

Preparation of PDP Red Phosphors by Impregnation Method and their Luminescence Properties

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(Received December 14 2006, Accepted February 18 2008)

The (Y,Gd)₂O₃:Eu phosphors were synthesized using the impregnation method in order to improve the performance of red-emitting phosphors for plasma display panels. (Y,Gd)₂O₃:Eu phosphors, with a particle size ranging from 150 and 200 nm, exhibited a strong red emission at around 615 nm. The emission intensity and particle size of the powders were controlled by adjusting the sintering temperature and raw material composition. The resulting particle size was very uniform and photoluminescence (PL) characteristic was excellent, being about twice that of commercial red phosphor.

Keywords : Red phosphor, (Y,Gd)₂O₃:Eu, Nanoparticles, Plasma display panels

1. INTRODUCTION

The phosphors which are used for plasma display panels requires an emission efficiency which is appropriate for the driving conditions of the display panel and which has a fast response time, short decay time, and superior color purity which is stable with heating. Currently, Y₂O₃:Eu and (Y,Gd)BO₃:Eu, which have been subjected to a doping process to obtain red phosphor, are in widespread use. As the latter has an inferior color purity and a long decay time, industries operating in this field are trying to develop phosphors which are more stable than boric acid salt phosphors and which have superior photoluminescence (PL) characteristics[1-5].

In order to prepare (Y,Gd)₂O₃:Eu phosphor, we used a precursor process with polymer precursors. In this way, it is possible to obtain phosphors with both a very high purity and an equalized structure, because the reaction is performed in the liquid phase. In addition, compared to the previous solid phase method, it is possible to control the crystallinity, morphology, particle size, and particle distribution of the product. We investigated the effects of Eu concentration, Y/Gd ratio, sintering temperature on the emission characteristic and crystal structure of the phosphors.

2. EXPERIMENTALS

2.1 Synthesis

YCl₃ · 3H₂O, GdCl₃ · 3H₂O, and Eu₂O₃ of high purity were used as starting materials for synthesis, which was performed using the precursor process with polymer precursors. Figure 1 presents the general precursor process used for the synthesis of (Y,Gd)₂O₃:Eu using polymer precursors. In this precursor process, firstly, YCl₃ · 3H₂O, GdCl₃ · 3H₂O, and Eu₂O₃ were dissolved in distilled water. To dissolve the mixed liquid perfectly, a small amount of nitric acid was added, after which the mixed solution was stirred at room temperature. The polymer precursor was added to the sol solution which was then dried at 70 °C for 24 hours and sintered at more than 1000 °C for 4 hours to afford a red phosphor. Herein, we report the characteristics of the (Y,Gd)₂O₃:Eu phosphors prepared by precursor process with polymer precursors.

2.2 Measurements

X-ray diffraction (XRD, Rigaku, D/MAX-2200V) was used to analyze the crystalline structure of the heat treated phosphor, and the results were checked by a joint committee on power diffraction standards (JCPDS) powder diffraction file. Cu-K α radiation was used and

