Photoluminescence Characteristics of Eu-doped Yttrium Oxide Submicron-sized Particles Prepared by Aerosol Pyrolysis

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Europium doped yttrium oxide submicron-sized particles were prepared by ultrasonic aerosol pyrolysis. To examine the size effect of submicron-sized-particle, the photoluminescence of the particles was investigated. The particle size was controlled by pH, reaction temperature, molar concentration of yttrium in precursor solution. The PL intensity of submicron-sized particles was decreased with particles size. When the particle size is above about 150 times of Bohr radius of Y_2O_3, the optical property of the particles shows the bulk characteristics.

Keywords : Submicron sized particle, Yttrium oxide, Phosphor

1. INTRODUCTION

Submicron-sized particles, and submicron-sized composites have drawn a continuous attention arising from the fundamental scientific interest in understanding the transition of material properties from the bulk to molecular-like clusters and their potential applications[1-3]. Areas of application that can be foreseen to benefit from the size effects of such small particles include quantum electronics, non-linear optics, photonics, chemically selective sensing, photochemical processing, and information storage. In the area of luminescent materials, the submicron-sized phosphors are known to have relatively high efficiency due to higher probability of optical transition by confining the charge carriers to the restricted volume of small particles. However, as the particle size approaches molecular regime, a large percentage of the atoms are on or near the surface [1-3]. The control of surface properties becomes critical for practical application.

A wide variety of techniques have been developed to prepare the submicron-sized particles of different systems. Great effort has been made in preparation and characterization of submicron-sized particles such as ZnS, CdS, ZnSe, CdSe and so forth [4-11]. Although there are a lot of pioneering works for synthesizing submicron-sized phosphors, only a few of them presented optical data. It seems that the Bohr radius is very small [1-3] and reflects difficulty in obtaining the substantial optical transition in atmosphere. However, these synthetic routes are usually energy-consumable and have limitation to scale up. The Europium-doped Yttrium Oxide particle is well-known as red emitting luminescent material. Submicroncrystalline structure of Y_2O_3 prepared by sol-gel processing and reverse microemulsions were reported [12-14].

In this work, Europium-doped Yttrium Oxides of submicron-sized particle sizes are prepared by aerosol pyrolysis method [16] and their PL characteristics would be investigated.

2. EXPERIMENTAL

As source materials, yttrium nitrate hexahydrate (99.99%) for host precursors and europium nitrate pentahydrate (99.9%) for activators were used [15]. The activator ions were added about 6 mol% of host materials. The molar concentration of yttrium nitrate hexahydrate about de-ionized water was changed to

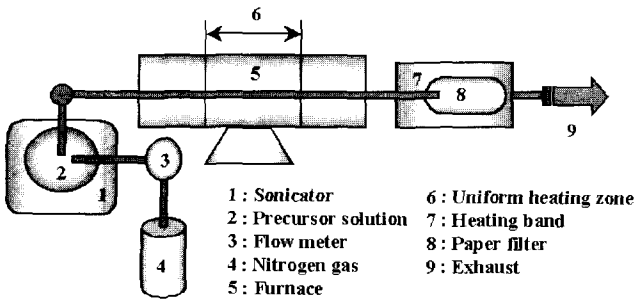


Fig. 1. Schematic of the ultrasonic aerosol pyrolysis system

control the particle size of the product [16]. To prevent the reaction in solution and control pH of solution, a proper amount of HNO_3 (99.99%) is added by proper mol% of solution. Schematic of the ultrasonic aerosol pyrolysis system is illustrated in Fig. 1. After dissolving precursors into deionized water, the solutions were stirred for several hours. The resulting solutions were aerosolized by ultrasonic transducer(1.67MHz), and carried into furnace with high temperature by carrier gas(N_2), which was volume-controlled. The aerosols which were made by ultrasonicator are about 7~10 ㎛ [17]. In the furnace, the aerosols were decomposed into submicron-sized particles. The residence time of the aerosols in heating zone was about 0.5~1 second. The temperature of furnace was 800℃~950℃. To avoid the aggregation of particles, annealing after reaction was not considered. Instead of annealing, reaction temperature of aerosol pyrolysis system for submicron-sized particles was taken rather high. The synthesized phosphor particles were captured by thimble filter, and kept at 80℃~100℃ to reduce condensation of water vapor.

