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# $Y_2SiO_5$: Ce Phosphor Particles 0.5–1.4 μm in Size with Spherical Morphology

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**Ce-doped $Y_2SiO_5$ phosphor particles with spherical morphology, small size, high crystallinity, and good photoluminescence (PL) intensity were prepared by spray pyrolysis. The characteristics of prepared particles were compared with those of commercial ones. The particles annealed above 1000°C had a clear crystallinity of $Y_2SiO_5$, and the crystal structure changed from $X_1$ to $X_2$ type after annealing above 1200°C. The mean size of the particles increased from 0.5 to 1.4 μm when the overall solution concentrations were varied from 0.045 to 0.9 mol/liter. The photoluminescence intensity and crystallinity of particles increased as the particle size and preparation temperature were increased. The annealed particles larger than 0.8 μm maintained a spherical morphology. Emission of blue light was observed after annealing above 1000°C on excitation with an UV light. The PL spectra particles annealed below 1100°C had maximum values at 450 nm, and shifted to the smaller wavelengths after annealing above 1200°C. The brightness of particles increased with increasing annealing temperatures due to favorable crystallization and had a maximum at 1400°C. The particles annealed above 1400°C exhibited intensities higher than those of particles produced commercially.** © 1999 Academic Press

***Key Words:*** **$Y_2SiO_5$:Ce; photoluminescence; blue phosphor; particles; spherical morphology.**

## INTRODUCTION

Various types of multicomponent oxide phosphors have been widely studied for use in display technologies such as high definition (HD), projection televisions (PTVs), and flat panel displays (FPDs). To improve the performance of these devices, the phosphor particles must have a narrow size distribution, a small particle size (about 1 μm), and a spherical morphology and, in addition, must be nonagglomerated, for good luminescent characteristics.

Phosphor materials are usually prepared via solid-state or aqueous reactions (1–5). The solid-state route requires high reaction temperatures, long heating times, and a milling process to obtain the pure phase of the multicomponent particles. Therefore, particles produced by this route are agglomerated particles of irregular shape. In addition, the milling process reduces the brightness due to destruction of the surface structure of the phosphor materials. By comparison, aqueous solution methods use low preparation temperatures; however, the resulting particles have an irregular and agglomerated morphology.

Yttrium silicate ($Y_2SiO_5$) is a good host material for cathodoluminescent phosphors. Some investigations on the luminescence properties of Tb- and Eu-doped $Y_2SiO_5$ phosphor materials prepared by solid-state reaction (6–8) and sol–gel method (9) have been reported. Others have reported on the properties of Ce-doped $Y_2SiO_5$, which produces a blue color when energized. Chakhovskoi *et al.* (10) investigated the luminescence properties of 12- and 30-μm-thick particulate layers of phosphors prepared by combustion synthesis. The brightness of the samples was found to be proportional to the thickness layer. Lee *et al.* (11) examined commercially available $Y_2SiO_5$:Ce phosphors prepared by solid-state reaction which had average particle sizes of 10 and 20 μm and a polyhedral shape. The luminescence properties of phosphors of different particle sizes were almost identical. No significant difference in luminescence behavior was detected after further sorting by settling in a centrifuge to obtain 4-, 6-, and 9-μm phosphor particles. They postulated that this lack of size dependence was due to the fact that all particles came from the same phosphor; e.g., the crystallite size is expected to be similar.

All of the commercial products are larger than 5 to 10 μm and of irregular morphology. The previous research was performed on particles on the order of 10 μm. Moreover, the previous studies did not show the morphology of their material. No detailed study relating morphology and crystallinity to the luminescence properties of the phosphor has been performed to date. In this study, we report on the

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preparation of spherical $Y_2SiO_5$:Ce phosphors with a particle size on the order of 1 μm or smaller. Particles are produced by spray pyrolysis. The effect of changes in particle size, crystallinity, and morphology on photoluminescence were investigated. In addition, the characteristics of the particles were compared with those of a commercial product.

## EXPERIMENTAL

Our experiments were conducted in an apparatus described in detail elsewhere (12). An ultrasonic nebulizer was used as the spray generator. A two-step process was used to prepare the multicomponent oxide phosphor particles: production of the particles from spray pyrolysis of a precursor solution into a hot-wall reactor followed by annealing in a second furnace to induce crystallization. Particles prepared by spray pyrolysis are generally spherical and nonaggregated because only one particle is produced per droplet. However, the multicomponent particles directly prepared by spray pyrolysis are amorphous and, thus, not activated due to their short residence time inside the hot-wall reactor. Therefore, an additional annealing step using a box-type furnace is necessary to induce crystallization. This crystallization of the particle is required for the dopant to enter the crystal structure, activating the phosphor.

