JOURNAL OF MATERIALS SCIENCE **37** (2002) 2721 – 2729

Preparation of Sr_2CeO_4 blue phosphor by ultrasonic spray pyrolysis: effect of NH_4NO_3 addition

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A blue emission Sr_2CeO_4 phosphor powder which has a one-dimensional structure was prepared from a nitrate starting solution by the ultrasonic spray pyrolysis process. To avoid the formation of hollow particles during spray pyrolysis, NH_4NO_3 was employed to change the mechanism of Sr_2CeO_4 formation from droplets, containing $Sr(NO_3)_2$ and $Ce(NO_3)_3$ in the required stoichiometric ratio. The mean particle size of as-prepared particle increased from 0.19 to 1.52 μm with a change in the overall concentration of the starting solution from 0.005 to 1.5 M. No hollow particles or particle fragments were observed when the ratio of overall concentration of the starting solution to NH_4NO_3 was equal to 1 : 1. The particles that were as-prepared with NH_4NO_3 had spherical morphology and a narrow size distribution. The emission spectrum of post heat-treated particles showed a broad maximum at 470 nm and the CIE Chromaticity coordinates were $x = 0.20$ and $y = 0.27$. The decay time of Sr_2CeO_4 phosphor powder was 58 μs, which is a long excited-state life time compared with *d-f* transitions for the Ce^{3+} excited state. *© 2002 Kluwer Academic Publishers*

1. Introduction

An unusual luminescent inorganic oxide, Sr_2CeO_4, was identified through combinatorial methods [1]. The structure of single-phase Sr_2CeO_4 shows one-dimensional chains of edgesharing CeO_6 octahedra that are isolated from one another by Sr^{2+} cations. Luminescence originates from a ligand-to-metal Ce^{4+} charge transfer and the emission maximum at 485 nm appears blue-white.

The previous methods of preparing Sr_2CeO_4 phosphor powder generally involve solid-state reactions of the corresponding metal carbonates or oxides at high temperature under air or oxygen atmosphere with subsequent milling of the products to reduce the particle size [2]. These approaches, however, do not allow good control over purity, size, composition, crystallinity or morphology. Liquid-phase routes were also used to prepare Sr_2CeO_4 phosphor powder using a chemical coprecipitation method with metal nitrates and ammonium oxalate. However, those particles prepared by the coprecipitation method have irregular shapes and require milling [3].

Recent studies and development have shown that spray pyrolysis can produce fine spherical particles with a narrow size distribution, high purity and high homogeneity [4–7]. One of the major problems of spray pyrolysis, however, is the formation of hollow particles, especially in methods using nitrates as the starting materials.

To obtain dense spherical particles, preparation conditions resulting in a flat temperature profile and sufficient heating time are considered to be desirable. These operation conditions, however, often lead to decreases in powder production. Another process to prevent the formation of hollow particles is by changing the type of salt. This can be achieved by causing reactions in the starting solution or in the droplets before the solvent completely evaporates. Hsuan-Fu *et al.* [8] introduced NH_3 into the spray pyrolysis process to react with the generated nitrate aerosol droplets. This gas is expected to change the corresponding reactions and formation mechanisms of aerosol-derived particles, resulting in the production of solid particles. The NH_3 in the carrier gas reacts with metal nitrates on the droplet surfaces. However, this is considered to accelerate the formation of a solid crust on the droplet surfaces and to result in hollow particles.

In this study, NH_4NO_3 was added to the starting solution to prevent the formation of hollow particles and fragments of particles. The effect of adding NH_4NO_3 on the morphology of particles and luminescence intensity is discussed.

2. Experimental procedure

The experimental apparatus used in this work is shown in Fig. 1. The starting solution was prepared by dissolving $Sr(NO_3)_2$ and $Ce(NO_3)_3 \cdot 6H_2O$ into distilled water. The overall concentration was varied from

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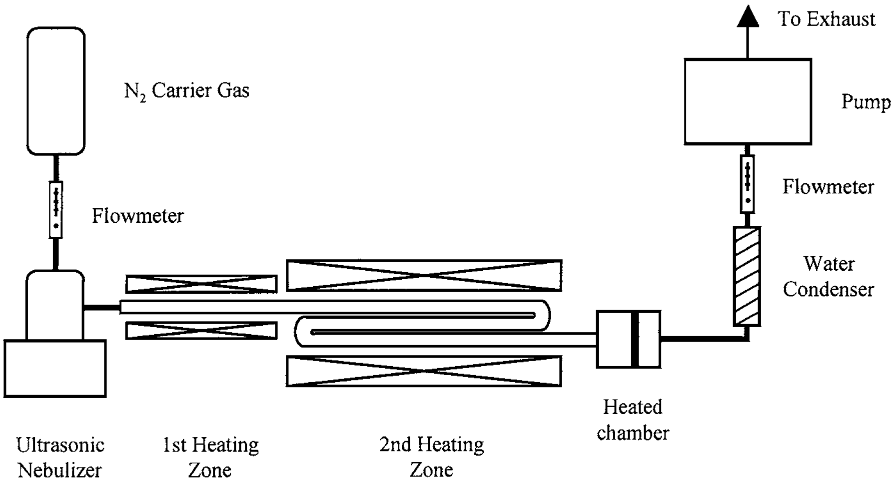


Figure 1 The experimental apparatus for ultrasonic spray pyrolysis.