The crystalline structure of particles was measured by x-ray diffractometer (Scintac XDS-2000, USA) and, the thermogravimetric property of particles was obtained by 2050 TGA analyzer. Particle size was measured by scanning electron microscopy(SEM : I.S.I - DS 130, Japan) and particle size analyzer(LPA-3100; Otsuka electronics), and photoluminescence(PL) properties of the phosphor were obtained with using Helium-Cadmium Laser(50mW, 325nm; OMNICHROME Co.), and photoluminescence spectrometer system(190nm~1.7 ㎛; SPEX 750M spectrometer).

3. RESULTS AND DISCUSSION

The particle size was controlled by yttrium concentration in precursor solution. At first, the crystallinity of as-synthesized particle was examined. Shown in Fig. 2 is the comparison between particle size and the x-ray diffraction data of yttrium-europium oxide formed by ultrasonic aerosol pyrolysis with different molar concentration for yttrium of precursors. The XRD intensity at 0.025 molar concentration is stronger than the others. As the particle size is decreased, the XRD intensity is decreased. However, dramatic decrease of XRD intensity was observed near 0.0025mole concentration, as shown in Fig 2.

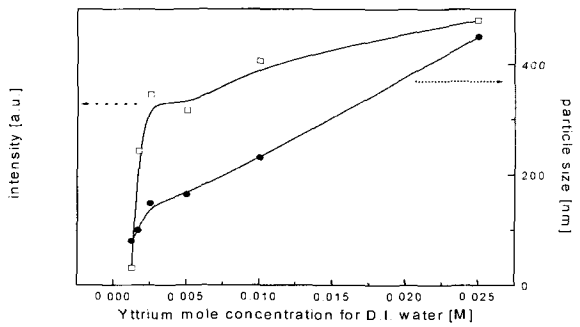
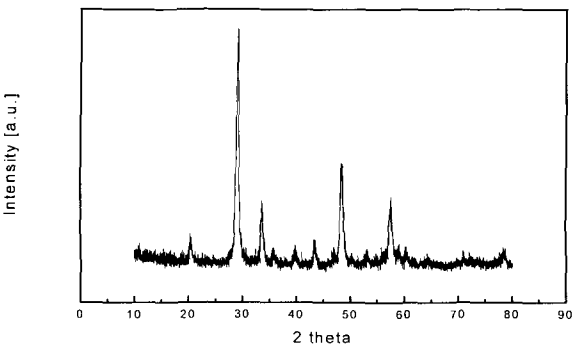
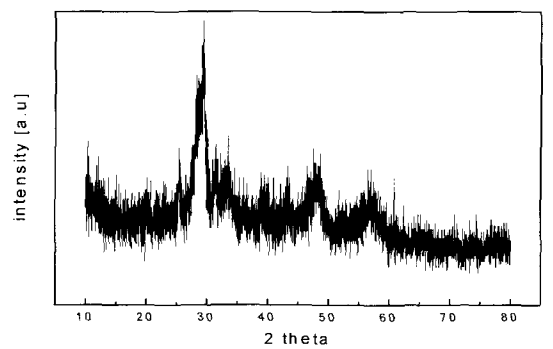


Fig. 2. Comparison between particle size and XRD intensity as molar concentration of Yttrium ions for D.I. water [reaction temperature : 850℃]