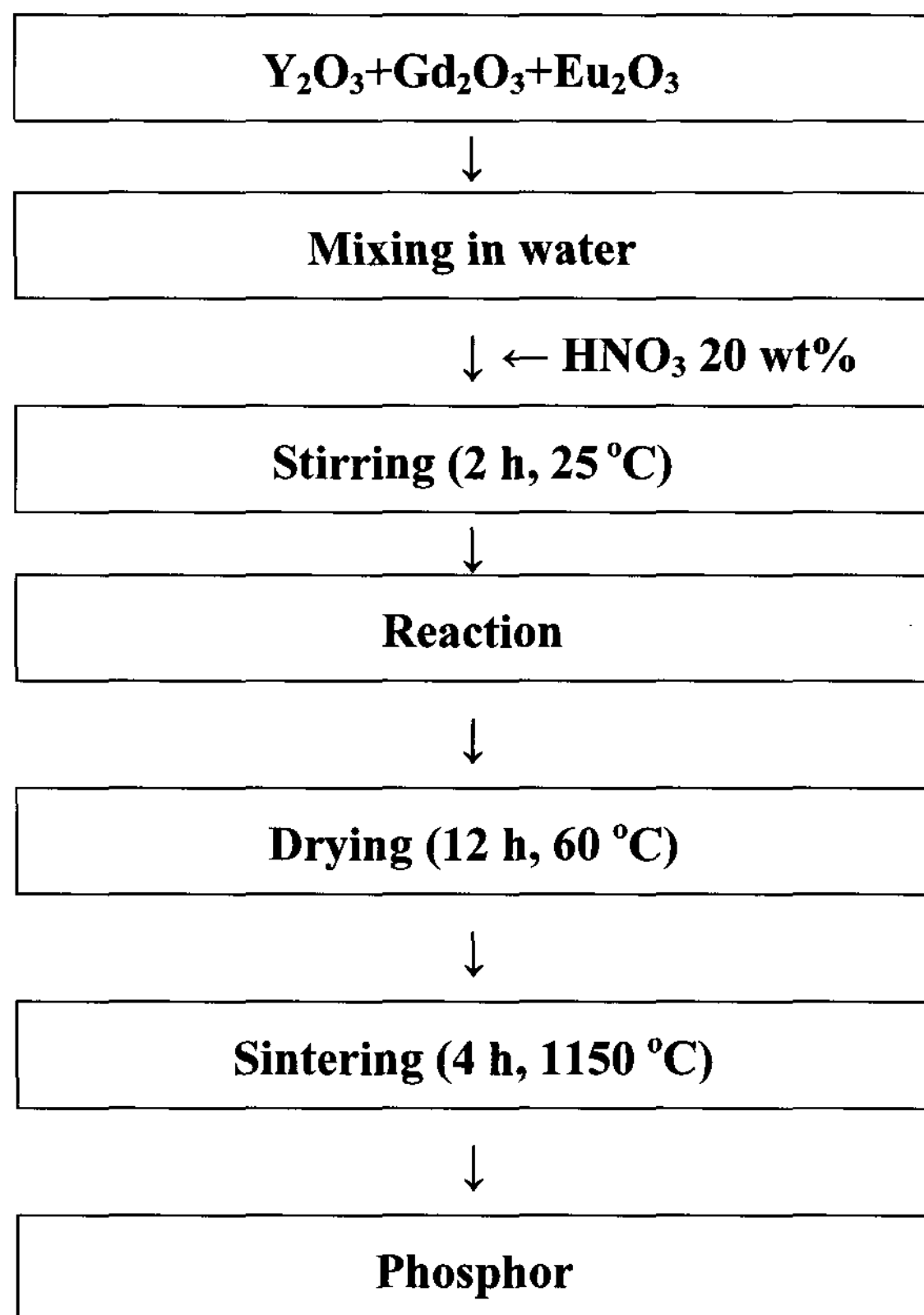


Fig. 1. Preparation procedure of $(Y,Gd)_2O_3:Eu$ phosphor by using polymer precursors.

the diffraction angle (2θ) was varied in the range of 5-80 degrees. The X-ray powder diffraction pattern was obtained at a scan speed of 5/min. Energy dispersive spectroscopy (EDS, Philips, XL30S FEG) was used to confirm the synthesis of the phosphors and to analyze the chemical components. Scanning electron microscopy (SEM, Philips, XL30S FEG) was used to estimate the particle size, morphology and particle size distribution of the synthesized phosphors. A vacuum ultraviolet (VUV, Professional Scientific Instruments, PTE-VUVD2L-1000) photoluminescence spectrometer with a D_2 lamp was used to investigate the emission characteristics of the synthesized phosphors.

3. RESULTS AND DISCUSSION

Figure 2 shows the chemical component of the phosphor, as determined by EDS. The peaks corresponding to the main components, Y and Gd, and the doping substance, Eu, are clearly observed. In addition, peaks were also observed corresponding to the Au coating, which originated from the pretreatment process performed prior to conducting the EDS measurements.

