Synthesis and Characterization of Y_2O_3:Eu Fine Particle

Ji-Koon Park[a] and Sang-Sik Kang
Department of Biomedical Engineering, College of Biomedical Science and Engineering, Inje University, Eobang-dong, Kimhae-si, Kyungnam 621-749, Korea

Min-Gi Kwak
Korea Electronics Technology Institute, Yatap-dong, Bundang-gu, Seongnam-si, Gyeonggi 463-816, Korea

Seung-Suk Choi
Department of Materials Engineering, Hankuk Aviation University, Hwajeon-dong, Deogyang-gu, Goyang-si, Gyeonggi 412-791, Korea

Jae-Hyung Kim and Sang-Hee Nam
Medical Imaging Research Center, Inje University, Eobang-dong, Kimhae-si, Kyungnam, 621-749, Korea

[a]E-mail : pjk@drworks1.inje.ac.kr

(Received May 3 2005, Accepted August 10 2005)

Y_2O_3:Eu powder was synthesized using a solution-combustion method by dissolving $(CH_3CO_2)_3Y$ and $(CH_3CO_2)_3Eu$ in methyl-alcohol solution. Results from X-ray diffractometery (XRD), thermogravimetry (TG)-differential thermal analysis (DTA) show that Y_2O_3:Eu crystallizes completely when the dry powder is sintered at 500 °C. The investigated optical properties were the photoluminescence emission spectra, the excitation spectra and luminescence decay curve. Europium (Eu) concentration had no observable effect on the optical spectrum which depended on the emission intensity. The mean lifetime of synthesized phosphors was 2.3 ~ 2.6 ms.

Keywords : Y_2O_3:Eu, Optical properties, Photoluminescence, Lifetime

1. INTRODUCTION

Yttrium oxide is an excellent substrate for phosphors because of its chemical stability. Recently, europium doped yttrium oxide (Y_2O_3:Eu^{3+}) as an efficient red-emission phosphor has been applied widely in high resolution projection devices, the cathode ray tube (CRT), fluorescent lights (FL), plasma display panels (PDP) and field emission displays (FED) and so on[1].

High efficiency phosphors with crystalline particles are the key for high resolution screens, and flat panels [2-4]. Therefore, the quality of the phosphor particles is very important, and phosphor pixel size as small as ~ 10 ㎛ in diameter are required for high resolution image devices. In practice, small particle sizes may improve aging by forming a densely packed film layer .

On the other hand, particle sizes smaller than a critical value decreases luminescence efficiency because of increasing light absorption and quenching effects by the surface layer. So, researches about synthesis of fine luminescence particles with high luminescence efficiency are needed.

Grinding is required to achieve the small particle size phosphor powders of high quality since particle sizes of phosphors synthesized by conventional high temperature solid-state reaction methods are too large. But, during this process, the particle morphology changes and the luminescence efficiency decreases. Therefore, various preparation schemes have been adopted to reduce the reactivity such as sol-gel, coprecipitation, etc[5,6].

In this paper, we report on the preparation of crystalline Y_2O_3:Eu phosphor particles using a modified low temperature solution-combustion technique. Structure and luminescence properties were carried out on the resulting phosphors with respect to varying europium (Eu) concentrations.

2. EXPERIMENT

Yittrium acetate hydrate [$(CH_3CO_2)_3Y$, 99.9 %, Aldrich], europium acetate hydrate [$(CH_3CO_2)_3Eu$, 99.999 %, Aldrich], and a methyl-alcohol solution were used as starting materials. Specified amounts of $(CH_3CO_2)_3Y$ and $(CH_3CO_2)_3Eu$ were dissolved in methanol separately and formed two solutions, and then mixed under stirring. This mixed solution containing yittrium and europium was evaporated by chemical evaporation method at 60 °C. After dried in air at 120 °C, the transparent powder was put into a covered 50 ml alumina crucible, and then this crucible was annealed at at 500 °C in furnace for 1 hour and cooled down to room temperature naturally in the chamber. The Y_2O_3:Eu^{3+} phosphor particles with europium concentration of 8 wt%, 10 wt%, and 15 wt% were fabricated.

