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Synthesis of Y_2O_3: Eu phosphor nanoparticles By RF thermal plasma method

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1. Introduction

Europium doped yttrium oxide particles are used in display devices and lamps as red phosphor, because they emit red light by UV excitation.[1, 2] It is important for phosphor particles to have fine size, spherical morphology, narrow size distribution and non-aggregation characteristics for high resolution and high efficiency.[3] Especially, non-aggregated fine particles have many advantages such as high packing density and good slurry property, and so, a thin and smooth phosphor layer can be made for good photoluminescent characteristics.[4] Like most of the phosphors, Y_2O_3:Eu phosphor particles are prepared by a conventional solid state reaction method. But the phosphor particles prepared by the solid state reaction method have irregular shape, large size distribution and aggregation characteristics.

Many different new techniques of phosphor particles preparation have been recently reported, e.g., sol-gel techniques, emulsion techniques, flame splay pyrolysis and combustion synthesis.[5-9] Howeber, it is difficult that nanometersized particles are produced in large quantities by these methods. On the other hand, RF thermal plasma is recommended as one of the effective method for industrial production of phosphor particles with narrow size distribution, aggregation-free and nanometer size.

The objectives of this work are to preparate Y_2O_3:Eu nanoparticles on a large scale, and to study the effect of Eu-doping concentration and calcination conditions on the photoluminescence (PL) of the as-prepared particles.

2. Experimental

The plasma reactor used in this work consists of a RF generator (frequency: 4 MHz, maximum RF power: 35 kW), a plasma torch, a quenching chamber, and a filter system. Starting precursor solution was prepared by dissolving Y and Eu nitrates into distilled water and it was fed to the gas atomization probe by a peristaltic pump. The overall solution concentration was 1.0 M and the doping concentration of Eu was varied from 3 to 7 mol% of Y component. The product nanoparticles were collected in the filter of the plasma reactor and post-treated at various temperatures for 1 hr.

The particle morphology was observed by scanning electron microscopy (SEM). The crystal structure of the powder was investigated by X-ray diffraction (XRD) and the particle crystallite size (D_{XRD}) was determined from the full width at half maximum of the (222) diffraction line using Scherrer's equation. The specific surface area (SSA) of the particles was measured by the BET technique. The BET-equivalent average primary particle diameter (D_{BET}) was obtained from the measured SSA and solid density (ρ) by $D_{BET} = 6/(SSA \cdot \rho)$, assuming solid spherical particles. The PL property of particles was measured by spectrofluorometer.

3. Results and discussions

Table 1 gives SSA, D_{BET}, crystal structure, D_{XRD} and the relative PL intensity of as-prepared particles, calcined particles at various temperatures for 1 hr, and the commercial Y_2O_3:Eu phosphor particles. The relative PL peak intensities of calcined particles were normalized by the PL peak intensity of the commercial particles. The crystal structure of as-prepared powder was a monoclinic phase, but it was transformed to a cubic phase after the calcination treatment above 800 ℃. D_{BET} and D_{XRD} increased with increasing the calcination temperature.

Table 1. The characteristic properties of as-prepared particles, calcined particles and commercial particles

Eu doping concentration	Calcination temperature	SSA (m^2/g)	D_{BET} (nm)	Crystal structure	D_{XRD} (nm)	Relative PL peak intensity
3.4 mol%	As-prepared	120	10	Monoclinic	No data	No data
3.4 mol%	800 ℃	45	27	Cubic	No data	11
3.4 mol%	900 ℃	33	37	Cubic	43	35
3.4 mol%	1000 ℃	24	50	Cubic	51	52
3.4 mol%	1100 ℃	15	83	Cubic	68	55
5.5 mol%	1000 ℃	23	52	Cubic	52	57
7.4 mol%	1000 ℃	24	50	Cubic	52	63
3.7 mol%	Commercial	0.69	1800	Cubic	99	(100)

In Figure 1, the PL spectra of the calcined particles at 800 ℃, 900 ℃ and 1000 ℃ with 3.4 mol% Eu concentrations are shown. The PL intensities of particles were measured under 254 nm UV light. The strongest emission appeared at 611nm. Figure 2 shows SEM images of the calcined particles at 900 ℃, 1000 ℃ and 1100 ℃ with 3.4 mol% Eu concentrations. The as-prepared particles and the calcined particles below 1000 ℃ have narrow size distributions, spherical morphology, and are non-aggregated. On the other hand, the calcined particles at 1100 ℃ are heavily aggregated, although their PL intensity is the highest of those of the calcined particles at other temperatures with 3.4 mol% Eu concentrations. These results indicate that the optimum calcination temperature, in this study, is 1000 ℃ to obtain non-aggregated phosphor nanoparticles.

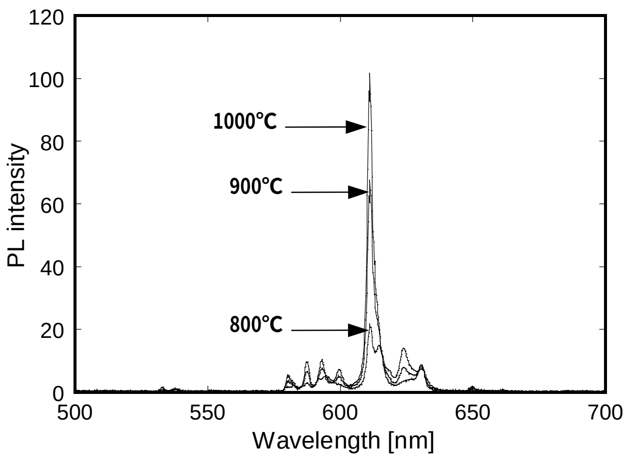

Fig. 1. PL spectra of calcined particles at 800 ℃, 900 ℃ and 1000 ℃ with 3.4 mol% Eu concentrations