The precursor chemicals used were tetraethyl orthosilicate (TEOS), yttrium nitrate, and cerium nitrate. A small amount of nitric acid was added to prepare homogeneous liquid solutions. The amount of cerium in solution was changed from 0.1 to 3 at.% to investigate which level of doping leads to optimum photoluminescence. The overall solution concentration ($C_s$) was varied (0.045, 0.15, 0.45, and 0.9 mol/liter) to change the mean size of the phosphor particles. The flow rate of the carrier gas and the temperature of the hot-wall reactor were 2 liters/min and 900°C, respectively. The residence time of particles inside the reactor was 1.6 s. The as-prepared particles were annealed at a variety of temperatures above 800°C for 5 h. The commercial product (P47) was fabricated by solid-state synthesis. However, the heating time and temperature have not been reported in detail. The particles were characterized by X-ray diffraction (XRD, Rigaku-Denki Corp., Model RINT 1000), scanning electron microscopy (SEM, Hitachi Corp., Model S-3100H2), and spectrophotometry (Shimadzu Corp., Model RF-53009c).

## RESULTS AND DISCUSSIONS

The particles prepared from the stoichiometric solution of TEOS and yttrium nitrate did not have a pure crystalline phase of $Y_2SiO_5$ in the XRD spectra due to the high volatility of TEOS. Because of the low boiling point (165°C) of TEOS, some TEOS may evaporate from droplets before the pyrolysis. Figure 1 shows the XRD spectra of particles

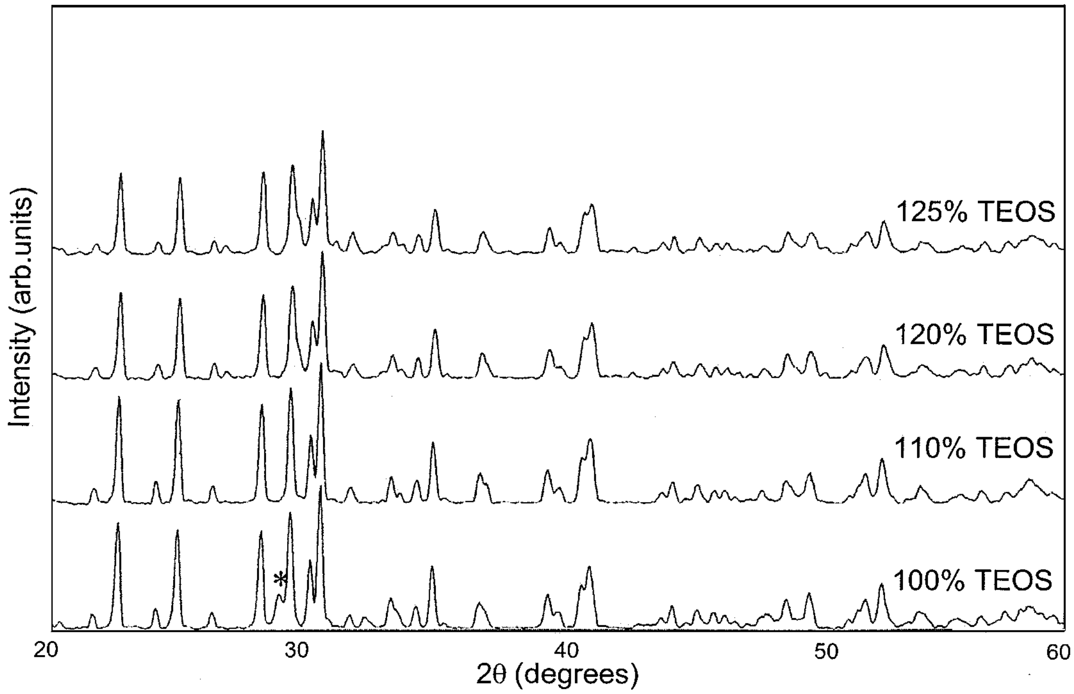

**FIG. 1.** XRD spectra of particles prepared from different ratios of TEOS to yttrium nitrate. The as-prepared particles ($C_s = 0.45$ mol/liter) were annealed at 1300°C for 5 h. The asterisk indicates the $Y_2O_3$ phase.

prepared from different ratios of TEOS of yttrium nitrate and a solution concentration ($C_s$) of 0.45 mol/liter. The as-prepared particles were annealed at 1300°C for 5 h. The particles prepared from the stoichiometric solution of TEOS and yttrium nitrate had small peaks corresponding to $Y_2O_3$ existing as an impurity. When the amount of TEOS was increased to 110–125% of the stoichiometric amount, the pure phase of $Y_2SiO_5$ was obtained.