X-ray diffraction patterns were obtained with a Rigaku D/Max-IIIA X-ray diffractometer (XRD) using Cu Kα . The thermal decomposition behavior of the dried powder was examined by means of thermogravimetry (TG) and differential thermal analysis (DTA) using the Setaram/ TGA92 analyzer. A JSM-6500F field-emission scanning electron microscopy (FE-SEM) was used to observe the particle morphology of the phosphors. The excitation and emission spectra of the phosphor powders were recorded using a FS900CDT spectrofluoremeter of Edinburgh Analytical. FL900CDT time-resolved fluorometer was used for measurements of luminescent decay curve.

3. STRUCTURE OF Y_2O_3:EU PHOSPHOR

The decomposition of the dry powder can be seen from the TG-DTA curve in Fig. 1. Several reactions occurred when the dry powder was heated. The weight loss below 200 °C corresponds to the removal of absorbed water. The weight loss from 350 to 450 °C was due to the combustion of redundant carbon from the decomposition of acetate hydrate, and there was a corresponding exothermic peak at 360 °C in the DTA curve. The dried Y-Eu composite powders are pro-gressively crystallized above 360 °C.

X-ray diffraction patterns for the decomposition products of the dry gel synthesized by the solution-combustion method at low temperature are shown in Fig. 2. X-ray diffraction patterns shows <222>, <400>, <411>, <332>, <511> peaks. These peaks are almost identical to typical Y_2O_3:Eu^{3+} phosphor crystal peaks. When sintered at 500 °C, a single phase of Y_2O_3 is obtained, with Eu_2O_3 entering the Y_2O_3 crystal lattice[4]. The SEM images of Y_2O_3:Eu^{3+} particles are shown in Fig. 3. The particles exhibited a wide distribution in particle size.

It can be seen from the SEM image that most of the particles were agglomerated after sintering. The average diameter of the particle used in the present study was

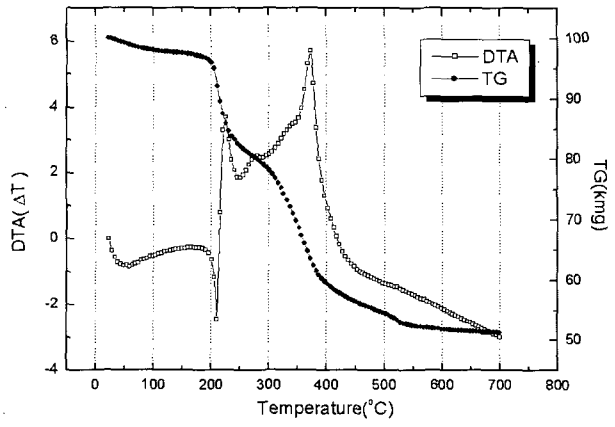

Fig. 1. TG-DTA curve of the dried Y-Eu powder.

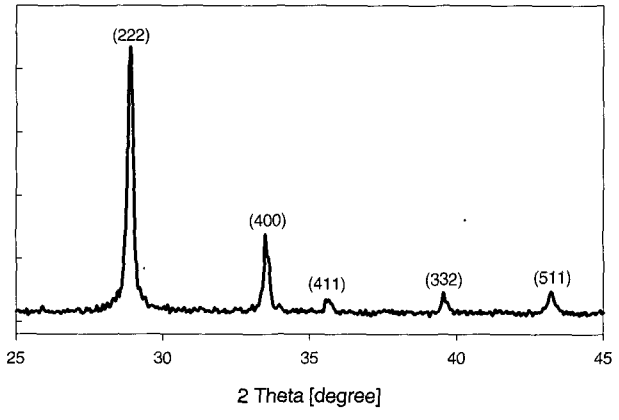

Fig. 2. X-ray diffraction spectra of Y_2O_3:Eu^{3+} particle after sintered at 500 °C for 1 h.

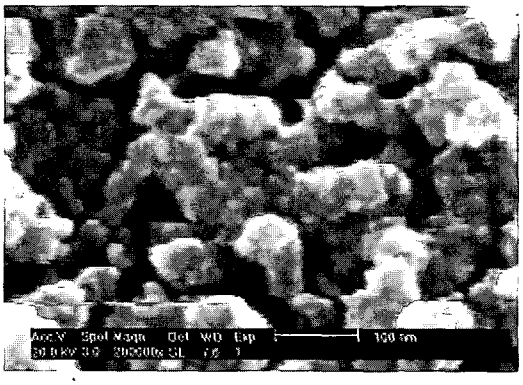

Fig. 3. Morphology of the Y_2O_3:Eu^{3+} particles after sintering at 500 °C for 1 hour.

determined to be about 30~40 nm. The calcination of the particles resulted in some contraction of the particles was probably caused by elimination of H_2O and CO_2 during the combustion process.