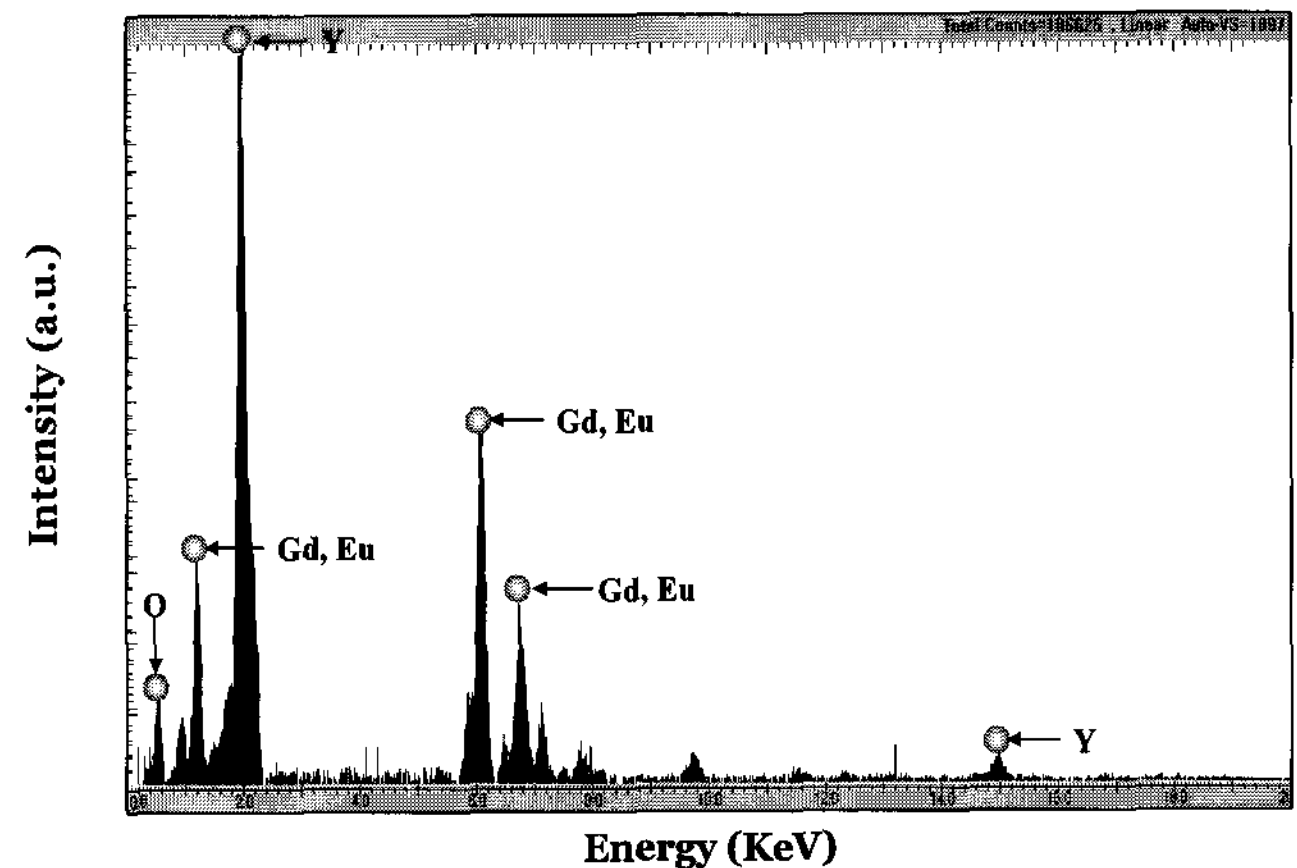


Fig. 2. EDS result of $(Y,Gd)_2O_3:Eu$ phosphor.

Figure 3 shows the XRD result obtained by comparing the XRD pattern of the $(Y,Gd)_2O_3:Eu$ phosphor to the corresponding JCPDS card (17-0341).

The main peak of the phosphor was (222) and it was comprised of a crystal phase consisting of the (400), (440) and (622) diffraction peaks. These peaks also indicated that the Gd_2O_3 monoclinic structure was changed to a cubic structure. The EDS and XRD results confirmed the successful preparation of the $(Y,Gd)_2O_3:Eu$ phosphor.

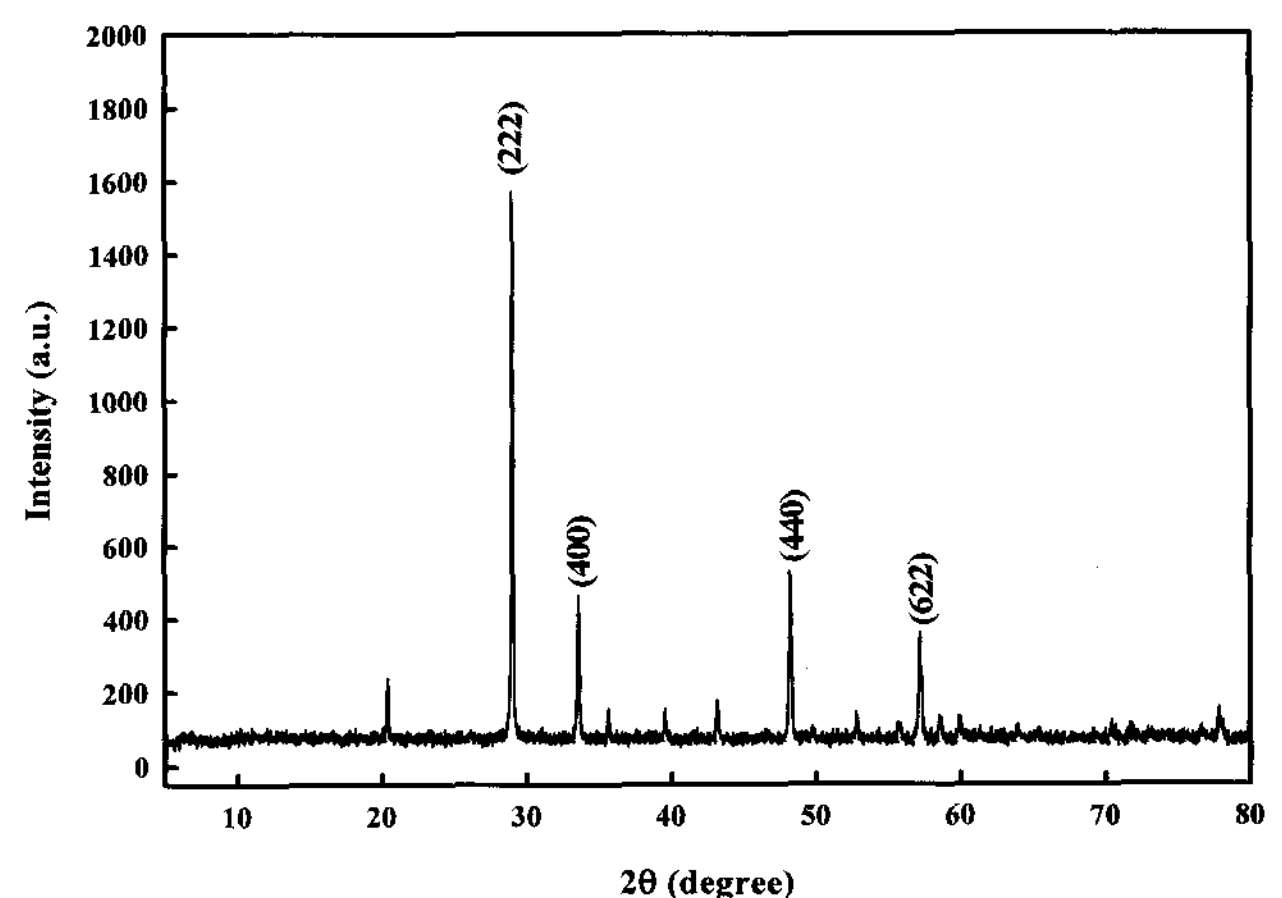


Fig. 3. XRD pattern of $(Y,Gd)_2O_3:Eu$ phosphor.