0.005 to 1.5 M, while the molar ratio of $Sr(NO_3)_2$ to $Ce(NO_3)_3 \cdot 6H_2O$ was kept at 2 : 1. Then, the NH_4NO_3 was added to the starting solution at various concentration. The starting solution was atomized using an ultrasonic nebulizer with a resonant frequency of 1.65 MHz. The aerosol stream was introduced into the first heating zone heated at 300°C to avoid the rapid heating of droplets, then the aerosol stream was passed into the second heating zone. The temperature of the second heating zone varied from 600 to 1100°C. The flow rate of nitrogen carrier gas was 1 ℓ/min. The residence time in the reactor varied from 3.4 to 4.1 s according to reactor temperature. The resulting particles were collected on a glass filter in a glass chamber heated at 300°C to prevent water condensation. As-prepared particles were post heat-treated for 2 h under a nitrogen atmosphere to complete the decomposition of any salts and increase the crystallinity. The post heat-treatment temperature varied from 900 to 1100°C. The crystallinity and morphology of particles were characterized by X-ray diffraction (XRD, Rigaku D/Max Rint 2000) and scanning electron microscopy (SEM, JEOL JSM-840A). The mean particle size and particle size distribution were measured by a particle size analyzer (Laser particle analyzer PAR-III,OTSUKA electronics). The luminescence characteristics of the

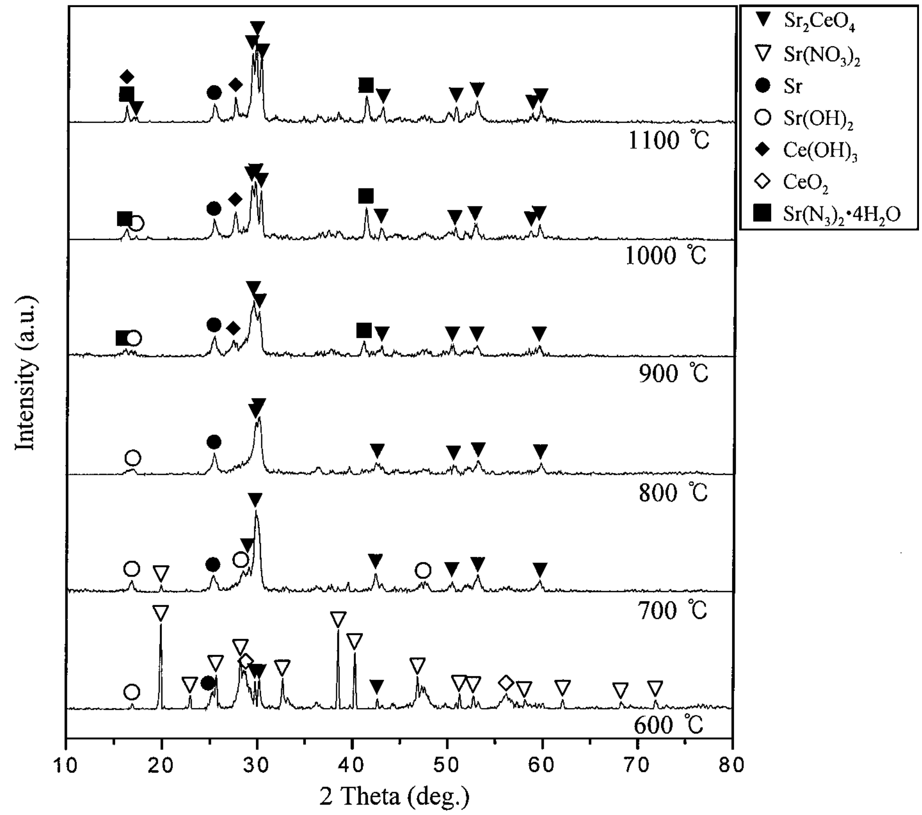


Figure 2 XRD patterns of particles as-prepared at various temperatures. JCPDS data files 22-1422, 25-0746, 15-0305, 27-0847, 19-0284, 34-0394 and 27-0833 were used to identify Sr_2CeO_4, $Sr(NO_3)_2$, Sr, $Sr(OH)_2$, $Ce(OH)_3$, CeO_2 and $Sr(N_3)_2 \cdot 4H_2O$, respectively.

phosphor powder were measured with a spectrophotometer (Perkin Elmer Luminescence Spectrometer, LS50) and time-correlated single photon counting (TCSPC, FL900CD, Edinburgh).

3. Results and discussion

The XRD patterns for particles as-prepared at various temperatures are shown in Fig. 2. Particles as-prepared at 600°C showed the presence of a $Sr(NO_3)_2$ phase. This means that the pyrolysis of the nitrate starting solution was not complete. The main peaks for Sr_2CeO_4 were observed above 700°C, and the crystallinity of the particles was improved by increasing the temperature. However, single-phase Sr_2CeO_4 did not form, even at 1100°C, because of the short residence time in the heating zone. The particles as-prepared at 1100°C

