

Precursor Process Designing to Synthesize Nano-sized Phosphors

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(Received November 1 2005, Accepted January 11 2006)

The nano-sized phosphors were prepared using precursor process in order to improve the performance of red and green emitting phosphors for plasma display panel (PDP). $Zn_2SiO_4:Mn$ and $(Y,Gd)_2O_3:Eu$ phosphors exhibit strong emissions around 520-530 nm, 615 nm respectively. The emission intensity and particle size of powders were controlled by sintering temperature and raw material composition. The single phase of each phosphor was obtained at lower temperature than prepared by solid-state reaction method. PL luminance of each phosphor was similar to the commercial material.

Keywords : Nano-sized phosphor, Nanoparticles, Photoluminescence

1. INTRODUCTION

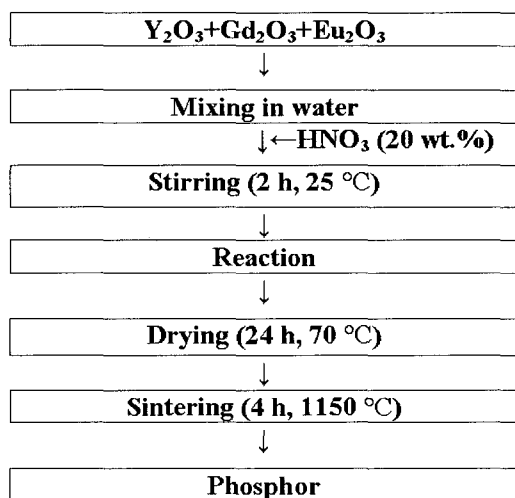
The physical properties such as electric conductivity, magnetic, optical and mechanical characteristics of nano-sized metal oxide particles are known to be substantially different from those of bulk materials. For the precise control of the morphology at the nanometric scale, the preparation methods of metal oxide nano-particles have been extensively studied[1-3]. An organo-polymeric precursor method is reported here. This process allows different patterns of particles to be prepared, because the morphology of the particle is dependent on the microstructure of the precursors, which are micelle or micro fibril. The particles have a nano-crystalline structure with a primary particle size of smaller than 100 nm. Multi-component metal oxide powder can be obtained homogeneously by introducing impregnated salts to the precursor before firing. This process does not include a co-precipitation operation as in the sol-gel process, neither does it involve alkali solutions. However, some efforts are required to remove corrosive gases generated by the pyrolysis of the impregnated precursor [4,5].

The phosphor which is used for PDP requires an emission efficiency which is appropriate for driving conditions and also which has a fast response time, a short decay time, and superior color purity which is stable with heat[6]. In order to prepare nano-sized phosphors, we used a precursor process with polymer precursors. By using precursor process with polymer

precursors, it is possible not only to get very high purity phosphor, but also to get phosphors with an equalized structure because the reaction is processed in the liquid. In addition, compared to the past solid phase method, we can control the crystals, morphology, particle size, and particle distribution of the product. We tried to investigate doping effect of various doping substance concentrations, the rate of host materials, characteristics according to the sintering temperature, and found out the emission characteristic and crystal phase.

2. EXPERIMENTAL

Highly pure metallic salts or metal oxides were used as starting materials. YCl_3 , $GdCl_3$, and Eu_2O_3 of high purity are used as starting material for red phosphor. In the case of green phosphor, pure $ZnCl_2 \cdot 6H_2O$, Ludox HS-40, $MnCl_2 \cdot 6H_2O$ were used as starting materials. Scheme 1 shows the general production process of $(Y, Gd)_2O_3:Eu$ phosphor. In this precursor process, first, metallic salts, and metal oxide of doping materials were dissolved in distilled water. To dissolve the mixed liquid perfectly, small amount of nitric acid was also added. Then, the mixed solution was stirred at room temperature. The polymer precursor was added to the sol solution. The solution of red phosphor was dried at 70 °C for 24 hours and sintered at more than 1000 °C for 4 hours. After the sintering, it was possible to get green and red phosphor.



Scheme 1. Preparation procedure of (Y,Gd)₂O₃:Eu phosphor.

On the other hand Green phosphor was sintered at 1200 °C for 5 hours, then, put thru reduction treatment at 900 °C for one hour. At this time, to change all of the Mn ions to Mn²⁺, 5 % H₂/N₂ (the gas mixture of nitrogen and a small amount of hydrogen 5 %) was used. After the reduction treatment, all the powder was white, so it was determined that when a Mn ion is in a state of oxidation, it exists as Mn²⁺.

The characteristics of nano-sized phosphors for PDP prepared by precursor process with polymer precursor have also been carried out detail. To check the crystal and crystalline structure of heat treated phosphor, an XRD analysis was carried out. Also a JCPDS powder diffraction file was used to check the results. XRD measurements were taken using Cu K α ($\lambda \sim 1.5418$) as the X-ray source, scanning range: 2θ from 0 ° to 80 ° scanning speed of 2θ ; 5 °/min. To confirm the chemical composition of the synthesized phosphor, EDS spectra were recorded. SEM was used to estimate the particle size, morphology and particle size distribution of the synthesized phosphor. A PL spectrometer with a D₂ lamp was used to see the emission characteristics of the phosphor.