Figure 4 shows the emission spectra of the $(Y,Gd)_2O_3:Eu$ phosphors under excitation at a wavelength of 147 nm, as a function of the Gd_2O_3 content. The highest emission intensity was obtained at a Gd_2O_3 content of 0.6 mol. In addition, the crystal growth of the $(Y,Gd)_2O_3:Eu$ was increased as Gd_2O_3 content was increased from 0.2 to 0.6 mol%. At 0.8 mol% Gd_2O_3 content, the emission intensity decreased due to the

crystal decay of $(Y,Gd)_2O_3:Eu$ phosphor, because the radius of the Gd ion (94 Å) is larger than that of the Yttrium ion (89 Å). According to the emission spectra, Eu^{3+} ion undergoes the following transitions: $^5D_0 \rightarrow ^7F_J$ ($J=0,1,2,3,4$), $^5D_1 \rightarrow ^7F_1$ (537 nm), $^5D_0 \rightarrow ^7F_1$ (593 nm) and $^5D_0 \rightarrow ^7F_2$ (619 nm). The transition $^5D_0 \rightarrow ^7F_2$, which is an energy level transition, makes the highest contribution to the emission of red spectra. In order to separate the emission of the 611, 615 and 619 nm radiation, which are released from the $^5D_0 \rightarrow ^7F_2$ transition, it is possible to identify the 5 different 7F_2 status values from the crystal field, which make it possible to distinguish these emissions by means of the special 7F_2 status[6]. The Gd_2O_3 was fixed to 0.6 mol%, the Eu doping concentration was varied from 1 to 10 wt. %, and the VUV PL emission spectra of the phosphor were recorded, as shown in Fig. 5.