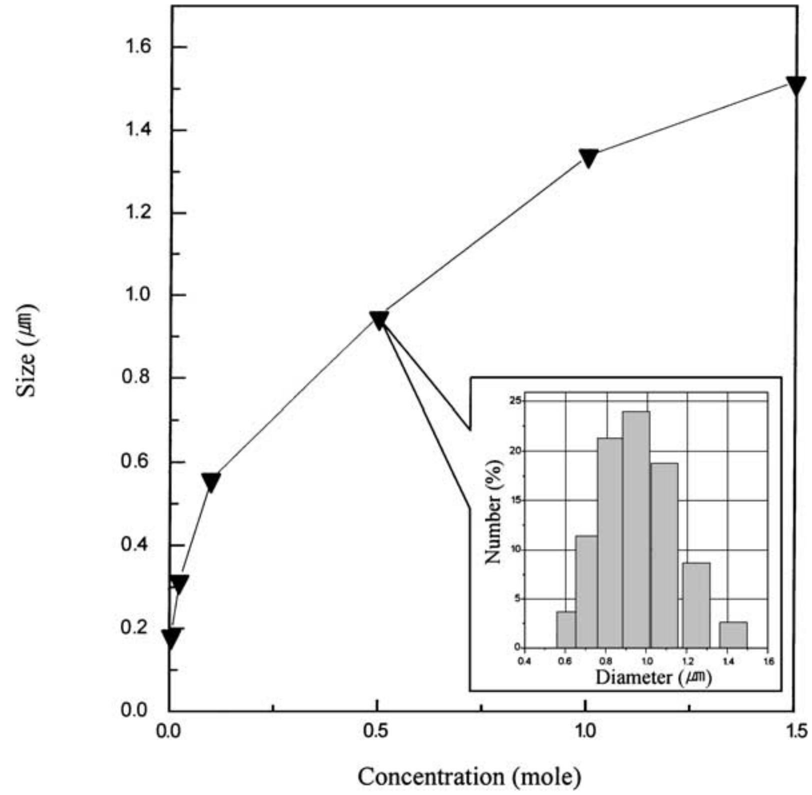
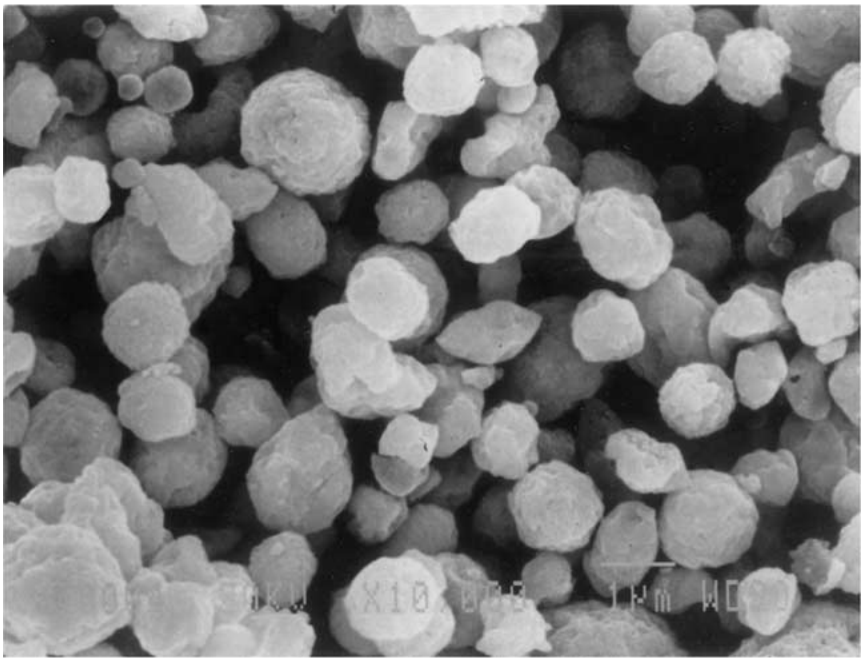


Figure 3 Average size of particles as-prepared with various concentrations of starting solution at 1100°C and particle size distribution of particles as-prepared with 0.5 M starting solution.



