

Preparation of Fine Sr_2CeO_4 Particles for a Blue Phosphor

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Fine Sr_2CeO_4 particles of a blue emission phosphor have been synthesized using a chemical co-precipitation technique, and the textual and optical properties were compared with the one synthesized by the conventional solid-state reaction method. Mean particle size of the prepared Sr_2CeO_4 fine particles was smaller than that given by the sample prepared from the solid-state reaction method. However, photoluminescence intensity was maintained in spite that it usually decreases with the particle size reduction.

Recently, Sr_2CeO_4 blue-white phosphor has been developed using the combinatorial techniques and the emission mechanism has been assigned to Ce^{4+} charge transfer luminescence.¹ This material was found to exhibit efficient luminescence under excitation with cathode and X-rays.^{1,2} In addition, it has also been established that Sr_2CeO_4 exhibits photoluminescence under excitation by UV light.³⁻⁵ Therefore, application of Sr_2CeO_4 as a blue phosphor in low pressure mercury vapor lamps and in cathode ray tubes is expected.

It is well known that phosphor particles of spherical morphology, sub-micrometer sizes, and narrow particle size distribution give higher packing densities than commercial products (a few μm in size) that usually fabricated by the solid-state reaction method, and are thus favorable in enhancement of the luminescence.⁶⁻⁹ However, decrease in size of phosphor materials by mechanical grinding induces formation of lattice defects and surface amorphous layers which appreciably lower the emission intensity of the photoluminescence.¹⁰

In the synthesis of the fine oxide powders, carbonates have been used as excellent precursors. Such carbonate precursors consist of fine primary particles that flock together making secondary loose agglomerated particles. The morphology of the carbonate precursors is favorable to obtain non-agglomerated oxide powders by the subsequent calcinations.¹¹ In this study, we synthesized strontium-cerium mixed carbonate as a precursor to obtain a low-agglomerated powder of Sr_2CeO_4 blue phosphor. The size, morphology, and luminescence properties of the oxide particles are then investigated.

Strontium nitrate and cerium nitrate hexahydrate were dissolved in deionized water and their concentration was adjusted to $1.0 \text{ mol}\cdot\text{dm}^{-3}$. A $0.5 \text{ mol}\cdot\text{dm}^{-3}$ solution of ammonium carbonate was used as a precipitant. Strontium and cerium mixed carbonate was precipitated by dripping of the mixture of 10 dm^3 of the strontium nitrate solution and 5 dm^3 of the cerium nitrate solution into 42 dm^3 of the ammonium carbonate solution. The obtained precipitate slurry was agitated with magnetic stirrer for 2 h at room temperature. After the filtration, the precipitate was washed with 0.05 wt% ammonium sulfate aqueous solution (twice) and then with acetone (twice). The resultant mixed carbonate powder was dried at room temperature overnight, and subsequently calcined at 1373 K in a flow of dried air with a

holding time of 2 h. The stoichiometry was confirmed with the inductively coupled plasma analysis (Shimadzu ICP-S1000IV) of the acid solution of the sample.

The powder samples of Sr_2CeO_4 were also prepared with conventional solid-state reaction method. Strontium carbonate and cerium oxide were used as starting materials. A stoichiometric mixture of the starting materials was thoroughly homogenized in an agent mortar for 1 h and then transferred to an alumina boat. The compound was fired in a flow of dried air at 1373 K for 2 h or at 1573 K for 24 h.

The obtained oxide particles were characterized by means of scanning electron microscopy (SEM, Hitachi S-800) and X-ray powder diffraction (XRD, 40 kV and 50 mA, Cu $\text{K}\alpha$, MacScience M18XHF-SHA). The mean size and the size distribution were estimated by measuring the diameters of 200 particles in the SEM photographs. The photoluminescence excitation and emission spectra were recorded at room temperature using a spectrofluorometer (Hitachi F-4500, Xe lamp). The emission spectra were recorded for excitation at 254 nm, and the excitation spectra were recorded measuring the emission at 479 nm.

Figure 1 shows X-ray diffraction (XRD) patterns of the Sr_2CeO_4 powders prepared by different processes and conditions. The sample synthesized by the calcination of the mixed carbonate for 2 h showed a single-phase of the Sr_2CeO_4 material. On the contrary, the one prepared by the solid-state reaction in air at 1373 K for 2 h showed phase separation into four phases such as Sr_2CeO_4 , SrCeO_3 , SrO , and CeO_2 . Heating at high

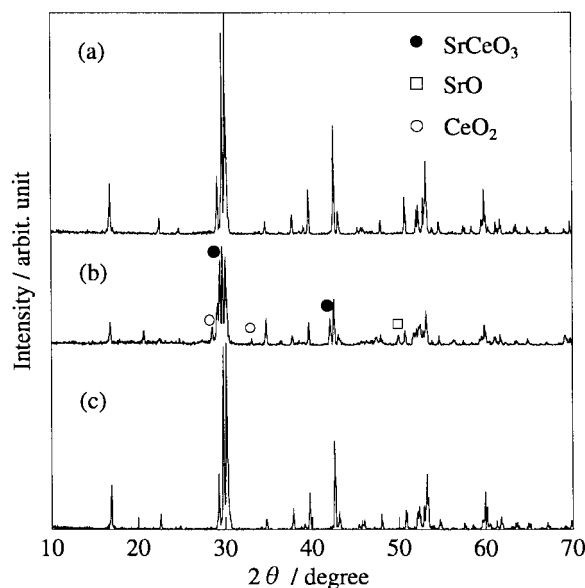


Figure 1. XRD patterns for Sr_2CeO_4 particles obtained by the (a) calcination of the co-precipitated carbonate at 1373 K, (b) solid-state reaction at 1373 K, and (c) solid-state reaction at 1573 K.