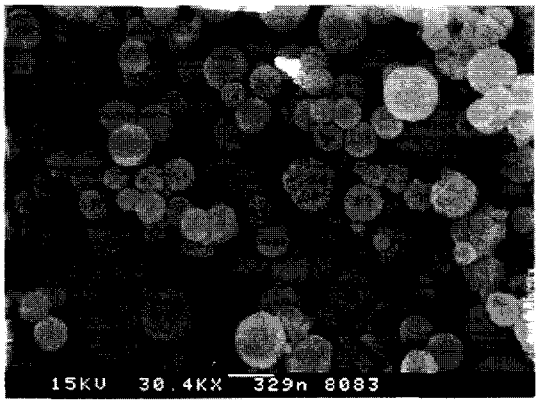
(a) pH4



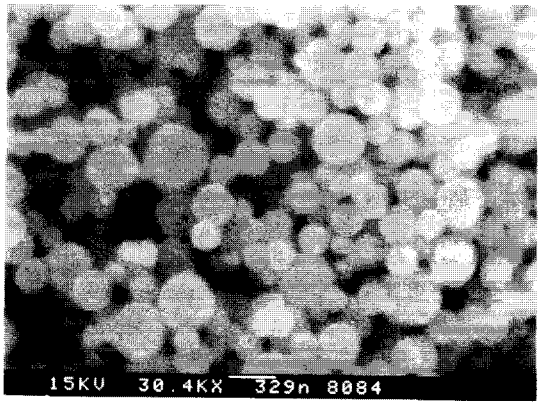
(b) pH7

Fig. 3. Typical XRD spectra of particles prepared by aerosol pyrolysis method.[reaction temperature : 850℃, molar concentration for yttrium : 0.0025M].

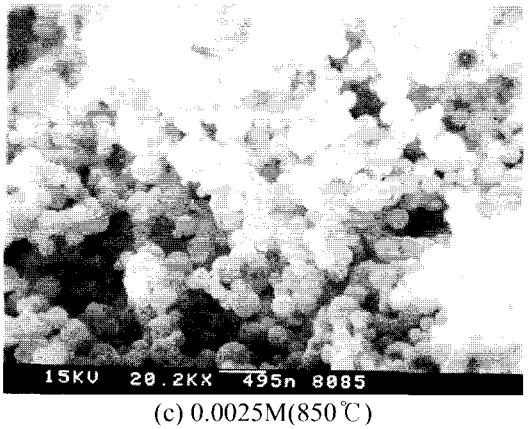
It seems that the properties of bulk material are changed to those of submicron sized-materials when the particle size is approached below 180nm which is about 150 times the Bohr radius of Y_2O_3. Fig. 3 presents the X-ray diffraction spectra about comparison between pH 7 and pH 4. It seems that before the aerosol enter into the furnace, reactions occurred. Actually, when the solution of pH7 is stirred for a long time at 30℃, colloids in the solution are found. It means that the pH control of solution plays major role that it prevents the solution from pre-reaction.



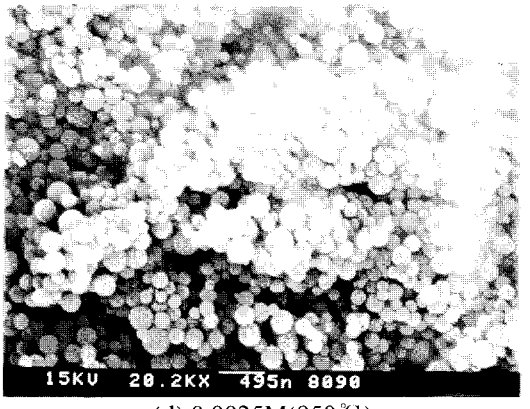
(a) 0.01M(850℃)



(b) 0.005M(850℃)

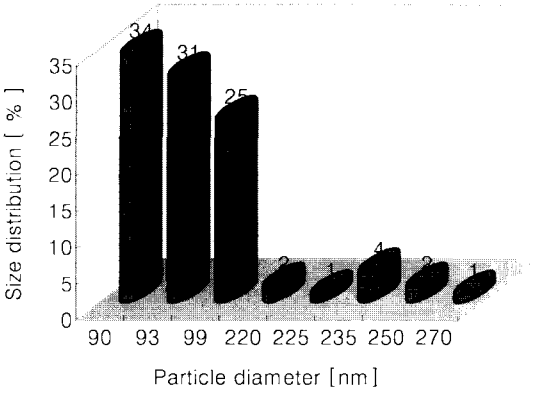


(c) 0.0025M(850℃)