Figure 2 shows the XRD spectra of particles ($C_s =$ 0.45 mol/liter) annealed at different temperatures. All of the particles in the figure were prepared from a solution in which the amount of TEOS was 125% above stoichiometric. The particles annealed at 900°C or below had poor crystallinity because of the amorphous structure of the as-prepared particles due to the short residence time inside the hot-wall reactor. However, the particles annealed above 1000°C had clear $Y_2SiO_5$ crystallinity. $Y_2SiO_5$ is polymorphic and crystallizes in either the monoclinic $X_1$ or $X_2$ type, depending on the synthesis temperature (6). In this work, the $X_2$ type appeared after annealing at 1200°C and particles with complete $X_2$ crystallinity were obtained above 1300°C. Using Scherrer's equation, crystallite size ($D_c$) of the samples was estimated from the XRD spectra. The results show that $D_c$ is approximately 28 nm for the particles annealed at 1100°C and 43 nm at 1300°C, and it increased to 46 nm after annealing at 1500°C. The commercial product (P47) has a $D_c$ of 48 nm.

Figure 3 comprises scanning electron micrographs of the particles prepared by spray pyrolysis ($C_s = 0.45$ mol/liter) annealed at various temperatures and the commercial product. The as-prepared particles (Fig. 3a) have spherical morphology, are submicrometer in size, are nonagglomerated, and have a narrow size distribution. For a solution concentration of 0.45 mol/liter, the mean size of the as-prepared particles measured from the scanning electron micrographs was 1.1 μm. Agglomeration of particles had not occurred, even after annealing at 1200°C. Particles began to agglomerate at an annealing temperature of 1300°C, and the degree of agglomeration increased with increasing annealing temperature. However, one can see from Fig. 3c that although agglomerated, the annealed particles at 1300°C maintained a spherical morphology. By comparison, the commercial particles (Fig. 3e) are irregular in shape and large (about 6 μm).

Figure 4 shows the emission spectra of $Y_2SiO_5$:Ce particles prepared from spray solutions with different ratios of TEOS to yttrium nitrate at an excitation of 366 nm. In Fig. 4, the as-prepared particles ($C_s = 0.45$ mol/liter) were annealed at 1300°C for 5 h. The emission spectra have broad peaks between 370 and 500 nm, resulting in the dominant blue emission. These emission characteristics of $Y_2SiO_5$:Ce particles coincide well with the results reported by Lee *et al.* (11). The photoluminescence (PL) intensities were strongly affected by the ratio of TEOS to yttrium