temperatures induced the homogenization of the sample and the Sr_2CeO_4 single-phase was obtained after the calcination at 1573 K for 24 h. As a result, it is elucidated that the single phase of Sr_2CeO_4 could be synthesized at lower temperature and shorter heating time in the present method than those needed to the solid-state reaction that is a general method to synthesize mixed oxide materials.

The SEM images of the Sr_2CeO_4 particles are shown in Figure 2. Figure 2 (a) shows the Sr_2CeO_4 sample prepared by the present precipitation method (P1). The particles are fine granular and measured $< 1 \mu\text{m}$ in diameter. Most of crystallites were separated to individual particle and a few multiple particles existed. On the contrary, SEM images of the sample synthesized by the conventional solid-state method are also presented for comparison (P2 and P3) in Figures 2 (b) and 2 (c). The differences of these photographs were calcination temperature and heating time. The former (P2) and the latter (P3) were calcined at 1373 K for 2 h and at 1573 K for 24 h, respectively. The primary particles do not have uniform shape and tightly aggregated one another to form large secondary particles. As the calcination time and temperature increased, the aggregation and sintering of the particles were enhanced to form larger secondary particles. The mean particle sizes of the P1, P2, and P3 were 0.8, 1.9, and 2.8 μm , respectively. From these results, it has been evidenced that the Sr_2CeO_4 particles prepared by the present precipitation method were fine compared with those prepared by the solid-state process.



Figure 2. SEM images for Sr_2CeO_4 particles obtained by the (a) calcination of the co-precipitated carbonate at 1373 K, (b) solid-state reaction at 1373 K, and (c) solid-state reaction at 1573 K.

The emission and excitation spectra of Sr_2CeO_4 particles prepared from the mixed carbonate and solid-state reaction are depicted in Figure 3, respectively. These excitation and emission spectra show broad bands and have peaks around 280 and 340 nm for excitation and 480 nm for emission. These peaks are assigned to the transition of Ce^{4+} between t_{1g} and f , where f is the lowest excited charge transfer state and t_{1g} is the orbital of the ligand in sixfold oxygen coordination.^{1,3} In Sr_2CeO_4 , two kinds of Ce^{4+} ions exist, that is, there are two different $\text{Ce}^{4+}-\text{O}^{2-}$ bond lengths in the lattice.¹ The two excitation peaks observed in the figure are thus attributed to the different charge transfer transitions, and the difference in profiles suggests the effects of particle size and morphology.

As mentioned above, generally the emission intensity of a phosphor decreases with the decrease in the particle size. However, the smaller particles prepared from the mixed carbonate showed no decrease in the emission intensity compared with the larger particles prepared by the solid-state method, probably due to the homogeneity of the morphology observed in the smaller particles.

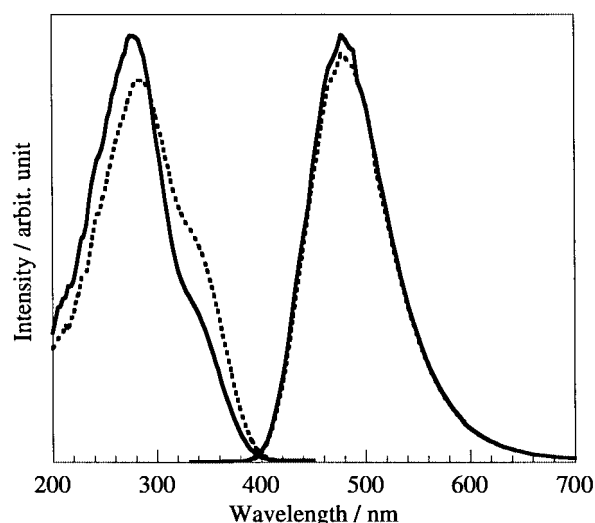


Figure 3. Excitation and emission spectra of Sr_2CeO_4 particles obtained by the calcination of the co-precipitated carbonate at 1373 K (solid line) and solid-state reaction at 1573 K (dotted line).

In addition, in the case of the solid-state reaction process, a grinding process is necessary to get powdered particles as fine as those obtained by the carbonate process. However, the grinding decreases the emission intensity. Consequently, it is considered that the emission intensity becomes smaller than that from the fine particles prepared from the carbonate. On the contrary, small particles with fine granular and uniform morphology were obtained without grinding by the carbonate process, and these features are suitable for a dense packing and coating on substrates. In conclusion, preparation of fine particles of Sr_2CeO_4 without reducing the emission intensity was successfully realized.

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