristics [1–3]. Nano-sized phosphors typically produce a high resolution on a display screen because the pixel size of the screen is continually reduced. Spherical particles are necessary for producing a high packing density and for minimizing light scattering on the surfaces of phosphor particles [4–8].

The phosphor particle characteristics, including particle morphology, size, crystallinity, and photoluminescence (PL), depend on the synthesis methods used and the preparation conditions. Phosphor particle size reduction, using a conventional solid-state milling process, often causes irregular shape and surface damage, which act as a nonradiative transition center and result in a reduction of luminescence efficiency [9].

In order to enhance the brightness and resolution of displays, developing phosphors with a controlled morphology and small particle size are required. There are several chemical methods that

can be used to prepare $Y_2O_3:Eu^{3+}$ nanophosphors with red emission; for example, using urea-based coprecipitation [4,9–11], wet chemical precipitation [12], a complexing soft chemical method [13], a microemulsion method [14], and a polyol method [15].

To inspect the excitation spectra of the $Y_2O_3:Eu^{3+}$ phosphor, the band structure at approximately 255 nm can be examined because it is a charge-transfer (CT) process that is related to the excitation of an electron from the oxygen 2p state to the $Eu^{3+}4f$ state. Direct excitation of Eu^{3+} can be observed from 285 to 500 nm. There are two main peaks at 394 and 466 nm corresponding to the transitions of ${}^7F_0-{}^5L_6$ and ${}^7F_0-{}^5D_2$ on a PL spectrum, respectively [1,16]. On the emission spectra, the corresponding emission peaks of $Y_2O_3:Eu^{3+}$ phosphor at 592, 611, 651, and 692 nm are attributed to the ${}^5D_0-{}^7F_1$, ${}^5D_0-{}^7F_2$, ${}^5D_0-{}^7F_3$, and ${}^5D_0-{}^7F_4$ transition of the Eu^{3+} ion, respectively [17]. In accordance with the theory of Judd and Ofelt [18,19], the strongest peak at 611 nm is attributed to the ${}^5D_0-{}^7F_2$ transition, which becomes an electric dipole type because of an admixture of opposite parity $4f^{n-1}5d$ states with an odd parity crystal-field component.

Microwave heating is used for processing materials because it is fast and saves energy and time, especially if the materials require low-temperature homogenization and crystallization. In several previous reports, europium (III)-doped yttrium oxide nanoparticles

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were prepared using microemulsion-microwave heating. The nanoparticles emitted a copious amount of strong red light at 611 nm under UV excitation [16]. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors were also synthesized using a rapid microwave-assisted solvothermal method. After performing calcinations at 600 °C, well-crystallized, spherical, and nano-sized grains were obtained [20]. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ hexagonal microprisms of uniform morphology and size were also successfully prepared using a quick microwave-assisted method followed by a subsequent heat treatment [21]. Serantoni et al. [22] synthesized sub-micrometer powder (100–150 nm in diameter) of Yb-doped yttrium oxide by using the microwave-assisted polyol (diethylene glycol, DEG) method. They then added the hydrolyzing agent to induce rapid nucleation followed by a controlled growth of nuclei.

Researchers who have studied the red emission of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors by using various specified chemical synthesis techniques and microwave-assisted methods focused on UV light excitation. However, thoroughly decompose the urea in organic solvents by using a simple microwave oven at an ambient atmosphere to prepare the luminescence enhancement of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors is an economical and uncomplicated process, which was used in the present study. The photoluminescence of phosphors excited by blue light or near UV light is used in the LED industry. If the phosphors excited by blue light can be used in FPDs such as PDP and LCD, the excited energy in PDP technology would be saved, and the energy in LCD technology would be reused to excite phosphors by using backlight. These developments are expected to occur based on the findings of this study. The nanophosphors were prepared using a urea-based precipitation method and combined with microwave energy to enhance the PL intensity in this work at a low processing temperature for a short processing time. The PL was excited by 466 nm (${}^7\text{F}_0\text{--}{}^5\text{D}_2$ transition) and correlated to nanophosphor particle size, morphology, and crystallinity, all of which were analyzed.

2. Experimental procedures

The reagents of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa, 99.9%) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa, 99.9%) were used as raw materials to prepare $\text{Y}_2\text{O}_3:7 \text{ mol}\% \text{Eu}^{3+}$. The molar ratio of urea ($(\text{NH}_2)_2\text{CO}$, Showa, 99%) to $\text{Y}_2\text{O}_3:7 \text{ mol}\% \text{Eu}^{3+}$ in a prepared aqueous solution was 6.5. This aqueous solution was heated at 80 °C for 2–6 h on a hot plate. The reagents mixed aqueous urea solution was also put into a commercial microwave oven (2.45 GHz) set at 1000 W for 20, 25, and 30 s and 100 W for 3.5 min. The precipitated powders obtained from the urea-hydrolyzed solution and microwave-treated urea solution were centrifuged and washed at least three times with alcohol. The powders were subsequently dried in an oven at 80 °C. The dried powders were then heat-treated at 600 °C and 800 °C for 2 h in an electrical furnace.