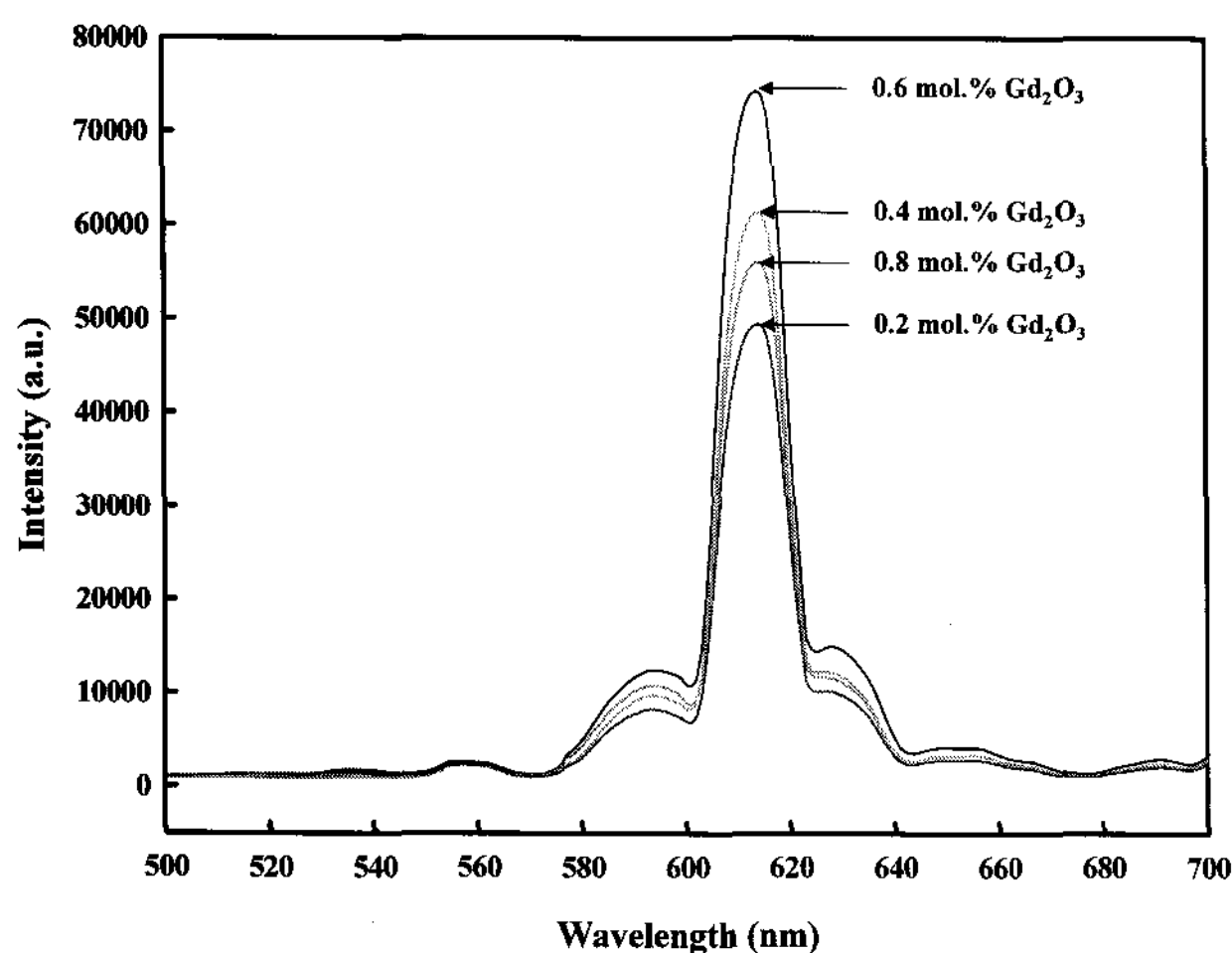


Fig. 4. Emission spectra (under 147 nm excitation) of $(Y,Gd)_2O_3:Eu$ phosphors with various Gd_2O_3 contents.

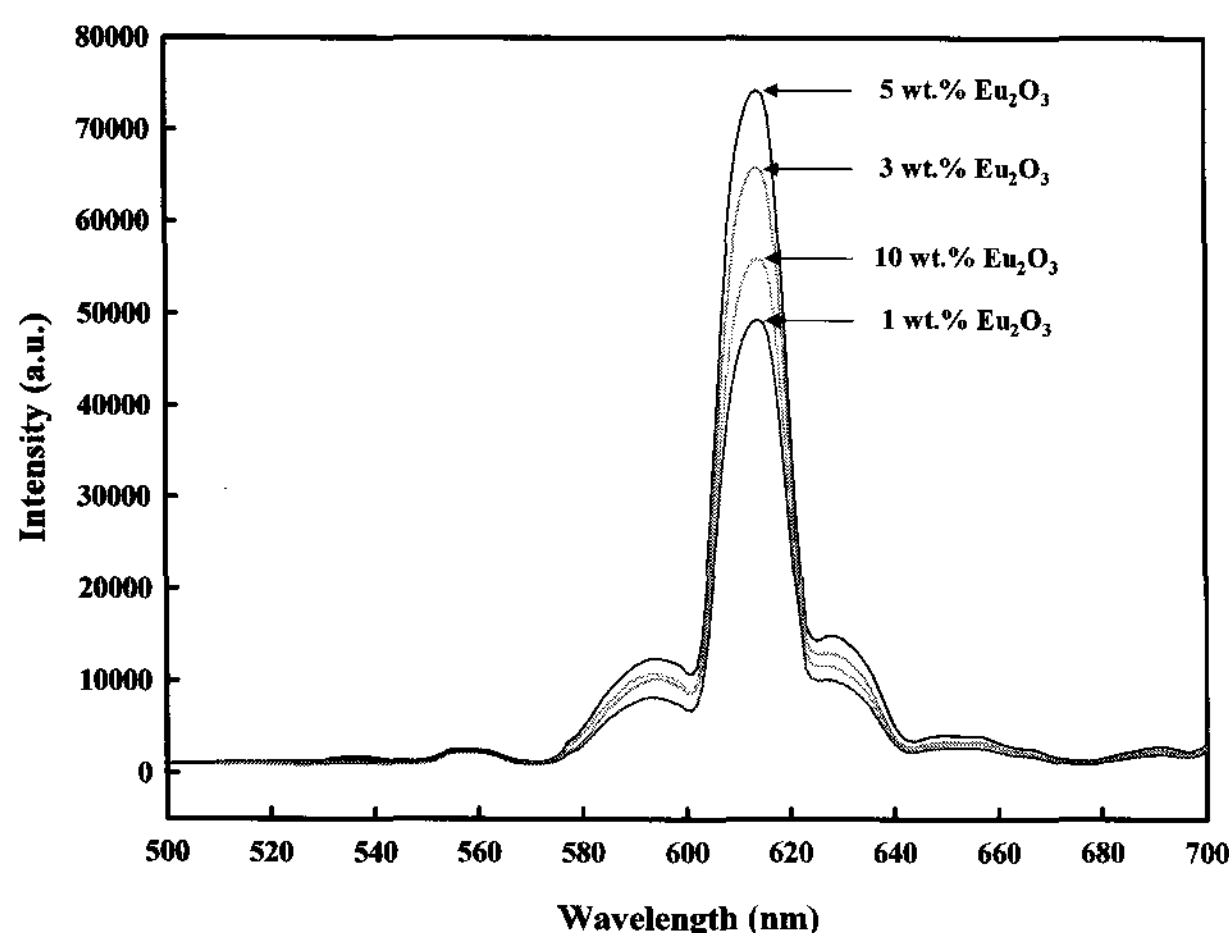


Fig. 5. VUV PL emission spectra of $(Y,Gd)_2O_3:Eu$ phosphors with various Eu_2O_3 concentrations.

