Sol-gel synthesis and photoluminescent characteristics of Eu doped Gd_2O_3 nanophosphors

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ABSTRACT

Eu^{3+}-ion doped Gd_2O_3 phosphor nanopowders were prepared by sol-gel method using $GdCl_3$ and $EuCl_3$ at 800-1100 °C. The dependence of structural and luminescent properties on the composition ratio of Eu/Gd and calcined temperature were investigated. The size of phosphors was about 50-200nm depending on the synthesis temperature for 2hrs. The phosphor was examined by XRD, FE-SEM, TEM, and the results showed that the materials possess a well-crystal and confirmed as $Gd_2O_3:Eu^{3+}$ particles. The photoluminescence (PL) measurement of the $Gd_2O_3:Eu^{3+}$ showed a red-emission at the main wavelength of 612 nm ($^5D_0 \rightarrow {}^7F_2$). It was found that 7% of Eu^{3+} is the best molar concentration to obtain the highest PL intensity for $Gd_2O_3:Eu^{3+}$.

Keywords: nanophosphor powders, sol-gel process, photoluminescence

1 INTRODUCTION

The development of high efficiency and high resolution displays has an urgent need for phosphors with enhanced optical properties. Rare-earth doped oxide particles have been extensively studied for application, such as field emission displays (FEDs) [1], plasma display panels (PDPs) [2], and cathode-ray tubes (CRT) [3]. Gd_2O_3 is a valuable host material and its crystallographic structure is of the same type as Y_2O_3, a known host lattice for efficient phosphors. Eu-doped Gd_2O_3 particles are well known as excellent red phosphors for applications in displays and lamps.

Phosphor materials have been prepared mainly by solid state reactions [4-5], co- precipitation methods [6-7], sol-gel methods [8-11] and spray pyrolysis process [12-15]. High reaction temperature, long heating time, and a milling process are required to obtain a pure phase of the phosphor by solid state reactions. Although phosphor can be obtained at low temperature via spray pyrolysis process, further annealing at high temperature is required to improve the luminescent properties of the particles. Therefore, development a novel synthesis method to prepare uniform size and high efficiency phosphor particles is important. The sol-gel method, owing to its advantages of easier composition control, better homogeneity and low reaction temperature is a route to manufacture fine powders. Due to these advantages, such as easy shaping, low reaction temperature, high purity and sample homogeneity.

In this process, a simple sol-gel process was adopted to fabricate nano-size $Gd_2O_3:Eu^{3+}$ phosphors. The photoluminescence and characterization property of $Gd_2O_3:Eu^{3+}$ material was investigated in this study.

2 EXPERIMENTAL

The $Gd_2O_3:Eu^{3+}$ nano-scale phosphors were prepared by sol-gel method. $GdCl_3$ (99.9% purity) and $EuCl_3$ (99.9% purity) were used as starting materials. First, 1g amount of $GdCl_3$ and different concentrations of $EuCl_3$ were dissolved in 20 ml D.I. water and then adding 20 ml ethanol solution at room temperature. Finally, 2 ml NH_3OH (28wt% purity) was added to this solution while stirring. The Eu^{3+}-doped specimens with different dopant concentrations of 0.03, 0.07 and 0.1 were added into the sol-gel solution. The precursor solution was stirred at room temperature for 4hrs. Then the solution was filtrated by D.I. water and dried at 120°C. The precursor was calcined at different temperature form 800, 1000 and 1100 °C individually, in air for 2 - 4hrs. Finally, we can obtain the nano-scale $Gd_2O_3:Eu^{3+}$ phosphors. X-ray diffraction (XRD) patterns for all samples were obtained using a diffractometer (Shimadzu, XRD-6000) with CuKα radiation in the range of 10°~80°. The grain sizes were estimated using the Scherrer's formula. The surface morphology was observed with a field emission scanning electron microscope (FE-SEM Hitachi, S-4800). For the photoluminescent analysis, the excitation and emission spectra of particles were measured using a fluorescence spectrophotometer (Hitachi, F-4500) using a Xe lamp (150W) as the excitation source. The wavelength range in the fluorescence spectrophotometer was from 200-1100 nm. All of these measurements were performed at room temperature.