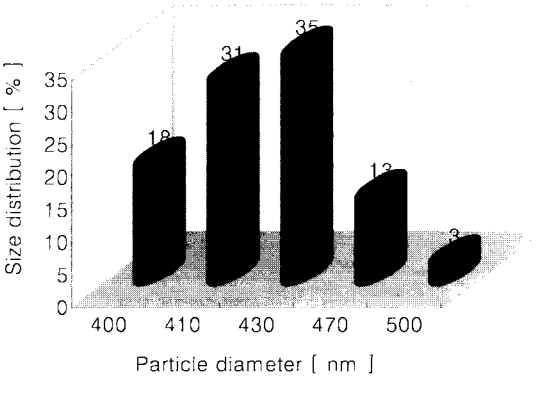


(d) 0.0025M(950℃)

Fig. 4. SEM photographs of luminescent particles synthesized by ultrasonic aerosol pyrolysis method were different mole concentration for yttrium and different reaction.



(a) 0.0025M



(b) 0.01M

Fig. 5. Particle size distribution of Y_2O_3 submicron-sized phosphors by aerosol pyrolysis method.
[molar concentration : reaction temperature : 850℃]

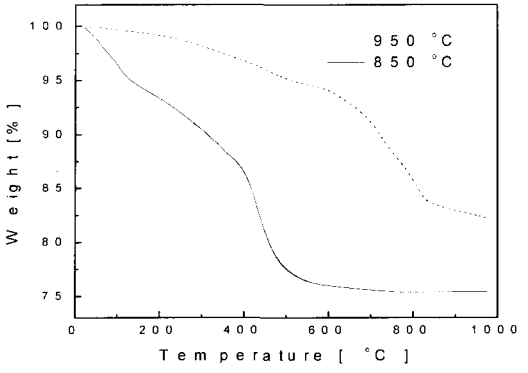


Fig. 6. The thermogravimetric curves as different reaction temperatures of Y_2O_3 submicron-sized phosphors by aerosol pyrolysis method. [molar concentration : 0.00125 M].

Figure 4 (a)~(c) shows the particle morphology and size of yttrium-europium oxide formed by ultrasonic aerosol pyrolysis with different molar concentration for yttrium; [0.01M(a), 0.005M(b), 0.0025M(c) : 850℃ of reaction temperature], respectively. They exhibit that particles had a narrow size distribution, spherical submicron-sized, together with a narrow size distribution as indicated in Fig. 5 (a) and (b). With the decrease in molar concentration of yttrium from 0.01 to 0.0025M, particles in the size range of 400~470nm were diminished to about 95nm, but the diminishment of the particles did not result in a change of shape. This result might be due to the fact that particles were synthesized in the limited region of aqueous droplets. Obviously, the particle size might be decreased as the molar concentration of yttrium is decreased. Also, Fig. 4 (c) and (d) shows morphology of particles about reaction temperature[(c) 850℃, (d) 950℃; 0.0025M of molar concentration]. Particle size of Y_2O_3:Eu synthesized at 950℃ reaction temperature was smaller than that of the particles at 850℃. The reason is found Fig. 6, which shows the themogravimetric curves about different temperature. Thermal stability at 950℃ is better than the one at 850℃. It means that Y_2O_3 at 950℃ contains a few impurities in comparison with the one at 850℃.

Figure 7 presents Fourier transformed infrared (FT-IR) spectra of particles prepared by aerosol pyrolysis method. As shown in Fig. 7(b), particles made at pH7 exhibited absorption bands around 3450, 1380, and 1270 cm^{-1}. These absorption bands were due to the pre-product made for stirring period, and hydrated water (hydroxide, 3450 cm^{-1}; aryl-O, 1380 cm^{-1}; O-NO_2, 1270 cm^{-1}). In Fig. 6(a), it was found that particles made at pH4 had no bands of the pre-product. It seems that the pH control is very important in the purification of the particle.