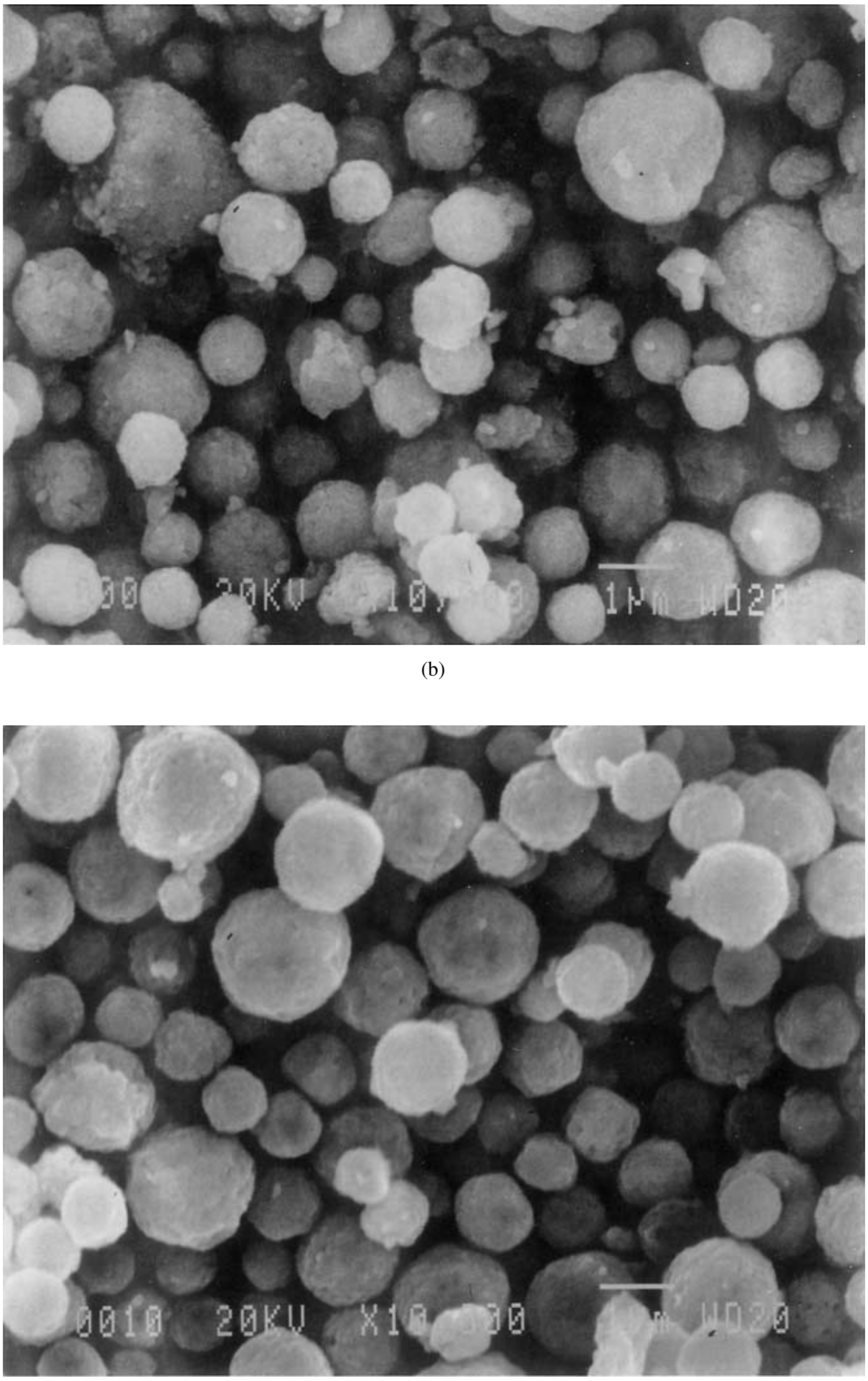
(a)

Figure 4 SEM images of particles as-prepared at 1100°C with various concentrations of NH_4NO_3: (a) none (b) 0.5 M (c) 1.5 M and (d) 3.0 M. *(Continued.)*

contained four different phases: $Sr(N_3)_2 \cdot 4H_2O$, Sr, $Ce(OH)_3$ and Sr_2CeO_4. This shows that the reactions between the intermediate products were not complete. Metal Sr was formed due to the reducibility of ammonia [9] as follows: at high temperatures, above 710°C, $Sr(OH)_2$ decomposes to SrO, which is further reduced to metal Sr by the ammonia in the atmosphere.

In the spray pyrolysis process, the mean size of the particles can be easily controlled from submicrometre to several micrometres in size by changing the concentrations of the starting solution or the type of droplet generator. Fig. 3 shows the mean particle size and particle size distribution of the particles as-prepared with various concentrations of starting solution at 1100°C. The mean particle size increases as the concentration of the starting solution increases. The mean size of as-prepared particles increased from 0.19 to 1.52 μm when the concentration of starting solution was changed from 0.005 to 1.5 mol and the as-prepared particles showed narrow particle size distributions.

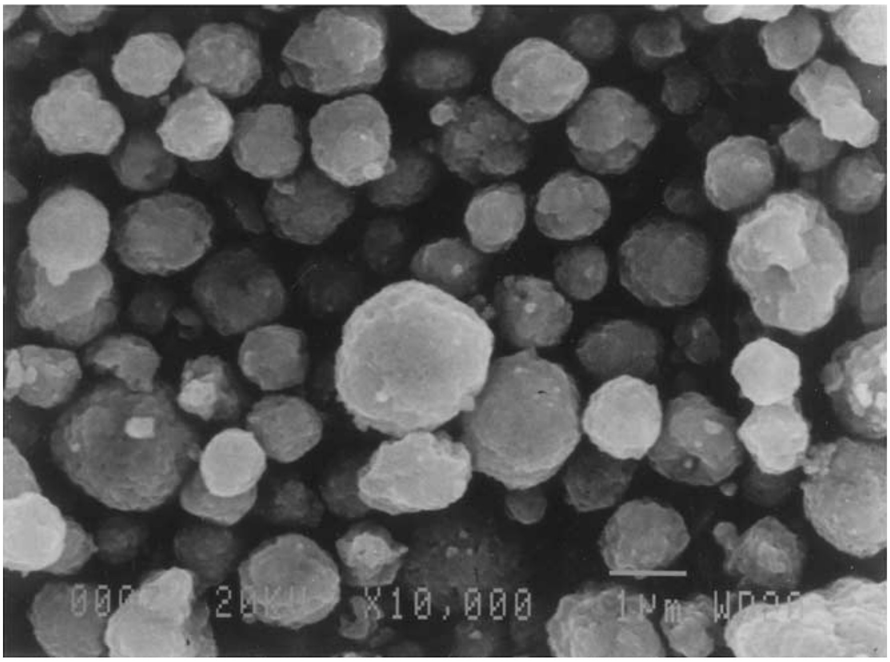
The particles had hollow and crumpled morphologies because of the liquefaction of the nitrate salt particles. This is a typical problem associated with the formation of hollow oxide particles by spray pyrolysis using nitrates as the starting materials [10, 11]. The



(b)

(c)

Figure 4 (Continued.)