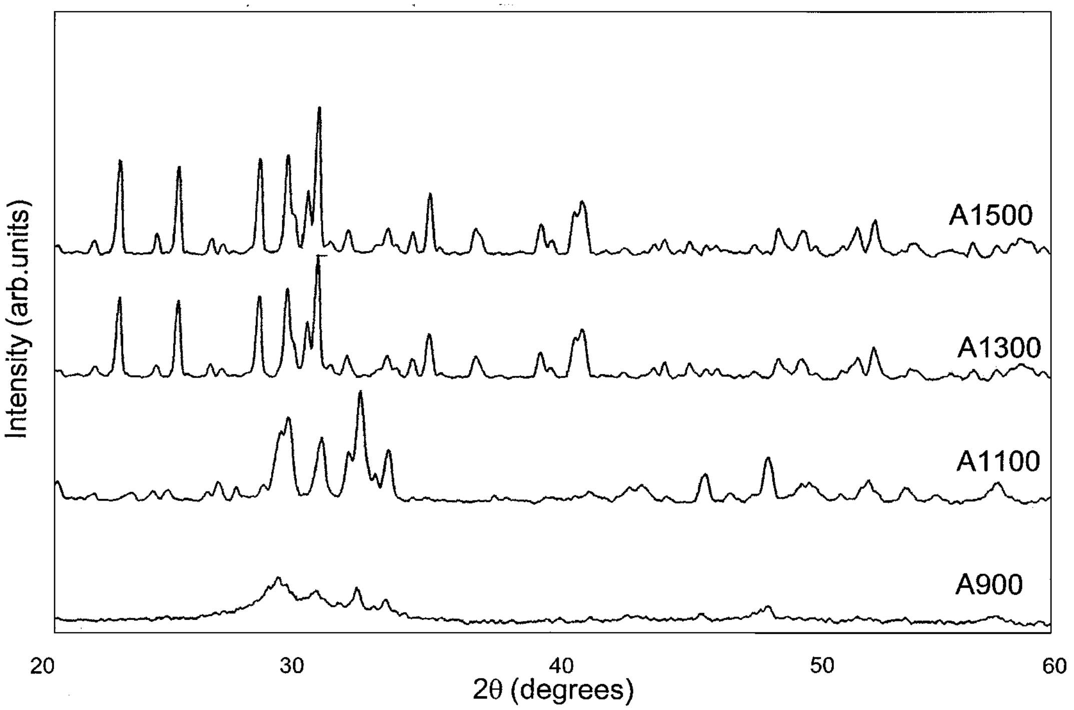

**FIG. 2.** XRD spectra of particles annealed at different temperatures. $C_s = 0.45$ mol/liter, TEOS = 125%.

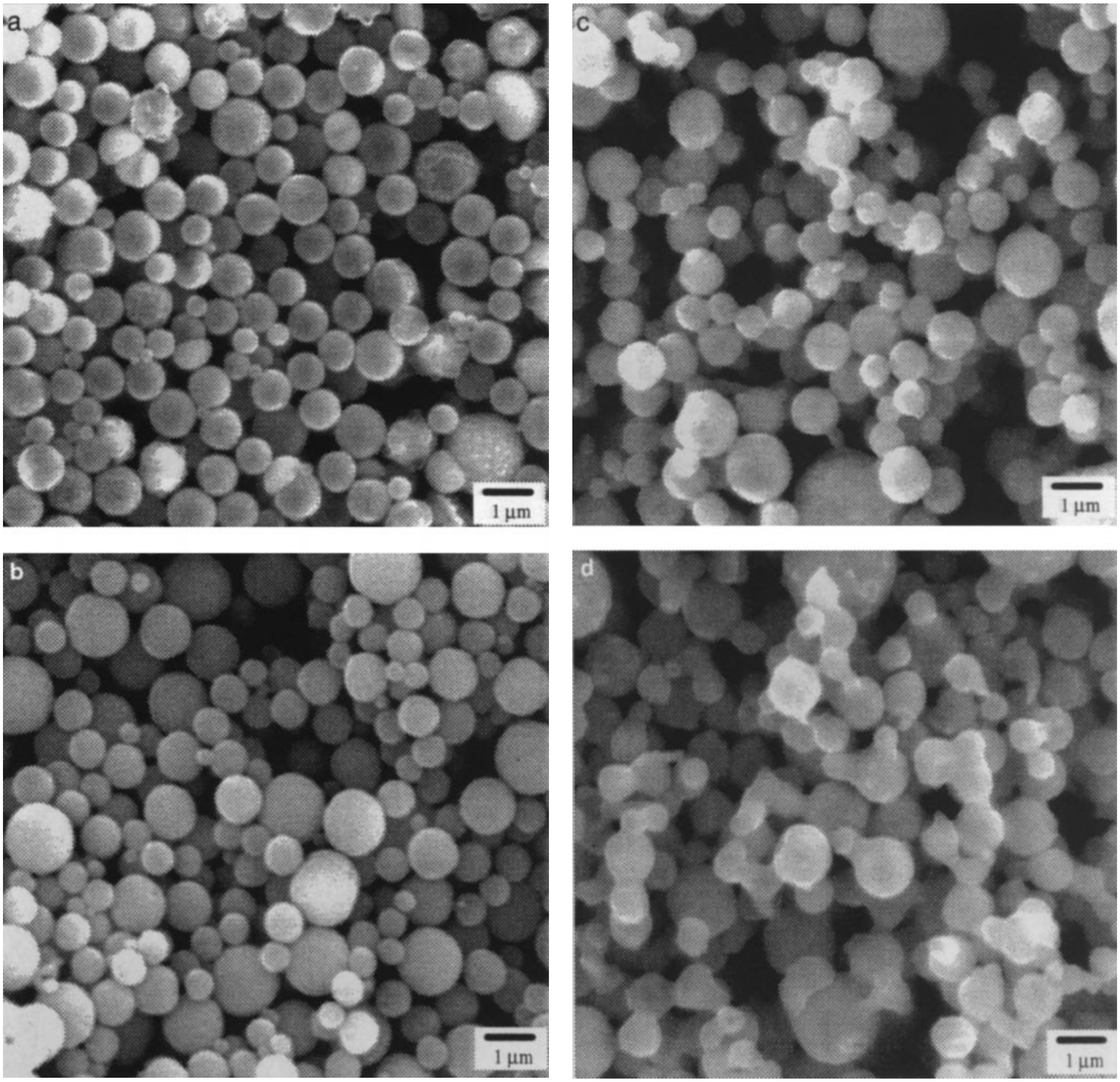

**FIG. 3.** Scanning electron micrographs of prepared ($C_s = 0.45$ mol/liter) and commercial particles: (a) as-prepared particles, (b) annealed at 1200°C, (c) annealed at 1300°C, (d) annealed at 1400°C, (e) commercial product (P47).

nitrate. The maximum PL intensity comes from particles prepared with a ratio of TEOS to yttrium nitrate of 125%, and is twice the intensity measured in particles prepared from the stoichiometric solution (100% TEOS).

Figure 5 shows the PL spectra of particles prepared at different doping concentration of Ce. It is apparent from the figure that the brightness of the emission from the particles was strongly affected by doping concentration. Optimum brightness was obtained at a doping concentration of 0.7 at%.