3. RESULTS AND DISCUSSION

Figure 1(a) is an XRD result by comparing the XRD pattern of the (Y,Gd)₂O₃:Eu phosphor to the JCPDS card (17-0341). The main peak of the phosphor is (222) and it is made of a crystal phase which consists of diffraction peaks (400), (440), (600). Also it was observed from those peaks that the monoclinic of Gd₂O₃ is changed to cubic structure, and from the results of

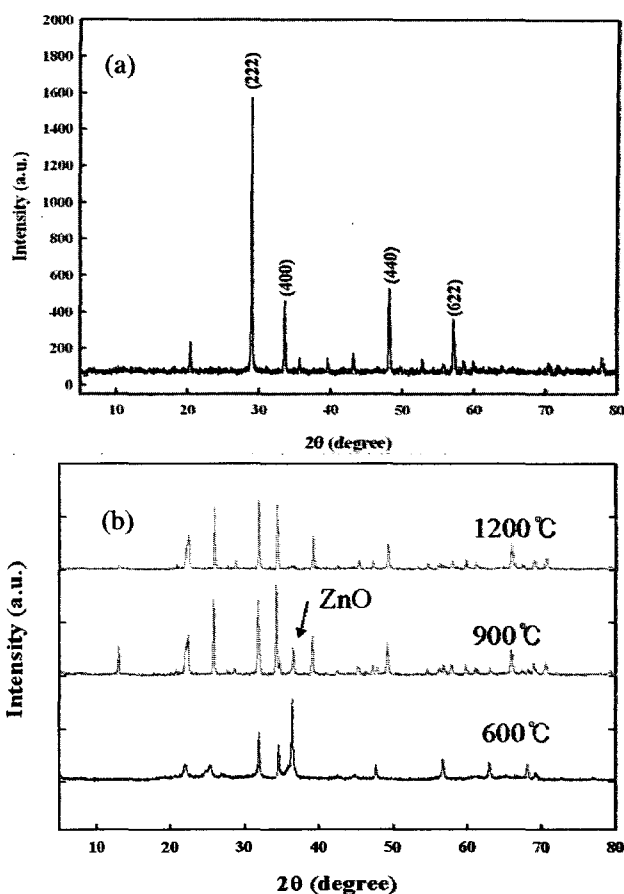


Fig. 1. XRD pattern of (a):(Y,Gd)₂O₃:Eu phosphor and (b): Zn₂SiO₄:Mn phosphors.

EDS and XRD, (Y,Gd)₂O₃:Eu phosphor was successfully prepared. Figure 1(b) shows an example of the X-ray diffraction analysis of the synthesized Zn₂SiO₄:Mn phosphor at various heat treatment temperatures. The ZnO peaks which did not react until 900 °C are visible. However, the non-reacted ZnO had totally disappeared at 1200 °C and only a single willemitte phase was visible. Therefore, compared to the solid state reaction, which is heat treated at more than 1300 °C, synthesized phosphor can be crystallized at a lower temperature, and it is also possible to see when the single phase is formed[7].

In order to check whether the application of different sintering temperature (800-1250 °C) results in the obtainment of different morphology of the (Y,Gd)₂O₃:Eu phosphor, SEM analysis was carried out and the results have been shown in Fig. 2. In Fig. 2(a), we can see that the particles were formed which were smaller than 100 nm when the sintering temperature was 800 °C, and in Fig. 2(b), we can see that when the sintering temperature became 1000 °C, the particle size increased and equalized. In Fig. 2(c), we can see that compared to 800 °C and 1000 °C, the particle size increased and

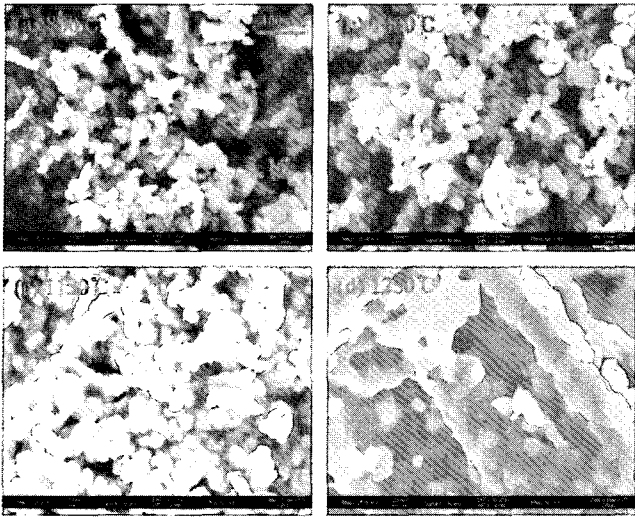


Fig. 2. SEM images $(Y,Gd)_2O_3:Eu$ phosphors prepared with different sintering temperature.