(d)

Figure 4 *(Continued.)*

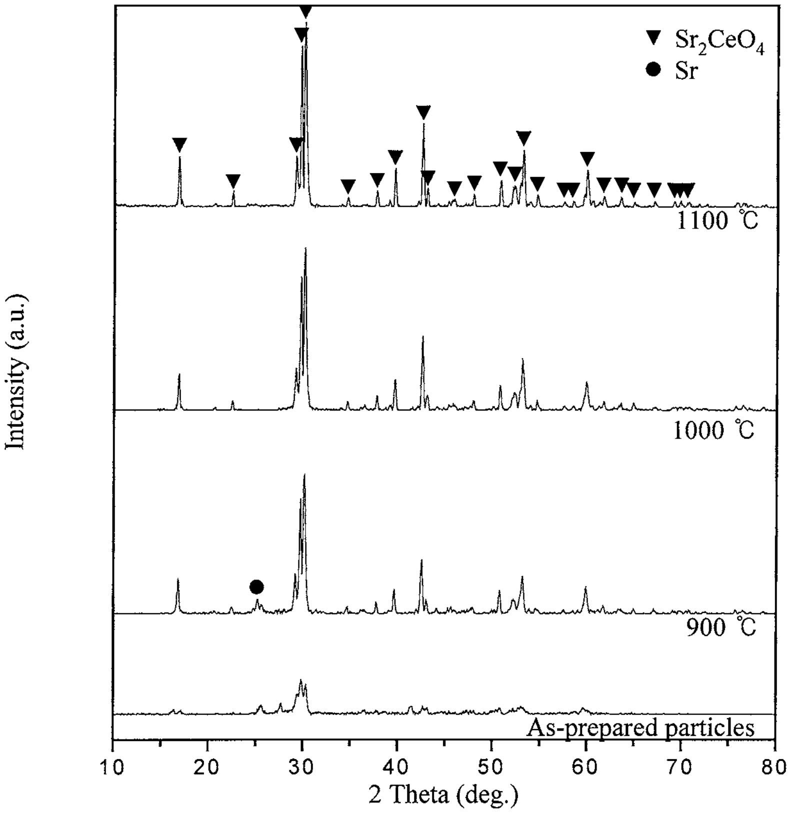


Figure 5 XRD patterns of particles post heat-treated at various temperatures for 2 h.

dried salt particles, which have low melting temperatures, form molten salts during the thermolysis stage and this causes low permeability for the removal of the remaining solvent. As a result of this process, explosion or foaming of the particles takes place and thus gives rise to hollow particles or particle fragments [4]. Che *et al.* [9] showed that the major problem with spray pyrolysis using nitrates as the starting materials can be solved by converting the nitrates into ammine complexes. NH_3 makes an ammine complex which decomposes and precipitates metal hydrate when the dropets are heated. This reaction takes place within the whole droplet instead of only on the surface of the droplet, thus giving rise to volume precipitation