4. LUMINESCENCE PROPERTIES OF Y_2O_3:Eu PHOSPHOR

Figure 4 shows the excitation and emission spectra of the Y_2O_3:Eu phosphor. Emission peaks are the same as commercial bulk phosphor's peaks[7]. As shown in Fig. 5, the excitation spectrum of the red fluorescence (λ=611 nm) shows a wide band with a peak at about 253.5 nm, which is attributed to transition towards the charge transfer state (CTS) due to Eu-O interaction.

The emission spectrum excited by 253.5 nm UV consists of lines in the red spectral area. These lines correspond to transition from the excited $^5D_0$ level to ^7F_J (J=0,1,2,3) level of the $^4F_6$ configuration of the Eu^{3+} ion. Figure 5 shows emission spectra excited by 253.5 nm UV with respect to changes of europium concentrations. As shown in Fig. 5, there are no changes to the emission peaks and in relative emission intensity, the Y_2O_3:Eu (10 wt%) has 1.56 times higher emission intensity than Y_2O_3:Eu (8 wt%) and Y_2O_3:Eu (15 wt%). The quenching concentration of Y_2O_3:Eu phosphors prepared by conventional synthesis is 6 wt% Eu, but for our samples the quenching concentration has apparently increased[8].

Because the quenching concentration is related to the energy transfer between the Eu ions, we think that the interface of the particles may hinder the energy transfer and, as a result, the quenching concentration increases.

To measure the lifetime of the Y_2O_3:Eu^{3+} phosphor, after excitation at a charge transfer band of 253.5 nm, the mean lifetime for the $^5D_0 \rightarrow {}^7F_2$ transition is measured at 611 nm. Fig. 6 shows the result of lifetime measurement with respect to europium concentrations. The mean lifetime is 2.3 ~ 2.6 ms which is relatively higher than the 1 ms mean lifetime of bulk phosphors. Also, europium concentration increases, decreases the mean lifetime, and the sintering environment has no relation to the mean lifetime. This increase of mean lifetime is caused by the radiative transition rate[8].

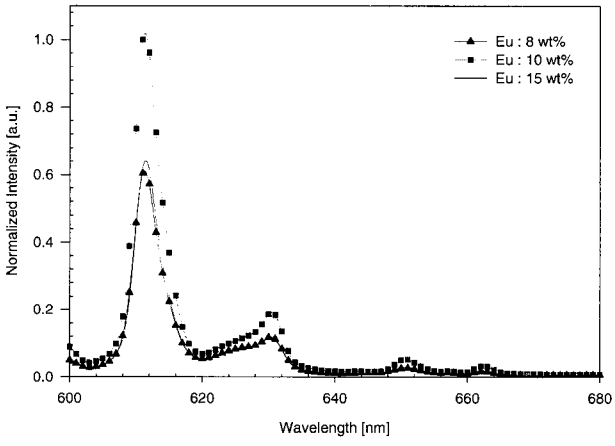

Fig. 5. Emission efficiency of the Y_2O_3:Eu phosphors after sintering at 500 °C for 1 hour in O_2 environment.

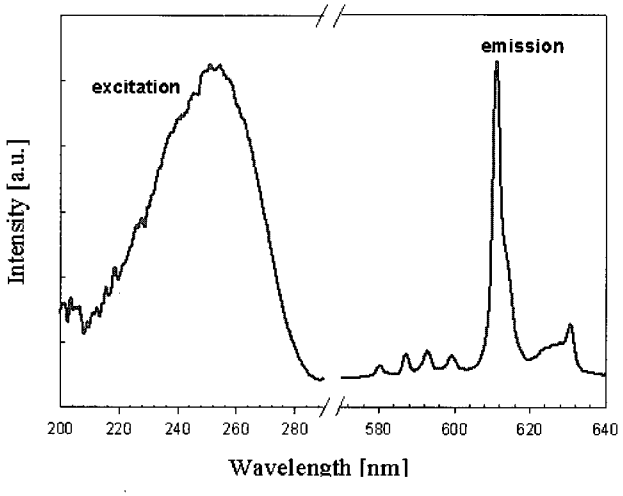

Fig. 4. Excitation and emission spectra of Y_2O_3:Eu phosphor phosphors after sintering at 500 °C for 1 hour in O_2 environment.