In Fig. 6, the effect of annealing temperature on the brightness of $Y_2SiO_5$:Ce particles is illustrated. The PL spectrum of the commercial product (P47) is shown for comparison. The particles prepared from a solution with a TEOS at 125% of stoichiometric were annealed at different temperatures for 5 h. The brightness of the emission

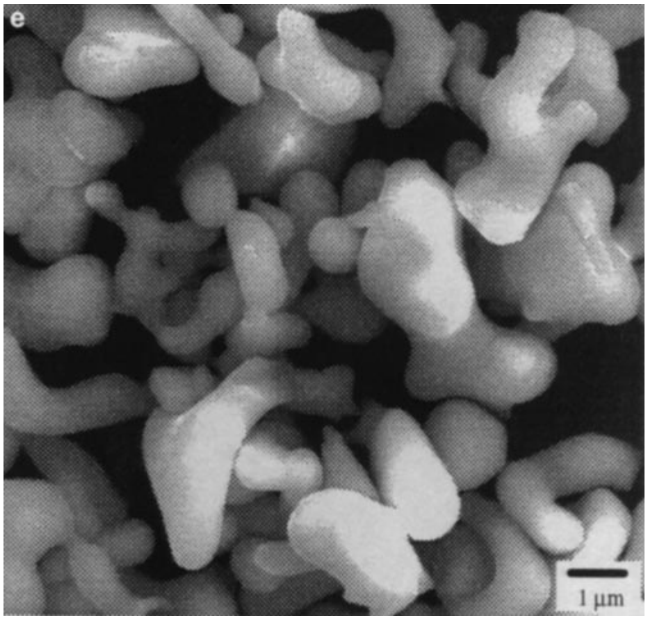

**FIGURE 3**—*Continued*

from the particles is strongly affected by the annealing temperature. Blue light was obtained after annealing at 1000°C when excited with UV light. The PL spectra of particles annealed below 1100°C had maximum values at 450 nm, and shifted to smaller wavelengths after annealing above 1200°C. The crystalline phase change of particles

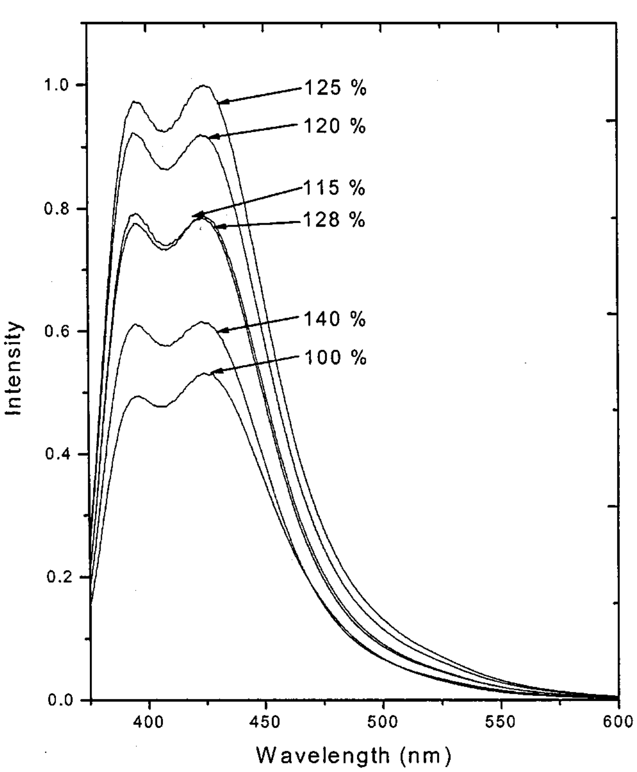

**FIG. 4.** PL spectra of particles from different ratios of TEOS of yttrium nitrate. The as-prepared particles ($C_s = 0.45$ mol/liter) were annealed at 1300°C for 5 h.

