

Synthesis and properties of Sr_2CeO_4 blue emission powder phosphor for field emission displays

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A blue emission powder phosphor Sr_2CeO_4 for field emission displays was prepared using a chemical coprecipitation technique, which is most suitable for large-scale production. The powders were fired at different temperatures to optimize the properties. Firing the powder at 1200 °C for 2 h gave the highest luminescence efficiency of 5.4 lm/W at 4 kV and 29.0 lm/W at 10 kV. The emission peak of this phosphor is at ~ 470 nm and Commission International de l'Eclairage coordinates are $x=0.19$, $y=0.26$. © 1999 American Institute of Physics. [S0003-6951(99)00812-8]

Field emission displays (FEDs) offer the potential of achieving comparable or superior levels of performance to the cathode ray tubes (CRTs). However, FEDs must operate at significantly lower excitation voltages (≤ 5 kV) and higher current densities ($10\text{--}100$ A/cm²) than CRTs. Thus the phosphors for FEDs are required to have a high efficiency at low voltages, high resistance to current saturation, long service time, and equal or better chromaticity than CRT phosphors.¹ For full color flat panel displays, it is difficult to find a suitable blue phosphor, because wide band gap materials are required and the eye sensitivity is quite low in the blue spectral region.^{2,3} Currently some of the new phosphor candidates being developed for FEDs are green $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$, and blue $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$.⁴ Unfortunately, sulfide phosphors emit and decompose sulfide gases during electron excitation, subsequently causing the cathode to deteriorate and the luminous efficiency of phosphors to decrease.⁵ In order to avoid these problems, new coating techniques are being developed for sulfide phosphors, such as coating with conductive oxides. However, after coating the luminous efficiency of the phosphors decreases dramatically, especially at low excitation voltages.⁶⁻⁸ In practice, oxides-based phosphors are probably the most stable under electron excitation, and then there is a continuous search for new oxide phosphors that can give blue emission with high efficiencies at low acceleration voltages.

Recently Danielson, etc.⁹ identified an oxide thin film blue phosphor (Sr_2CeO_4) by a combinatorial materials synthesis technique. The phosphors were prepared by electron beam evaporation with multiple targets and moving masks. It was also determined that the crystal structure of Sr_2CeO_4 is orthorhombic with one-dimensional chains of edge-sharing CeO_6 octahedra, and that the luminescence originates from a ligand-to-metal Ce^{4+} charge transfer. It was also reported that the emission peak of this material was at 485 nm with CIE chromaticity coordinates $x=0.198$, $y=0.292$. Although this new material opens up a new direction in the search for a blue emitter, for industrial applications, powders synthesized by chemical methods are more attractive than thin films

for large-scale production. In this letter, we report the synthesis of Sr_2CeO_4 powders using a chemical coprecipitation method. The cathodoluminescent properties and particle morphologies were also investigated.

In the chemical synthesis, strontium nitrate [$\text{Sr}(\text{NO}_3)_2$, Aldrich, 99+ %], cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Johnson Matthey, 99.5 %] and ammonium oxalate [$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, Fisher, 99+ %] were used as raw materials. First, dissolving $\text{Sr}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with different $\text{Sr}^{2+}:\text{Ce}^{3+}$ ratios, and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in deionized water, and filtering these solutions, nitrate and oxalate solutions were formed, respectively. The concentrations of nitrate solution and oxalate solution were 1.0 and 0.67 N, respectively. Oxalate is 20% more than theoretically needed. By titrating the oxalate into the nitrate solution at a rate of ~ 15 ml/min, white precipitates were formed. The precipitates were separated by filtering the solution, then the precipitates were washed with deionized water and absolute ethanol to remove residual chemicals and water. After drying at ~ 80 °C, the precursors were fired at different temperatures (1000, 1200, and 1400 °C) for 2 h. The phases formed were determined by x-ray diffraction (Rigaku D-MAX-B). Morphologies at different firing temperatures were observed from scanning electron microscopy (Hitachi S-4100) and the cathodoluminescent properties were measured by using a deep patch method as reported previously. (Direct current electron beam, current density is 1 nA/cm².)¹⁰