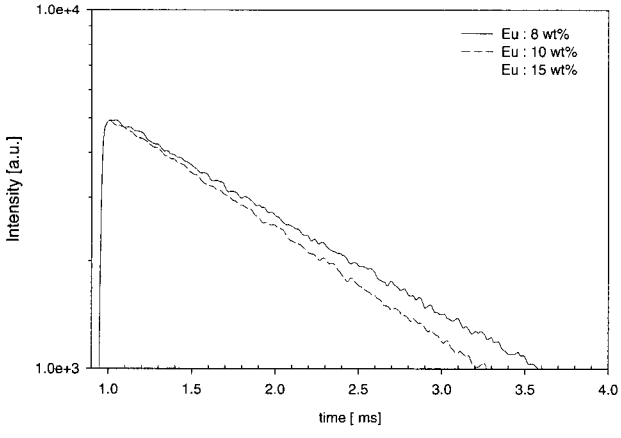

Fig. 6. Time resolved PL-emission intensity of the Y_2O_3:Eu phosphors after sintering at 500 °C for 1 hour in O_2 environment.

5. CONCLUSION

In this paper, Y_2O_3:Eu^{3+} phosphors are synthesized using a solution-combustion method. From TG-DTA analysis, the phosphor crystallizes completely at 500 °C Some contraction of the particles was probably caused by elimination of H_2O and CO_2 during the combustion process. There are no changes to the emission peaks and in relative emission intensity, the Y_2O_3:Eu (10 wt%) has 1.56 times higher emission intensity than Y_2O_3:Eu (8 wt%) and Y_2O_3:Eu (15 wt%). Furthermore, all our samples exhibited a lifetime of 2.3~2.6 ms which is longer than commercial bulk phosphor lifetime. This increase in mean lifetime is caused by the radiative transition rate.

ACKNOWLEDGMENTS

This work was supported by a 2004 INJE University Post-Doctor Research Grant.

REFERENCE

[1] R. P. Rao, "Growth and characterization of Y_2O_3: Eu^{3+} phosphor films by sol-gel process", Solid State Communications, Vol. 99, No. 6, p. 439, 1996.

[2] A. Jean, L. Laperriere, A. Legros, H. Mani, Z. Shukri, and H. Rougeot, "New cesium iodide-selenium x-ray detector structure for digital radiography and fluoroscopy", SPIE., Vol. 3659, p. 298, 1999.

[3] J. K. Park, S. S. Kang, J. H. Kim, C. W. Mun, and S. H. Nam, "Zinc sulfide-selenium x-ray detector for digital radiography", Trans. EEM, Vol. 3, No. 4, p. 16, 2002.

[4] J. K. Park, S. S. Kang, D. G. Lee, J. Y. Choi, J. H. Kim, and S. H. Nam, "Study on electrical properties of x-ray sensor based on CsI:Na-selenium film", Trans. EEM, Vol. 4, No. 3, p. 10, 2003.

[5] J. Zhang, Z. Zhang, Z. Tang, Y. Lin, and Z. Zheng, "Luminescent properties of Y_2O_3:Eu synthesized by sol-gel processing", J. Materials Processing Tech., Vol. 121, p. 265 , 2002.

[6] Y. D. Jiang, Z. L. Wang, F. Zhang, H. G. Paris, and C. J. Summers, "Synthesis and characterization of Y_2O_3:Eu^{3+} phosphor by a hydrolysis techque", J. Mater. Res., Vol. 13, No. 10, p. 2950, 1998.

[7] V. Pelova, K. Kynev, T. Petrova, and T. Piperov, "Luminescence of Y_2O_3:Eu and Gd_2O_3:Eu depending on precursor and activation temperature", Cryst. Res. Technol., Vol. 33, No. 1, p. 125, 1998.

[8] Z. Qi, C. Shi, and W. Zhang, "Local structure and luminescence of nanocrystalline Y_2O_3:Eu", Applied Physics Letters, Vol. 81, No. 15, p. 2857, 2002.