3 RESULTS AND DISCUTIONS

Fig. 1 presents the XRD patterns of $Gd_2O_3:Eu^{3+}$ phosphor particles by different thermal treatment from 800, 1000 and 1100 °C, individually. For structure characterization of the $Gd_2O_3:Eu^{3+}$ nano-particles, XRD

patterns are taken as shown. For the particle sintered at 800 °C, weak peak and impurity phase is observed. As the temperature increased to 1000 °C, a complete cubic structure of Gd_2O_3 exists. The typical and intense diffraction peaks of cubic $Gd_2O_3:Eu^{3+}$ phosphor particles appear for particles calcinations at higher temperature. The crystallite sizes D of $Gd_2O_3:Eu^{3+}$ phosphor particles was estimated by Scherrer's formula ($D = 0.9\,\lambda / \beta \cos\theta$). Where λ is the wavelength of CuKα radiation (0.15418 nm), β is the full width in radians at half-maximum (FWHM) of the peak at $2\theta = 28.56$ and θ is the Bragg angle of the X-ray diffraction peak. The crystallite size of $Gd_2O_3:Eu^{3+}$ phosphor particles increases with the calcination temperature, which is 12, 34 and 34 nm at 800, 1000 and 1100 °C, respectively. The calculated grain sizes of $Gd_2O_3:Eu^{3+}$ phosphor particles sintered at different temperatures are shown in table1.

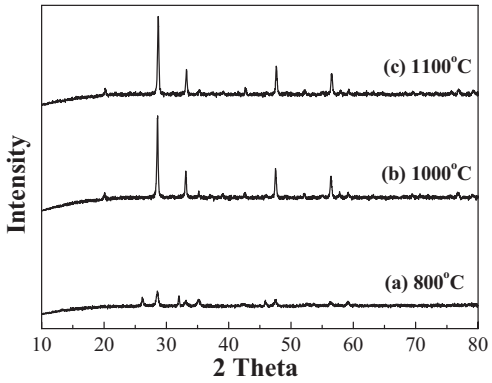

Figure 1: XRD spectra of $Gd_2O_3:Eu^{3+}$ powders calcined at different reaction temperature (a) 800, (b) 1000 and (c) 1100 °C for 2hrs.

Calcination conditions (temperature)	Mean particle size dp (nm)	Crystallite size D (nm)
800℃	50-120	12
1000℃	80-180	34
1100℃	90-190	34

Table 1: Crystalline and particle size of $Gd_2O_3:Eu^{3+}$ phosphors calcined at various temperature.

The morphology of $Gd_2O_3:Eu^{3+}$ phosphor particles were used to study by transmission electron microscopy. In Fig. 2, the morphological characteristics and particle size of $Gd_2O_3:Eu^{3+}$ phosphor particles were investigated at different calcination temperature. The particle size and aggregation degree of particles increased with calcination temperature. At below 1000 °C, the nano-sized particles were separated well, and the particle size distribution was between 50-200 nm. When the calcination temperature increased to 1000 °C, the particles present the highly aggregated. Fig. 3 exhibits the TEM images of $Gd_2O_3:Eu^{3+}$ phosphor particles prepared at 1000 °C from 2 to 4hr. The average particle size not obvious increases as the calcination time increase.