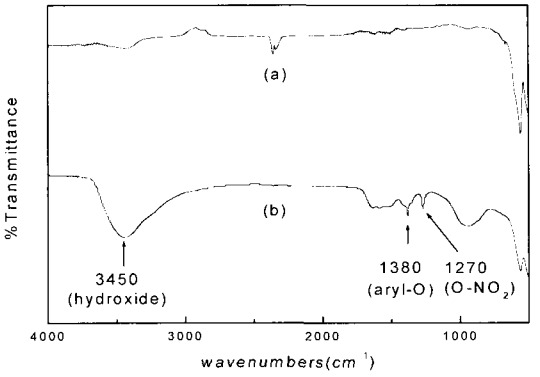


Fig. 7. FTIR spectra of Y_2O_3:Eu particles synthesized through a micro emulsion system. pH4(a) and pH7(b).

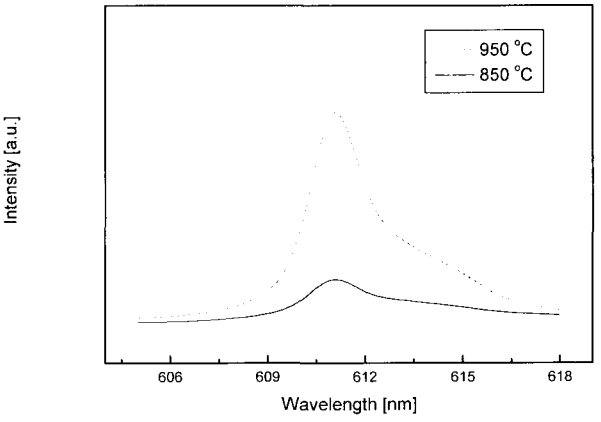


Fig. 8. Photoluminescence (PL) of Y_2O_3:Eu particles performed with an excitation wavelength 325nm as different reaction temperatures.

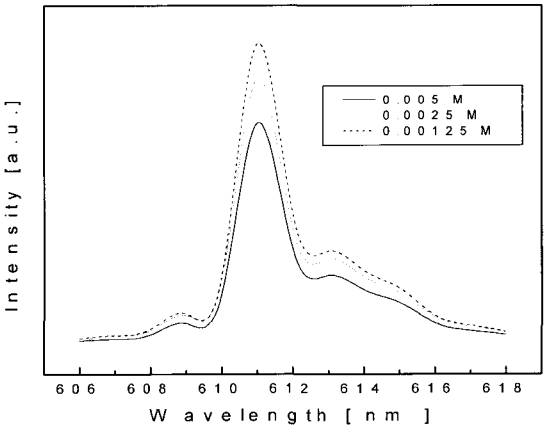


Fig. 9. Photoluminescence (PL) of Y_2O_3:Eu particles performed with an excitation wavelength 325nmas variable molar concentration of yttrium.

Figure 8 shows PL emission spectra of Y_2O_3:Eu phosphors which are prepared with different reaction temperature; 850℃(solid line), 950℃(dotted line), respectively. As the reaction temperature was increased from 850℃ to 950℃, the PL intensity was increased 4 times. It might be due to the impurity densities as shown in Fig. 5(c) and (d). Fig. 9 exhibits PL emission spectra of Y_2O_3:Eu phosphors which are prepared with variable molar concentrations. The measurements were performed at the same conditions for all particles. As shown in Fig. 8, the emission spectra were the same shape with the peak position at 611nm, quite similar to those by other groups. These emission lines are assigned to the transition from $^5D_0$ excited state to $^7F_2$ states within the $4f^6$ configuration of europium. As the particle size is decreased, the emission peak is increased. This result might be attributed to the size effect, which comes from high probability of optical transition as expected. This assertion may be supported by the fact that the PL intensity is increased even though XRD intensity is dramatically decreased as shown in Fig. 2.

4. CONCLUSION

In conclusion, europium doped yttrium oxide submicron-sized particles were successfully prepared by ultrasonic aerosol pyrolysis method. The particles had a narrower size distribution, spherical shape. The PL efficiency of submicron-sized particles formed was inversely increased with size due to the quantum effect, which may be ascribed to the submicron-size. However, when the particle size is fallen above about 150 times of Bohr radius of Y_2O_3, the properties of the particles shows the bulk properties.

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