Figure 3 shows the relative PL intensity and D_{XRD} of the calcined particles at 1000 ℃ for 1 hr as a function of Eu concentration. The Eu concentration in the calcined particles was measured by using energy dispersive X-ray fluorescence spectrometer. From Figure 3, it is clear that the PL intensity of

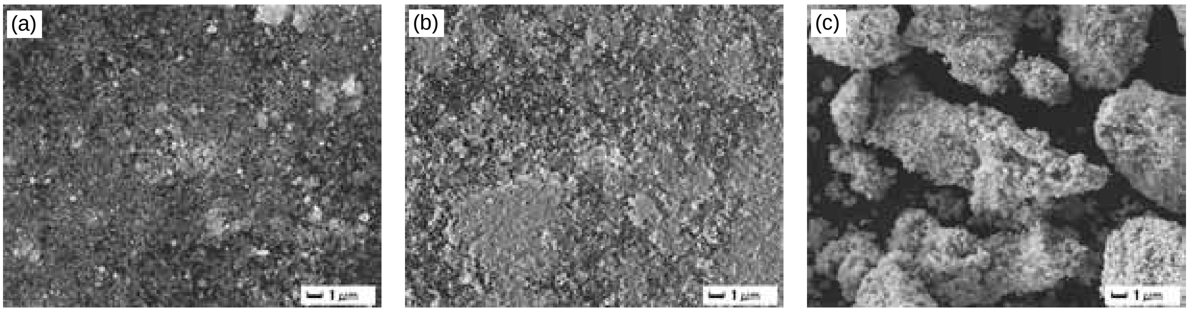

Fig. 2. SEM images of calcined particles at (a) 900 ℃, (b) 1000 ℃ and (c) 1100 ℃ with 3.4 mol% Eu concentrations

the calcined particles with 7.4 mol% Eu concentrations is the highest of those of the calcined particles with different Eu concentration, although D_{XRD} of the calcined particles with 7.4 mol% Eu concentrations is similar to that of other calcined particles. These results prove that the Eu-dopant material is highly dispersed inside the Y_2O_3 host matrix of nanometer size by RF thermal plasma method.

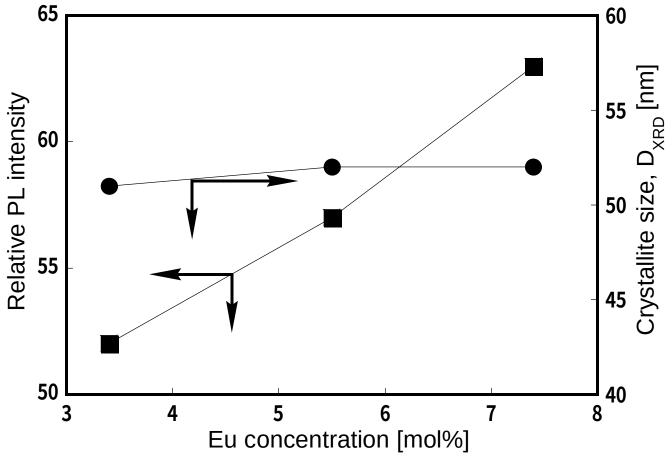

Fig. 3. Relative PL intensity and crystallite size (D_{XRD}) of calcined particles at 1000 ℃ for 1 hr as a function of Eu concentration

4. Conclusions

Y_2O_3:Eu nanoparticles were synthesized by RF thermal plasma method in this study. The as-prepared Y_2O_3:Eu nanoparticles had non-aggregated spherical shape and had a monoclinic phase with poor luminescence intensities. In order to improve the luminescence characteristics of the particles, the as-prepared particles were calcined at various temperatures. It is found that the crystal structure of particles was transformed to a cubic phase after calcination above 800 ℃ and the particles did not be sintered below 1000 ℃. The PL peak intensity of the calcined particles at 1000 ℃ for 1 hr with 7.4 mol% Eu concentration was the highest in this study. This value was 63% of the PL peak intensity of the commercial particles. The results show that RF thermal plasma method has the high possibility for the industrial production of phosphor nanoparticles.

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References

1 R. P. Rao: Solid State Commun., 99, 439 (1996).
2 Y. C. Kang, S. B. Park, I. W. Lenggoro and K. Okuyama: J. Mater. Res., 14, 2611 (1999).
3 H. K. Chang, I. W. Lenggoro, K. Okuyama and T. Kim: Jpn. J. Appl. Phys., 43-6A, 3535 (2004).
4 D. J. Seo, Y. C. Kang and S. B. Park: Appl. Phys. A, 77, 659 (2003)
5 A. Nakamura, N. Nambu, K. Kawahara, S. Ohshio and H. Saitoh: J. Ceram. Sci. Jpn., 111, 0142 (2003)
6 L. Sung, C. Qian, C. Laio. X. Wang and C. Yan: Solid State Commun., 119, 393 (2001)
7 Y. C. Kang, D. J. Seo, S. B. Park and H. D. Park: Jpn. J. Appl. Phys., 40, 4083 (2001)
8 P. K. Sharma, M. H. Jilavi, H. Schmidt and V. K. Varadan: Int. J. Inorganic Mater., 2, 407 (2000)
9 Y. Tao, G. Zhao, W.Zhang and S. Xia: Mater. Res. Bull., 23, 501 (1997)