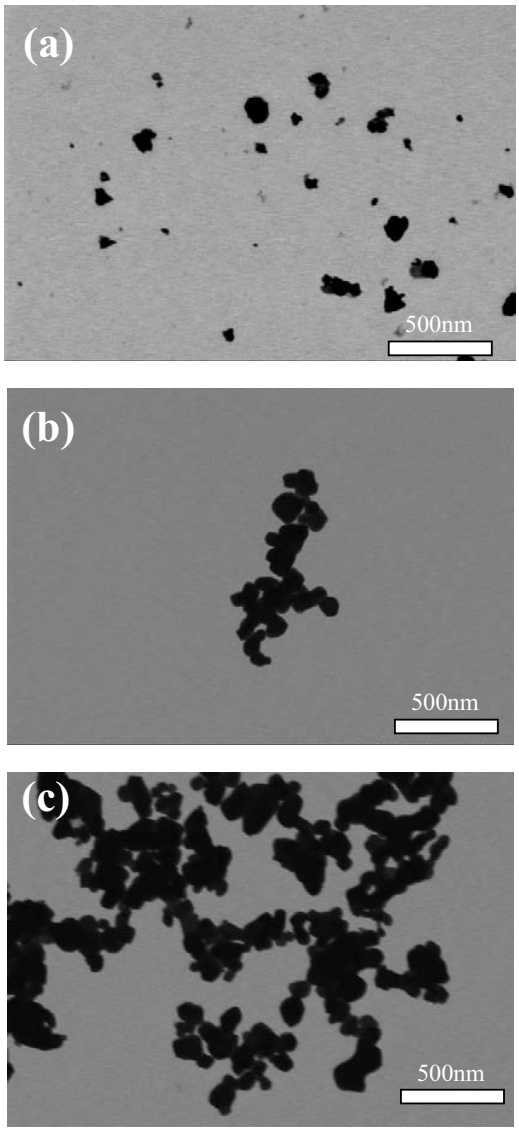

Figure 2: TEM images of $Gd_2O_3:Eu^{3+}$ particles sintered at different temperatures: (a) 800°C, (b) 1000°C and (c) 1100°C.

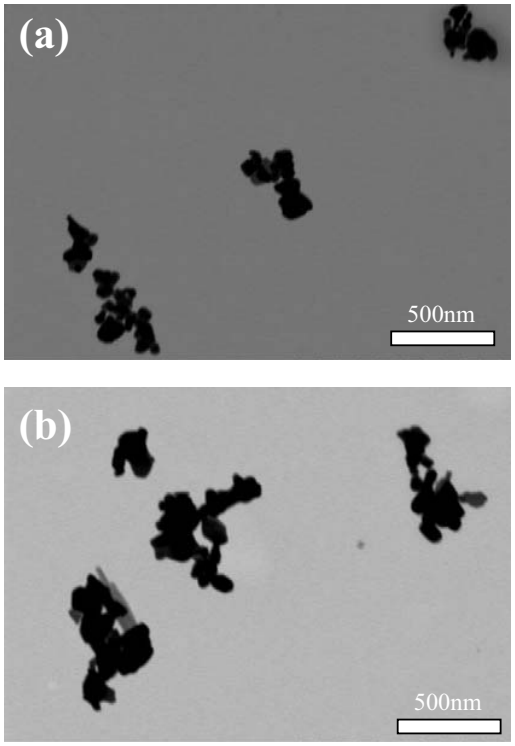

Figure 3: TEM images of $Gd_2O_3:Eu^{3+}$ particles sintered at 1000°C for (a) 2hrs and (b) 4hrs.

Figs. 4 show the excitation spectra of $Gd_2O_3:Eu^{3+}$ phosphor sintered at different temperature. The excitation spectrum shows a wide band with the peak at about 254 nm which is attributed to transition toward the charger transfer due to Eu-O interaction [16]. Furthermore, it is the excitation from the ground state of the 4*f* levels to a Eu-O charge transfer state. The peaks near 365 nm, 380 nm and 390 nm can be assigned to the higher energy level (*f-f*) transitions of Eu^{3+} [16]. In Fig. 5, the effect of calcination temperature on PL emission of $Gd_2O_3:Eu^{3+}$ phosphor particles were investigated. The synthesized were excited by UV light of 254 nm wavelength while main emission peak was 612 nm, corresponds to the red emission. This peak is due to the electron dipole transition of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$), induced by the lack of inversion symmetry at the Eu^{3+} site. The emission near 590 nm is due to the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$, which is insensitive to the site symmetry.