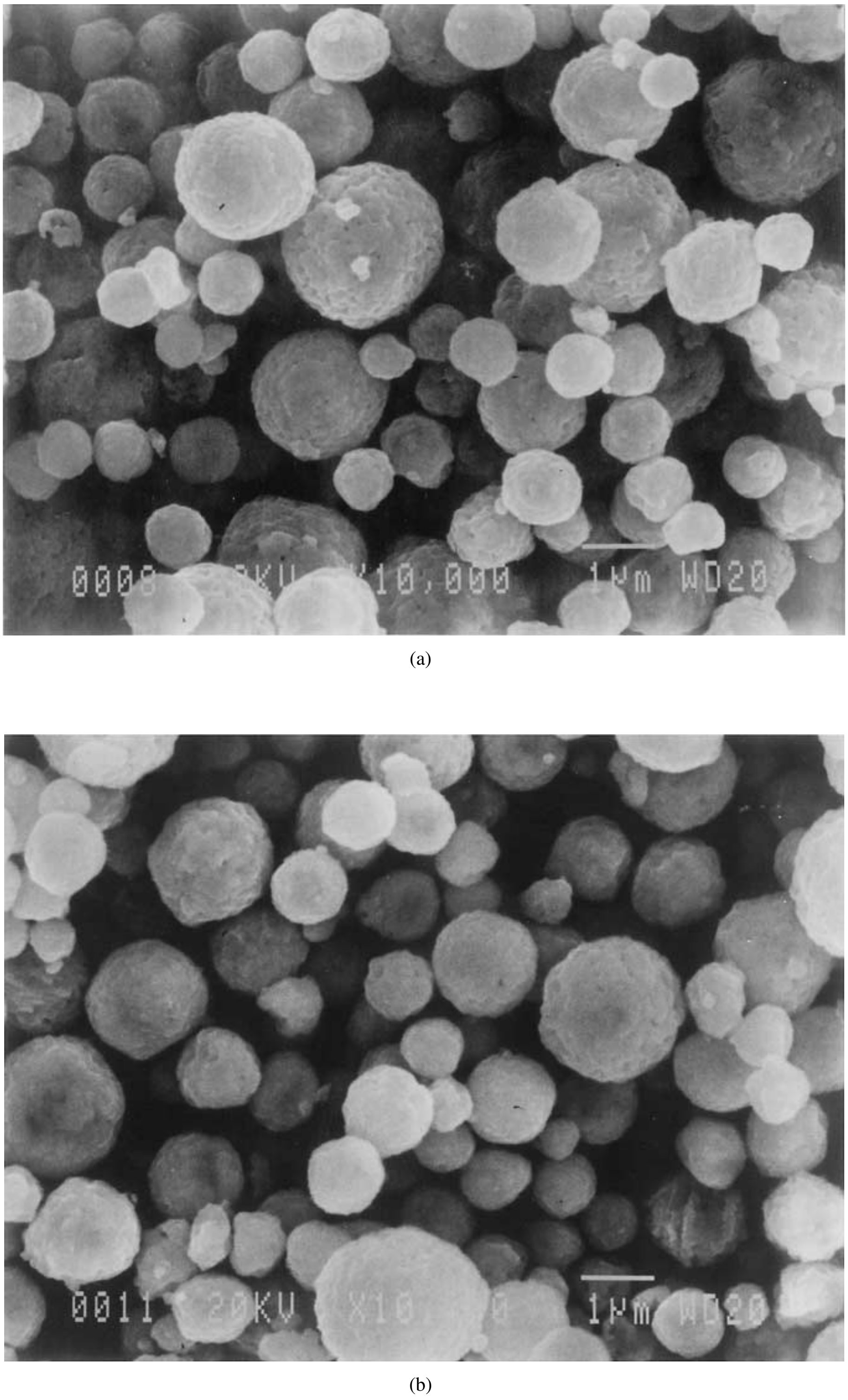
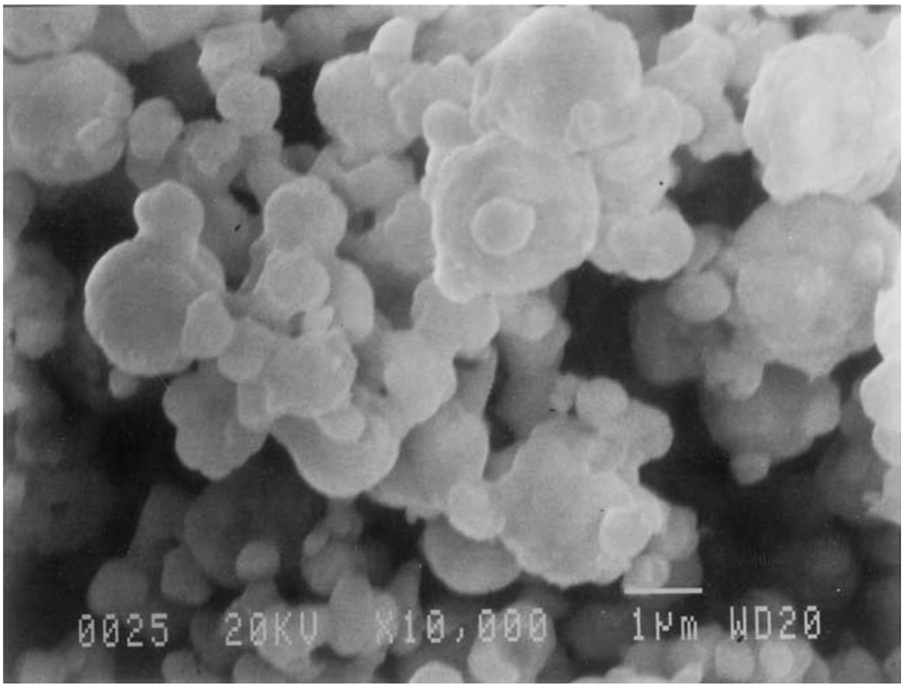


Figure 6 SEM images of particles post heat-treated at various temperature for 2 h: (a) 900°C (b) 1000°C and (c) 1100°C. *(Continued.)*

which is advantageous to the formation of dense particles.

Fig. 4 shows the SEM images of particles as-prepared at 1100°C with various concentrations of NH_4NO_3. The overall concentration of the starting solution was 0.5 M. In the case of particles as-prepared without NH_4NO_3, hollow and fractured particles were observed. As NH_4NO_3 was added to the starting solutions, as-prepared particles had a spherical morpholog and there were no fractured particles. When the ratio of overall concentration of the starting solution to NH_4NO_3 was not equal to 1 : 1, fractured particles and particle fragments were observed.

As-prepared particles were post heat-treated with a view to completing the decomposition and improving the crystallinity of the particles. The XRD patterns of the particles post heat-treated above 900°C for 2 h are presented in Fig. 5. In these cases, particles were as-prepared at 1100°C. The particles post heat-treated above 1000°C show a single-phase of Sr_2CeO_4. It was also found that the crystallinity of the post heat-treated particles increased with increases in temperature.



(c)

Figure 6 (*Continued.*)