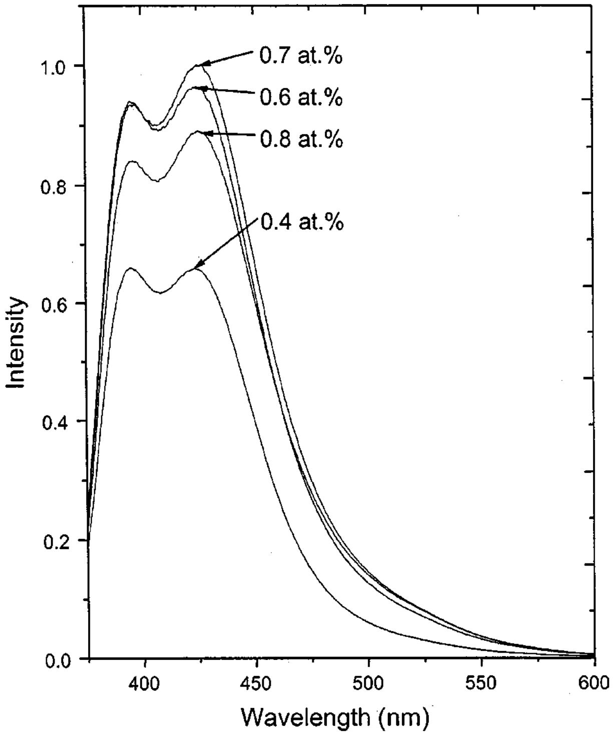

**FIG. 5.** PL spectra of particles at different doping concentration of cerium. $C_s = 0.45$ mol/liter.

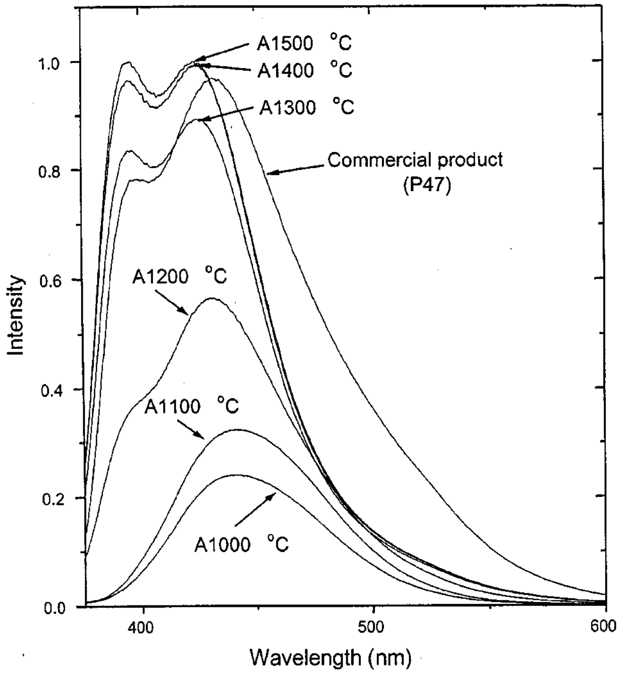

**FIG. 6.** PL spectra of particles obtained at different annealing temperatures at 5 h. $C_s = 0.45$ mol/liter, TEOS = 125%.

above 1200°C caused the shift of PL peaks. As previously discussed the $X_2$ crystalline type appeared after annealing above 1200°C, and particles with complete $X_2$ type were obtained above 1300°C. The brightness of particles increased with increasing annealing temperatures and had a maximum value at 1400°C. The PL intensity of particles annealed at 1300°C for 5 h was 92% that of the commercial particles (P47).

The mean size of particles produced by spray pyrolysis can be controlled by changing the solution concentration. Figure 7 comprises scanning electron micrographs of the as-prepared particles obtained from different solution concentrations. As the concentration increases from 0.045 to 0.9 mol/liter, the particle size increases from 0.5 to 1.4 μm. These as-prepared particles were annealed at 1300°C for 5 h. The results show that smaller particles, shown in Figs. 7c and 7d, tend to agglomerate more readily during the annealing process.

Figure 8 shows X-ray diffraction patterns of $Y_2SiO_5$:Ce particles obtained from different solution concentrations under the same conditions as used in Fig. 7. All peaks assigned to the complete $X_2$-type phase can be seen for all solution concentrations, but the peak height tends to decrease with decreasing solution concentration, corresponding to a decrease in crystallite size. The value of $D_c$ is around 49 nm for 0.5- and 0.8-μm particles, 41 nm for 1.1-μm particles, and approximately 66 nm for 1.4-μm particles. As a reference, the spectra of the commercial product (P47), having a $D_c$ around 48 nm, are also shown.

Figure 9 shows the PL spectra of the phosphor particles obtained by varying the solution concentration. The PL intensity of phosphors seems to increase with increasing