The higher PL intensities of $Gd_2O_3:Eu^{3+}$ phosphor particles were obtained with reaction temperature up to 1000°C. It can found other energy transition peaks for Eu^{3+} corresponding to $^5D_0 \rightarrow {}^7F_2$ (near 630 nm) and $^5D_0 \rightarrow {}^7F_3$ (near 650 nm). In Fig. 6 the influence of Eu^{3+} content on the PL intensities of $Gd_2O_3:Eu^{3+}$ phosphor was investigated. The Eu^{3+} dopant molar concentration was varied form 3 to 10%. The optimum doping molar concentration of Eu^{3+} showing the maximum intensity was 7%. When the Eu^{3+} concentration higher than 7% the emission intensity was decreased by PL measured. This is caused by concentration quenching phenomena. This leads to effective energy transfer among the Eu^{3+} dopants, which may cause the migration of the excited states to the quenching site.

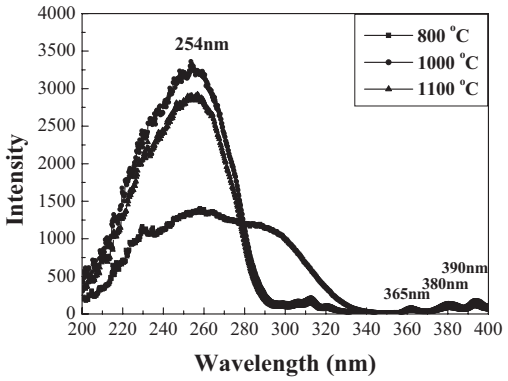

Figure 4: Excitation spectra of the $Gd_2O_3:Eu^{3+}$ phosphor with different reaction temperature.

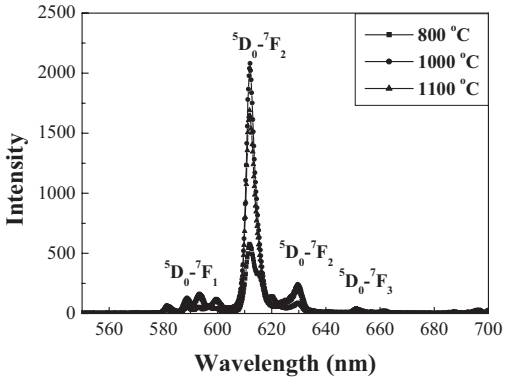

Figure 5: Emission spectra of Gd2O3:Eu particles with different reaction temperature.

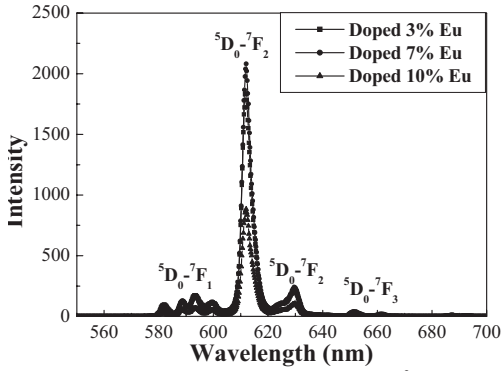

Figure 6: Emission spectra of $Gd_2O_3:Eu^{3+}$ particles at different doping concentration.

4 CONCLUTION

In summary, we have optimized the procedure parameters and Eu^{3+} molar concentration to obtain Gd_2O_3:Eu^{3+} phosphor particles with efficient emission intensity by sol-gel method. The XRD results show that the pure crystalline phase Gd_2O_3 could be formed at 1000 ^oC. The optimum Eu^{3+} dopant molar concentration is 7%. Furthermore, the influences of calcination temperature and calcination time on the photoluminescent properties of Gd_2O_3:Eu^{3+} phosphor particles have been investigated. The results confirm that the Gd_2O_3: 7%Eu^{3+} phosphor particles calcination at 1000 ^oC product the highest photoluminescent emission intensity.

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