The spectra shown in Fig. 5 indicate that the emission at the 612 nm always follows the $^5D_0 \rightarrow ^7F_2$ transition, irrespective of the doping concentration, and that the highest emission intensity was obtained at a doping concentration of 5 wt.%. When the Eu doping concentration was varied from 1-5 wt.%, the emission intensity increased with increasing Eu content, but then decreased at concentrations above 5 wt.% because of the concentration quenching effect.

Figure 6 shows the VUV PL emission spectra of the $(Y,Gd)_2O_3:Eu$ phosphors according to the sintering temperature. Concerning the emission spectra of the $(Y,Gd)_2O_3:Eu$ phosphors, the main peaks were observed at 612 nm for all calcining conditions, due to the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} , and the phosphor sintered at 1150 °C showed the highest emission intensity. The emission intensity increased with the increasing sintering temperature for the following reasons. The important factors determining the emission efficiency of phosphors are the chemical structure, particle size, and the arrangement and optimization of powder morphology[7]. Therefore, when the sintering temperature is increased, the particle size will increase and the structure will become more equalized. This is important, because large particles with an equalized structure have less surface scattering but a higher packing density[8,9].

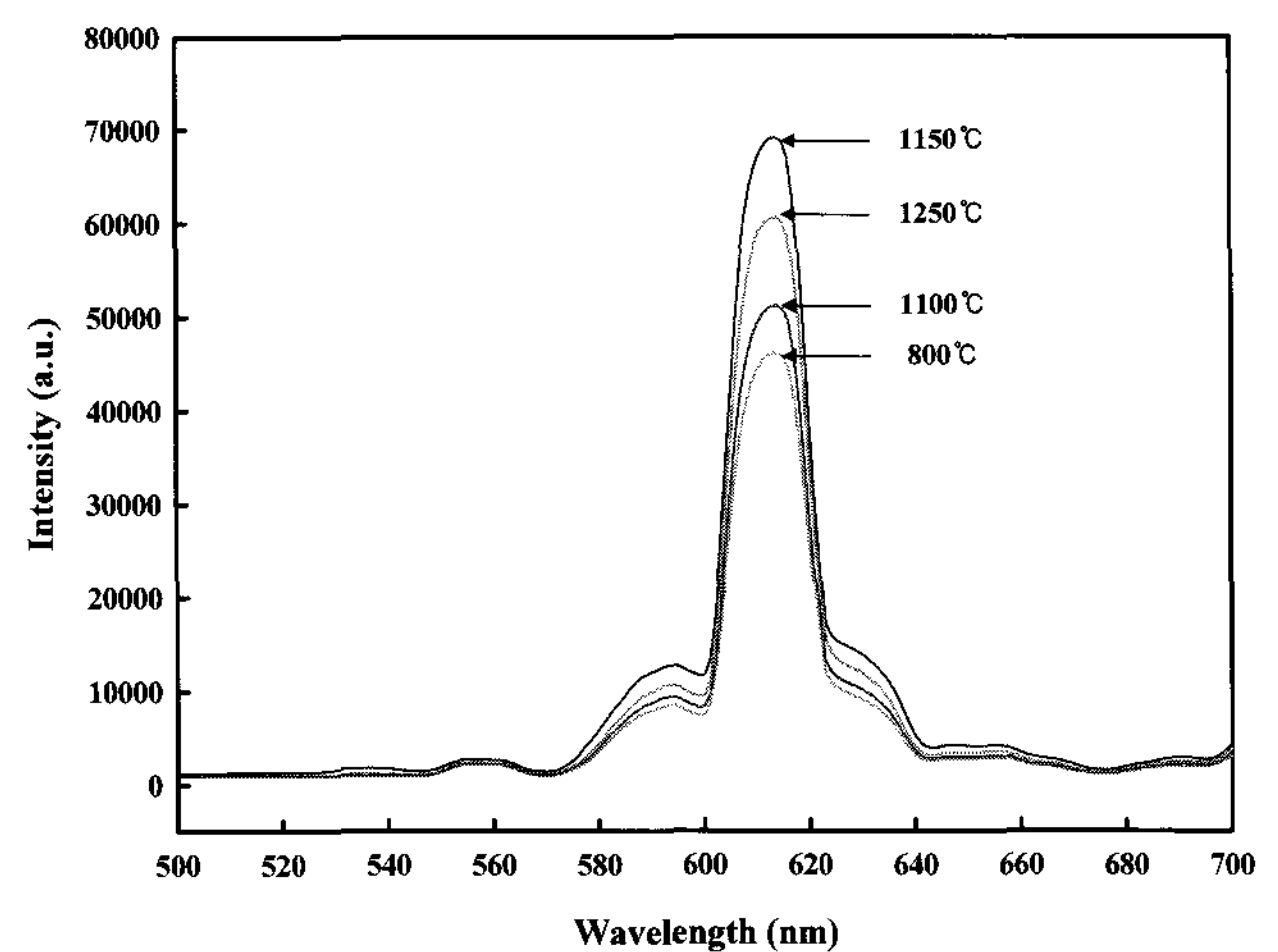


Fig. 6. VUV PL emission spectra of $(Y,Gd)_2O_3:Eu$ phosphors at various sintering temperatures.