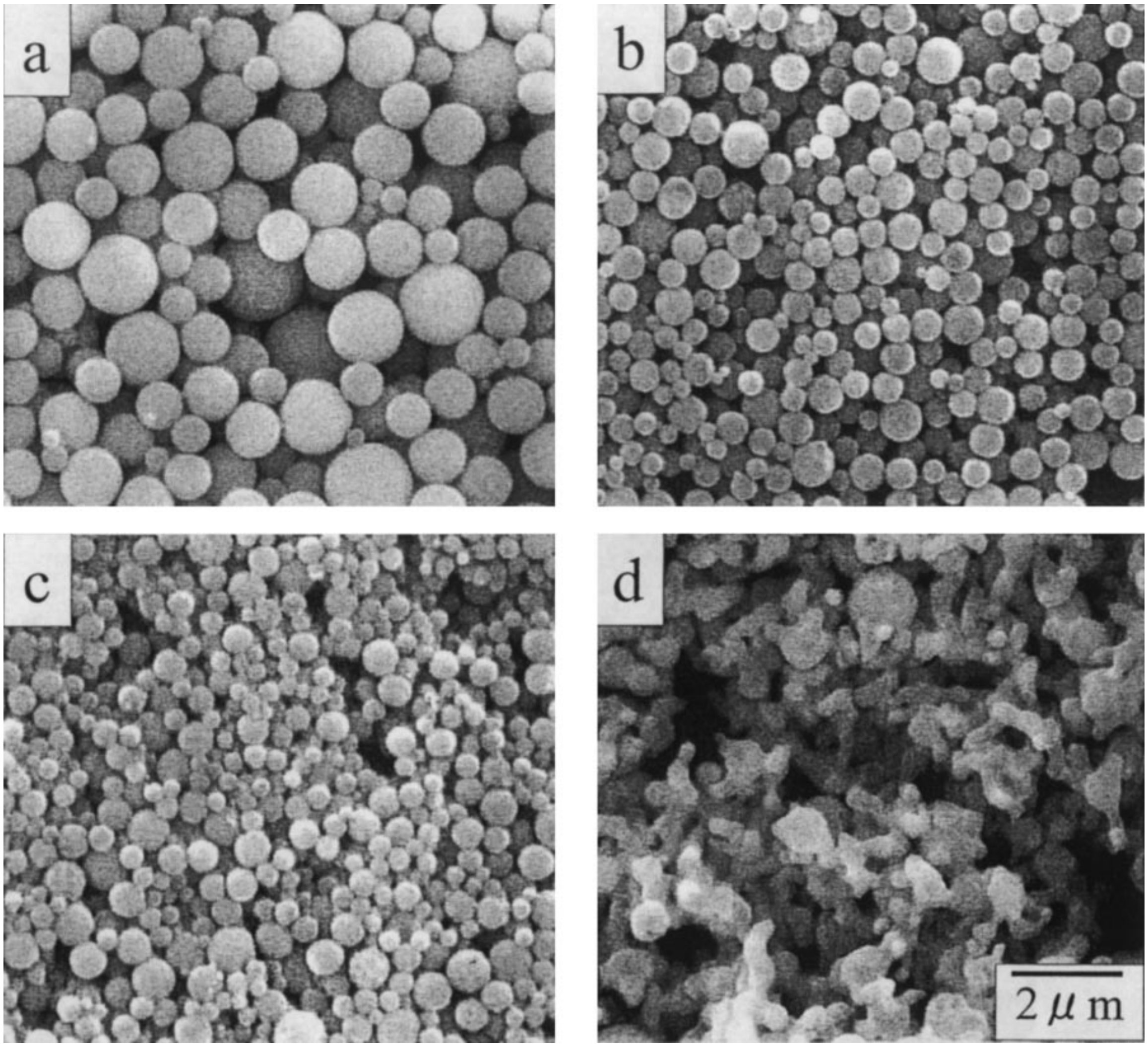

**FIG. 7.** Scanning electron micrographs of as-prepared particles from solution concentrations of (a) 0.6, (b) 0.1, (c) 0.03 mol/liter. (d) Annealed particles of (c). Experimental conditions: TEOS = 125%, Ce = 0.7 at.%, annealing temperature = 1300°C (5 h).