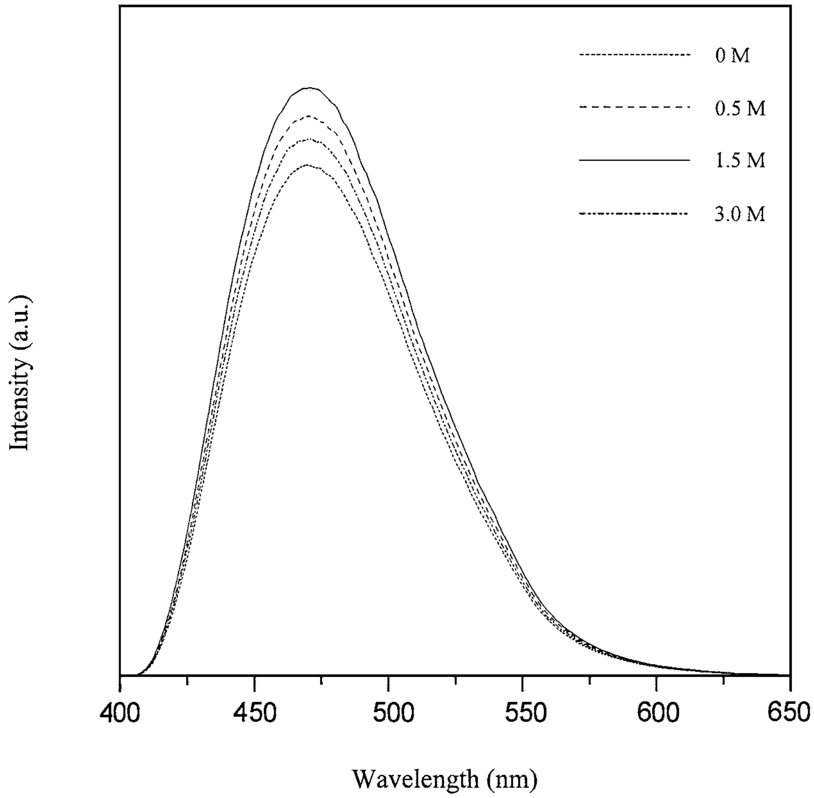


Figure 7 Emission spectra of particles post heat-treated at 1000°C with various concentrations of NH_4NO_3 for 2 h.

Fig. 6 shows the SEM images of the post heat-treated particles. The particles as-prepared at 1100°C were post heat-treated for 2 h with the temperature varying from 900 to 1100°C. The particles post heat-treated up to 1000°C were discrete as sintering of the particles had not yet begun. Therefore, milling was not necessary for the preparation of fine-sized, phase-pure Sr_2CeO_4 phosphor particles by spray pyrolysis. However, it was observed that a neck was formed between the spherical particles and hard agglomerates were observed at 1100°C.

The luminescence characteristics of the phosphor particles depend on the morphology of the particles and other properties including size, crystallinity and defects. The particles prepared by spray pyrolysis had little brightness due to the short residence time of the

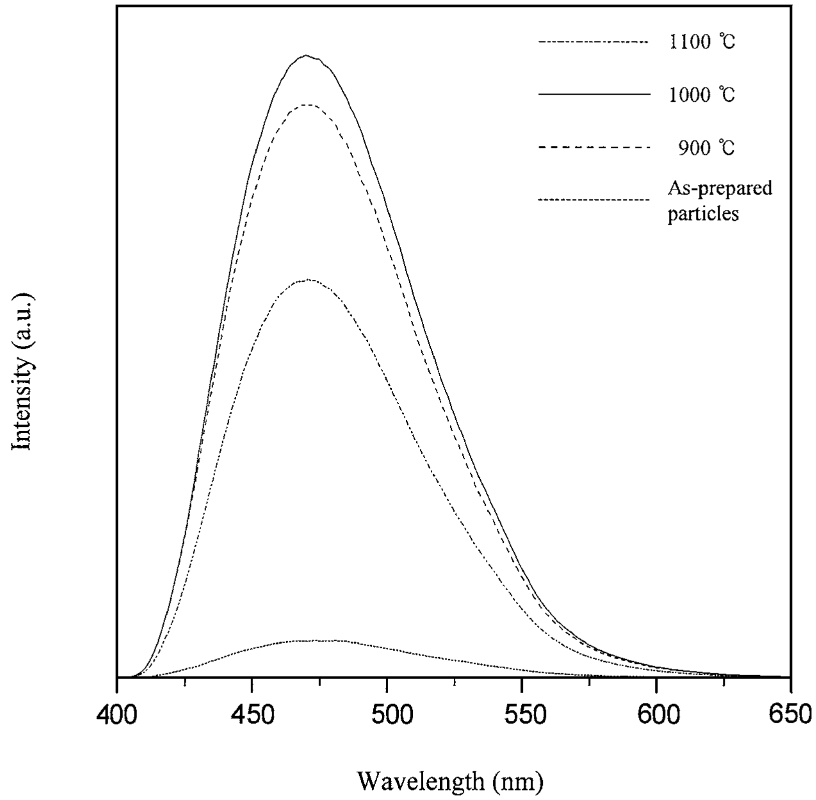


Figure 8 Emission spectra of particles post heat-treated at various temperatures for 2 h.