Ten milliliters of the urea and $\text{Y}_2\text{O}_3:7 \text{ mol}\% \text{Eu}^{3+}$ aqueous solution were added to ethylene glycol (EG) to form an organic EG solution. This organic-based solution was put in a commercial microwave oven set at 100–500 W for 1–3.5 min. The high boiling point of EG allowed the solution to sustain high temperatures for a prolonged period of time during microwave heating. To increase the rate of precipitation of the organic EG solution in the microwave, 1 M KOH of EG solution was added to the organic-based solution to form EG + KOH solution. This EG + KOH solution was then treated in the same microwave oven at 100 W for 3.5 min. In addition, this EG + KOH solution was treated at 300 W for 1 min and at 500 W for 1 min, respectively. These microwave-treated EG and EG + KOH solutions were centrifuged and washed at least three times with alcohol to obtain the precipitated powders. The powders were subsequently dried in an oven at 80 °C. The dried powders were then heat-treated at 600 °C and 800 °C for 2 h in an electrical furnace.

To compare the particle size reduction to PL degradation of phosphors, $\text{Y}_2\text{O}_3:7 \text{ mol}\% \text{Eu}^{3+}$ powders were prepared by mixed oxides (Y_2O_3 and Eu_2O_3) using the ball milling method. The prepared powders were sintered at 1600 °C for 4 h. The sintered powders were then pulverized by ball milling. The pulverized powders were subsequently sieved using a 60 (approximately 250 μm), 80 (approximately 177 μm), and 325 (approximately 44 μm) meshed screen to distinguish the particle sizes of the milled particles.

The microstructures and morphologies and particle sizes of the precipitates and the various furnace-heated and microwave-treated phosphors were determined using a field emission scanning electron microscope (JEOL JSM-6500F) and a transmission electron microscope (Hitachi HT7700). The crystal structures of the powders were characterized using X-ray diffraction (XRD, Philips PW1700, Cu K α

radiation wavelength $\lambda = 1.5405 \text{ \AA}$, scan speed of 2.5 deg/min). The photoluminescence (PL) spectra of the phosphors were measured using a fluorescence spectra analyzer (Horiba, Fluoromax-4). The molecular bonding energies were determined using Fourier-transform infrared spectroscopy (Bruker, FTIR Tensor 27).

3. Results and discussion

3.1. Solid state and urea coprecipitation preparation

The particle size of the 1600 °C-sintered phosphors was reduced using the ball milling process. Various particle sizes were separated by sieving the pulverized powders with 60, 80, and 325 meshed screens, which indicated an equivalent particle size of 250, 177, and 44 μm , respectively, in accordance with the ASTM E11:01. The decrease in particle size is shown in Fig. 1. According to the XRD peak (222) intensity of the pulverized Y_2O_3 phosphors, the crystallinity decreased rapidly as the particle size was reduced. Fig. 1 also shows the rapid decrease in PL intensity as the Y_2O_3 phosphor particle size was reduced. These results demonstrate that the changes in phosphor particle size, determined using a top-down method involving conventional solid-state milling, often led to irregular shape and surface damage on phosphors. Consequently, the luminescent intensity decreased because of the nonradiative transition center increase on the defectively small nanophosphors surface.

The isotropic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor precursor particles were precipitated at 80 °C for 2–6 h by using a urea coprecipitation process, as shown in Fig. 2(a). The particle size was slightly larger than 100 nm and the particles possessed an amorphous structure by XRD analysis. The particle size decreased after the particles were heat-treated at 800 °C for 2 h compared with the 80 °C as-precipitated particles, as shown in Fig. 2(b). The 800 °C heat-treated phosphors were characterized with a well-crystallized Y_2O_3 phase and an agglomerate particulate morphology. The decrease in particle size after the 800 °C heat treatment may be attributed to the decomposition of the urea precipitates caused by residual basic carbonates. Grain growth occurred when the heat-treating temperature reached 1200 °C in 2 h. The large particle size of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor is shown in Fig. 2(c). In addition, the grain growth of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors demonstrated crystal development and possible defect elimination. However, the findings of this study reveal that the large particle size accompanied by particle agglomeration and particles necking after the 1200 °C heat treatment is not beneficial for nano-sized applications in FPDs.

During the solvation and the hydrolysis reaction of the urea to precipitating $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ precursor particles, water hydrolyzed the urea to decompose and release precipitating ligands (mainly OH^- and CO_3^{2-}) slowly and homogeneously [4,11,23,24]. It required reaction time to achieve uniform phosphor precursor particle

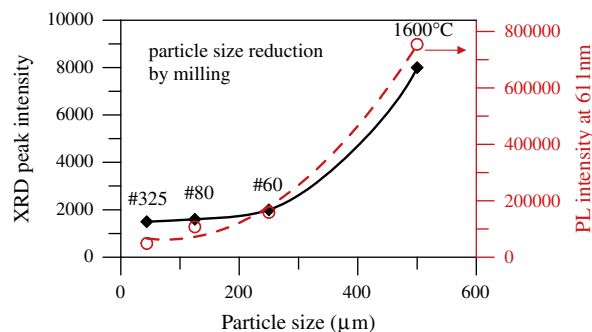


Fig. 1. XRD peak (222) intensity and PL intensity of 611 nm red emission under 466 nm excitation as a function of particle size of pulverized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors sintered at 1600 °C.

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