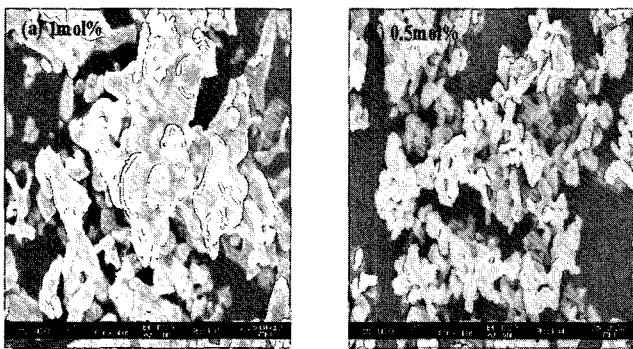


Fig. 3. SEM image of Zn_2SiO_4 doped with different Mn concentration.

equalized even more at 1150 °C, its size is about 150 nm, even though it has a surface structure. It means that when the sintering temperature increases, the response of the particles is more active. However, in Fig. 2(d), when the sintering temperature is 1250 °C, it shows rapid agglomeration of particles.

Figure 2 comprises SEM of the $Zn_2SiO_4:Mn$ particle at various concentrations. Generally, it is known that controlling the particle size and morphology of the phosphor has an effect on the brightness of the emission. This means that when the phosphor is in the best particle size condition, and when morphology is round, the efficiency in the quantum energy of the absorbed light energy can increase. The phosphor doped with 0.5 mol% has a regular distribution with a regular shape. Whereas particles doped with 1 mol% Mn become aggregated and show an irregular shape.

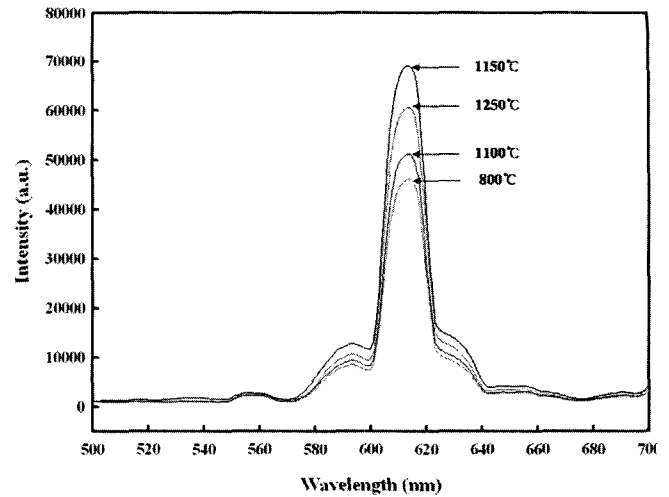


Fig. 4. PL emission of $(Y,Gd)_2O_3:Eu$ phosphors for various sintering temperature.

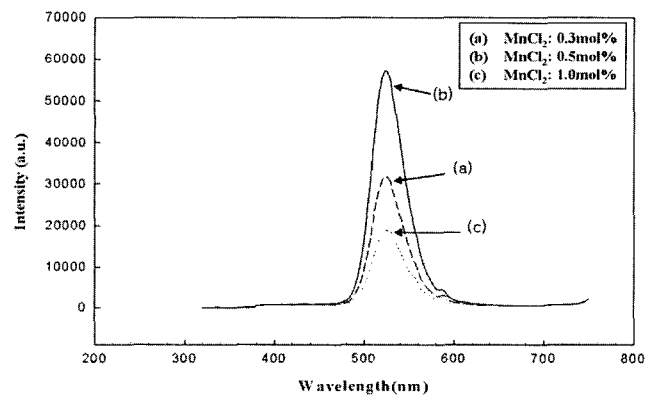


Fig. 5. Emission spectra of Zn_2SiO_4 doped with various Mn concentrations.

Figure 4 shows the PL emission spectra of $(Y,Gd)_2O_3:Eu$ phosphor according to the sintering temperature. Concerning the PL emission spectra of the $(Y,Gd)_2O_3:Eu$ phosphor, the main peaks are shown at 612 nm due to the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} at all the calcining conditions, and also sintering at 1150 °C showed the best emission intensity. With an increase in sintering temperature, the emission intensity is also increased. This phenomenon can be explained as follows. The important factors for emission efficiency of phosphors are chemical structure, particle size, arrangement and optimizing of powder morphology[8].

Figure 5 shows the emission spectra according to the different Mn concentrations. The PL characteristics were examined under the excitation of 147 nm. As a result, the phosphors emit very intensive green light with a narrow

band in the wavelength range between 520 to 530 nm, and especially 0.5 mol% Mn doped Zn₂SiO₄ shows the best emission characteristics.

4. CONCLUSION

In this study, the impregnation process was used by using polymer precursor to make (Y,Gd)₂O₃: Eu and Zn₂SiO₄: Mn phosphors and the rate of host materials, doping substance concentration, emission characteristics and crystalline structure of the surface were examined according to the sintering temperature. The best concentrations of green phosphor starting materials were obtained, and especially the maximum emission intensities were found to be 0.5 mol% Mn concentration. Also, in the case of red phosphor, when the Gd is 0.6 mol.%, the Eu is 5 wt.%, the emission intensity become maximum. With the increase of the sintering temperature, the emission efficiency increases because the crystallization of the phosphor is improved.

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