However, the phosphor which was sintered at 1250 °C showed decreased emission intensity, due to rapid particle agglomeration and crystal decay. In order to study the variation of the morphology of the $(Y,Gd)_2O_3:Eu$ phosphor over the sintering temperature range of 800-1250 °C, the SEM images shown in Fig. 7 were examined. In Fig. 7(a), which corresponds to a sintering temperature of 800 °C, particles smaller than

100 nm were formed, while the particle size was increased and equalized at a sintering temperature of 1000 °C (Fig. 7(b)). Figure 7(c) shows that the particle size was further increased and even more equalized at 1150 °C, attaining a size of about 150 nm, compared to the phosphors sintered at 800 °C and 1000 °C, indicating that the particle response becomes more active with increasing sintering temperature. However, rapid agglomeration of particles occurred at a sintering temperature of 1250 °C (Fig. 7(d)).

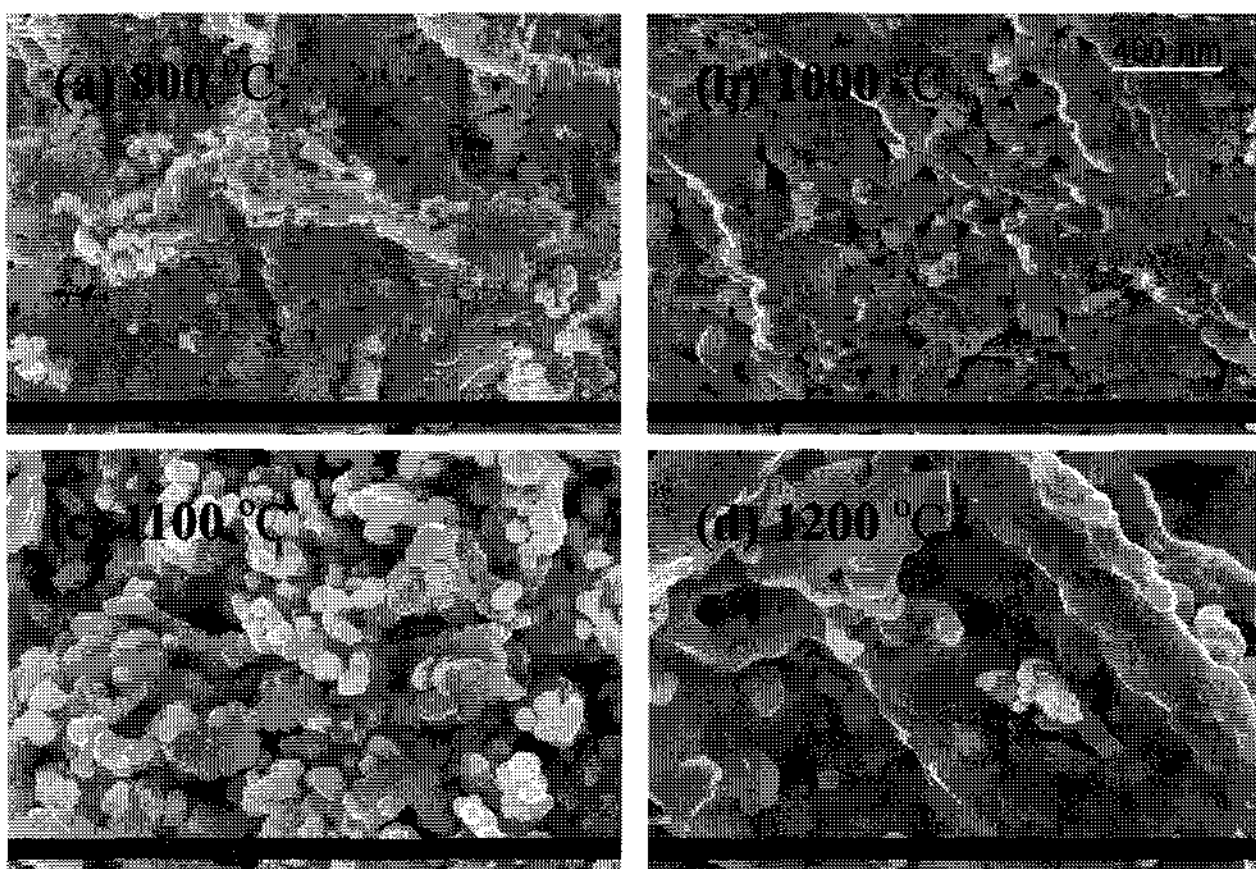


Fig. 7. SEM images of $(Y,Gd)_2O_3:Eu$ phosphors prepared with different sintering temperatures.