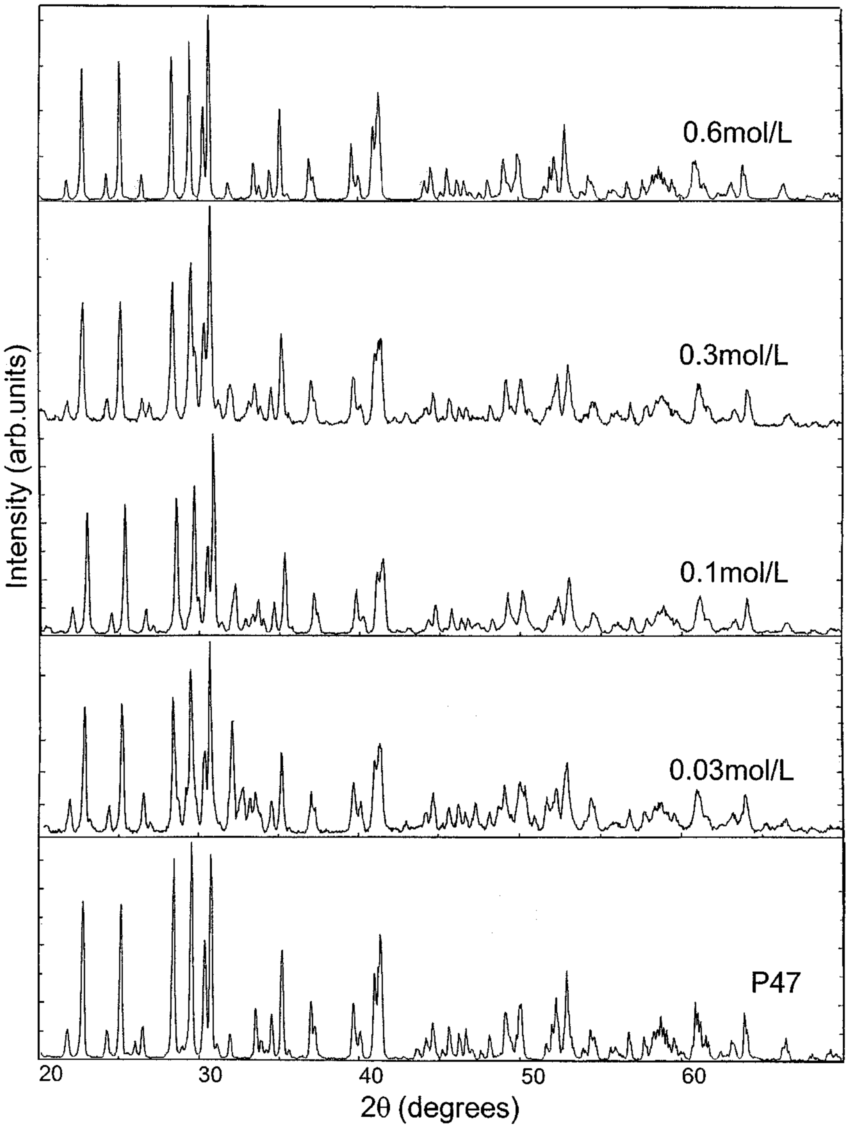

**FIG. 8.** XRD spectra of annealed particles of different size prepared by varying solution concentrations (the legend) and commercial product (P47). Experimental conditions are the same as in Fig. 7.

particle size. There is currently no theory that describes the influence of particle size on photoluminescence characteristics. Therefore, it is difficult to discuss the relation between PL and particle size or morphology.

A direct comparison between our results and those for the commercial product is not entirely appropriate, in that the commercial product was optimized for a specific application. However, it should be noted that the particles annealed above 1400°C had PL intensities as high as that of the commercial product. We can conclude that the phosphor particles obtained by spray pyrolysis in the current study had characteristics such as crystallinity and morphology that produced good photoluminescence. The results highlight the fact that spray pyrolysis has many advantages for the preparation of multicomponent phosphor particles. More research is needed to increase our understanding of the effect of particle size and crystallinity on the performance characteristics of the phosphors to support innovations in the field.

## CONCLUSIONS

Fine particles of cerium-doped yttrium silicate phosphors of different size were prepared by an ultrasonic spray-pyrolysis technique using various concentrations of the precursor solutions. Well-crystallized phosphor particles were obtained after annealing of the as-prepared, amorphous nonactivated particles. The characteristics of the particles

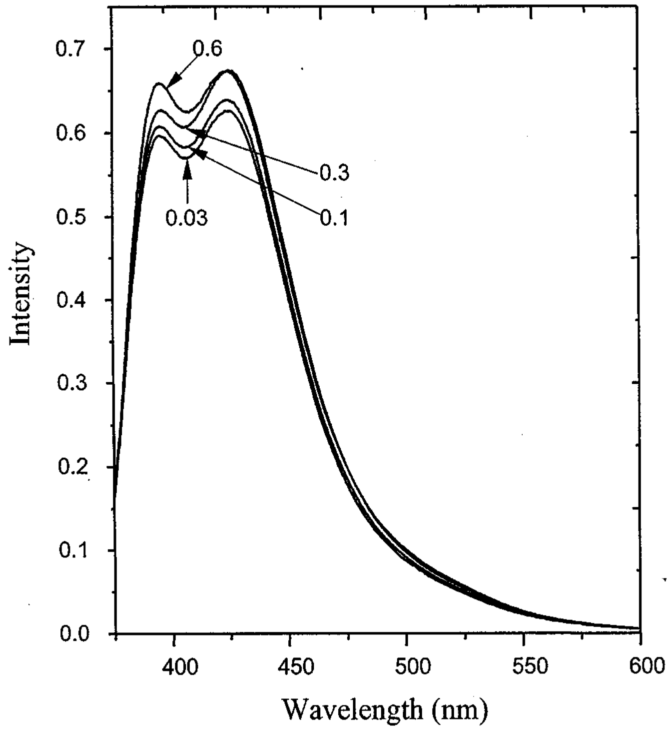

**FIG. 9.** PL spectra of particles from different solution concentrations (the legend is in mol/liter). PL intensity is normalized to that of the commercial product. Experimental conditions are the same as in Fig. 7.

obtained by spray pyrolysis such as PL intensity, mean size, and morphology were measured and compared with those of the commercial product. The $Y_2SiO_5$:Ce phosphor particles prepared by spray pyrolysis showed spherical morphology, small size, and good PL intensities. The particles were relatively uniform in size and composition. Additionally, the annealed particles were nonagglomerated after annealing at 1300°C, a temperature that also resulted in good crystallization and PL intensity of the phosphor particles. This study also indicates that changing the concentrations of starting solutions affected the size, crystallinity, and photoluminescence behaviors of the particles.

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