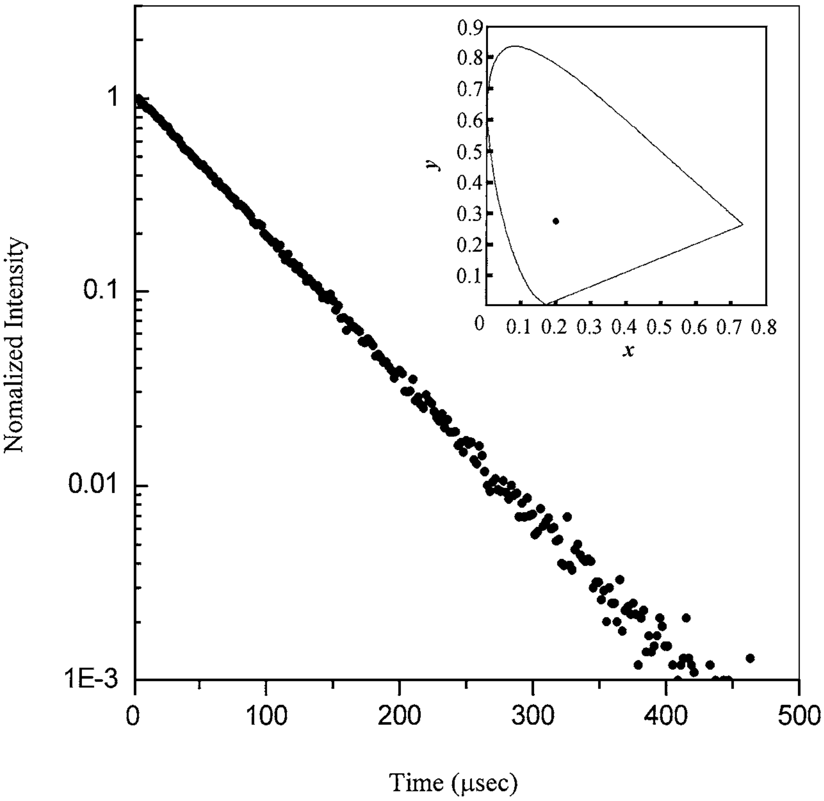


Figure 9 Decay curve and the chromaticity of particles post heat-treated at 1000°C for 2 h.

particles inside the heating zone. Figs 7 and 8 illustrate the relative luminescence of the Sr_2CeO_4 particles with various concentrations of NH_4NO_3 and post heat-treatment temperatures. The emission spectra of Sr_2CeO_4 displayed broad maxima at 470 nm. When NH_4NO_3 was added in an equal amount to the overall concentration of the starting solution, the luminescence intensity was at its highest. This is because the morphology of the spherical particles lowers the light scattering. The intensity of luminescence increased dramatically with increases in post heat-treatment temperatures up to 1000°C. This is because a higher post heat-treatment temperature yields better crystallinity. In the case of the particles post heat-treated at 900°C, the low luminescence intensity was attributed to unreacted intermediate products and insufficient crystallization of the particles. When the post heat-treatment temperature was 1100°C, the particles lost their spherical shape and began to sinter. The decrease in luminescence above 1000°C resulted from the formation of hard agglomerates. It is known that hard agglomerates yield low density packing of the phosphor which causes a strong light scattering [12].

The CIE chromaticity and decay time of the Sr_2CeO_4 particles post heat-treated at 1000°C for 2 h are shown in Fig. 9. The CIE chromaticity indices were $x = 0.20$ and $y = 0.27$. This shows that the emission of Sr_2CeO_4 powder appears blue-white to the eye. The decay time for Sr_2CeO_4 was 58 μs, which is an uncharacteristically long excited-state life time compared with d-f transitions with the Ce^{3+} excited state.

4. Conclusions

Sr_2CeO_4 phosphor particles were prepared by ultrasonic spray pyrolysis. The Sr_2CeO_4 particles had a fine size, a spherical morphology and were non-agglomerated. The mean particle size was controlled from a submicrometre to micrometre size by changing the concentration of the starting solution. The addition of NH_4NO_3 to the starting solution was an effective method of preparing dense spherical particles without any hollow particles or particle fragments. The Sr_2CeO_4 phosphor particles maintained their spherical shape and unagglomerated characteristics after heat-treatments at temperatures below 1000°C for 2 h. The use of spherical particles should increase the screen brightness because of the lower scattering of the evolved light and higher packing density compared with irregularly-shaped particles obtained by conventional methods.

Acknowledgements

This work was supported by Brain Korea 21 through the Korea Research Foundation (KRF).

References

1. E. DANIELSON, M. DEVENNEY, D. M. GIAQUINTA, J. H. GOLDEN, R. C. HAUSHALTER, E. W. MC FARLAND, D. M. POOJARY, C. M. REAVES, W. H. WEINBERG and W. D. WU, *Science* **279** (1998) 837.
2. *Idem.*, *J. Molecular Structure* **470** (1998) 229.
3. Y. D. JIANG, F. ZHANG, C. J. SUMMERS and Z. L. WANG, *Appl. Phys. Lett.* **74** (1998) 1677.
4. G. L. MESSING, S. C. ZHANG and G. V. JAYANTHI, *J. Amer. Ceram. Soc.* **76** (1993) 2707.
5. N. TOHGE, M. TATSUMISAGO, T. MINAMI, K. OKUYAMA, M. ADACHI and Y. KOUSAKA, *ibid.* **74** (1991) 2117.
6. Y. C. KANG and S. B. PARK, *J. Aerosol Sci.* **26** (1995) 1131.
7. M. NYMAN, J. CARUSO, M. J. HAMPDEN-SMITH and T. T. KODAS, *J. Amer. Ceram. Soc.* **80** (1997) 1231.
8. H. F. YU and A. M. GADALLA, *J. Mater. Res.* **11** (1996) 663.
9. S. CHE, K. TAKADA and N. MIZUTANI, *J. Mater. Sci. Lett.* **17** (1998) 1227.
10. S. JAIN, D. J. SKAMSER and T. T. KODAS, *Aerosol Sci. Tech.* **27** (1997) 575.
11. S. CHE, K. TAKADA, O. SAKURAI, K. SHINOZAKI and N. MIZUTANI, *J. Mater. Sci.* **34** (1999) 1313.
12. Y. C. KANG, S. B. PARK, I. W. LEGGORO and K. OKUYAMA, *J. Electrochem. Soc.* **137** (1999) 2744.

Received 4 June 2001
and accepted 13 March 2002