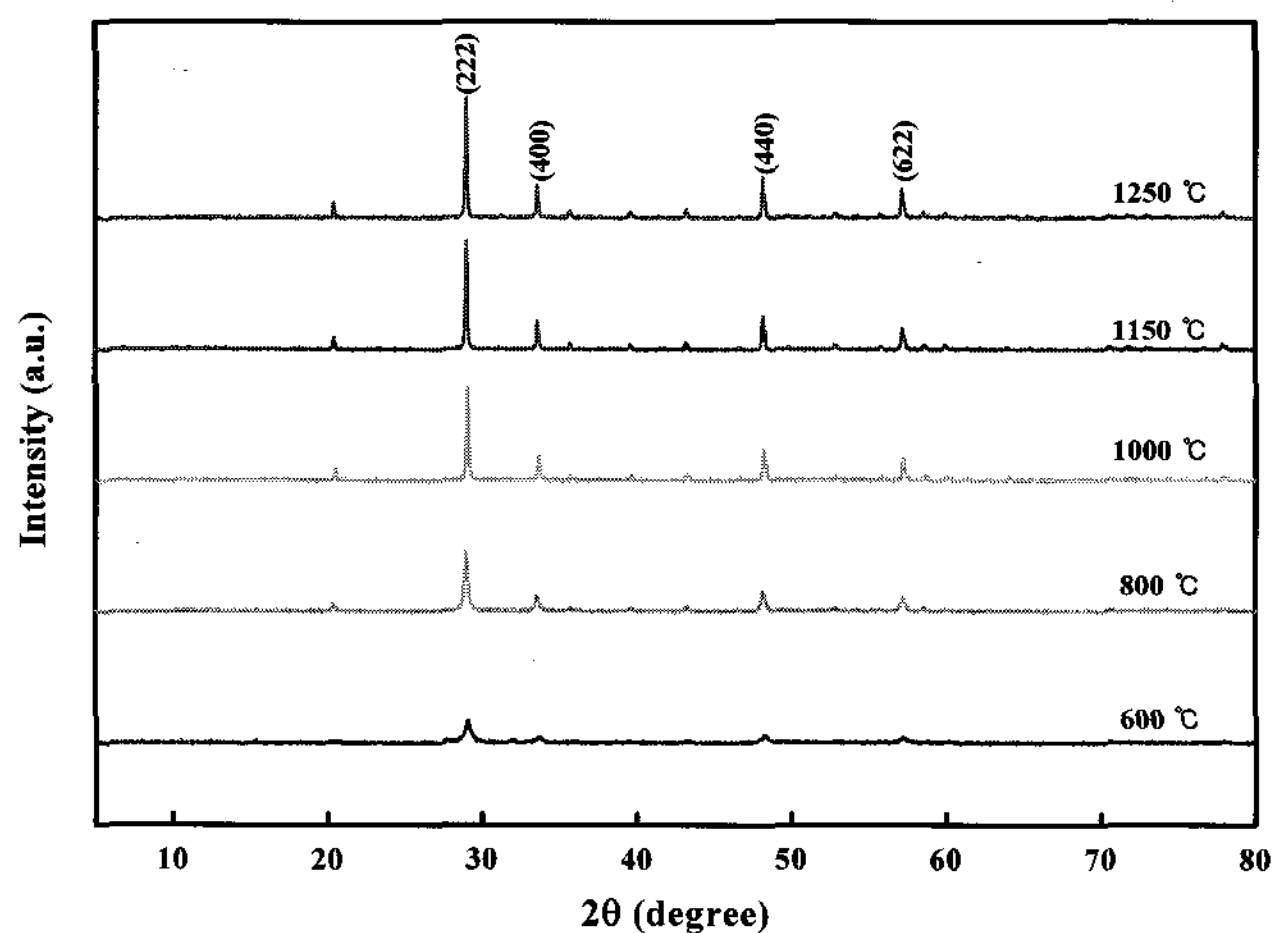


Fig. 8. XRD patterns of $(Y,Gd)_2O_3:Eu$ phosphors at various sintering temperatures.

Figure 8 show the XRD patterns of $(Y,Gd)_2O_3:Eu$ phosphors which were sintered at 600 °C, 800 °C, 1000 °C, 1150 °C and 1250 °C. The $(Y,Gd)_2O_3:Eu$ crystal phase began to form 600 °C and the crystal growth of $(Y,Gd)_2O_3:Eu$ continued up to 1150 °C. The main peak

for all of the $(Y,Gd)_2O_3:Eu$ phosphors was maintained at (222), irrespective of the sintering temperature, and they also incorporate a crystal phase consisting of the (400), (440) and (622) peaks. The Full Width at Half Maximum (FWHM) was decreased with increasing sintering temperature and greater intensities of the main (222) peaks, indicating an improved crystallinity of the phosphors with increasing sintering temperature[10].

4. CONCLUSION

In this study, the impregnation process was used to prepare $(Y,Gd)_2O_3:Eu$ phosphors from a polymer precursor and the Y/Gd ratio, Eu doping concentration, emission characteristics and crystalline structure of the surface were examined as a function of the sintering temperature. The $(Y,Gd)_2O_3:Eu$ phosphors showed a maximum emission intensity at 612 nm, due to the $^5D_0 \rightarrow ^7F_2$ transition, irrespective of the Eu doping concentration and the sintering temperature. Furthermore, the emission intensity was maximized with Gd and Eu concentrations of 0.6 mol% and 5 wt.% Eu, respectively, but decreased at higher concentrations because of the crystal decay and concentration quenching effect. In addition, the particles obtained a more rounded out and equalized shape with superior emission intensity when the sintering temperature was increased from 800 °C to 1150 °C. At sintering temperature above 1150 °C, however, the emission efficiency decreased with increasing sintering temperature, because of the rapid particle growth. Therefore, the emission efficiency increased with increasing sintering temperature due to the improved crystallization of the phosphor.

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