Figure 1 shows the morphologies of (a) precursor and powders fired at (b) 1000 °C, (c) 1200 °C, and (d) 1400 °C for 2 h. The particle shape of the as-prepared precursor is irregular, and the particles are composed of very fine plate-like crystallites. After firing the particles became smooth, and with increasing firing temperature the particle size increased significantly, from ~ 4.0 μm at 1000 °C to ~ 7.5 μm at 1400 °C. The particle shape also became more regular with increasing firing temperature. Also at the firing temperature of 1400 °C, hard agglomerations were observed between particles. Figure 2 is an x-ray diffraction pattern of the powder fired at 1400 °C for 2 h and the standard peaks from

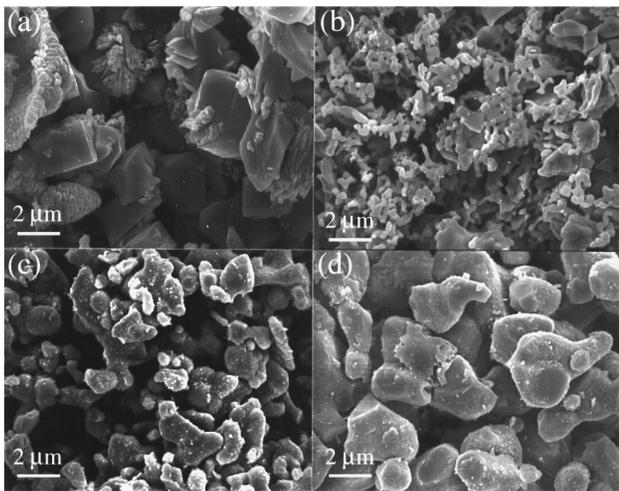


FIG. 1. Morphologies of (a) precursors and particles fired at (b) 1000 °C, (c) 1200 °C, and (d) 1400 °C for 2 h, showing increased particle size and improved particle shape with the increase of firing temperature.

the Joint Committee on Powder Diffraction Standards (JCPDS) card. JCPDS card shows the crystal structure of Sr_2CeO_4 is triclinic. Danielson, etc.⁹ reported the structure of Sr_2CeO_4 to be orthorhombic.

The relationship between cathodoluminescent efficiency and firing temperatures was shown in Fig. 3. The powders fired at 1200 °C for 2 h have a highest luminous efficiency at all acceleration voltages, especially at voltages above 5 kV. Lower or higher firing temperature than 1200 °C caused the efficiency to decrease. The main reason is that at lower temperatures the crystallization of the powders was not complete, and there are some defects in each particle which can trap or scatter the emitted light. At higher temperatures, very hard agglomerations were formed, and this led to a low density packing layer of the phosphor which caused a strong light scattering, so the luminous efficiency decreased. Figure 4 shows the luminous efficiency versus acceleration voltage of powders prepared with two different $\text{Sr}^{2+}:\text{Ce}^{3+}$ ratios.

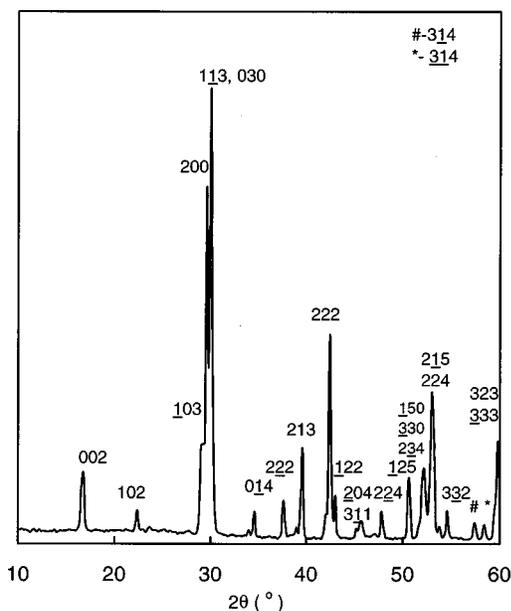


FIG. 2. X-ray diffraction pattern of the powder $2\text{SrO}\cdot\text{CeO}_2$ fired at 1400 °C for 2 h, proving a triclinic crystal structure.

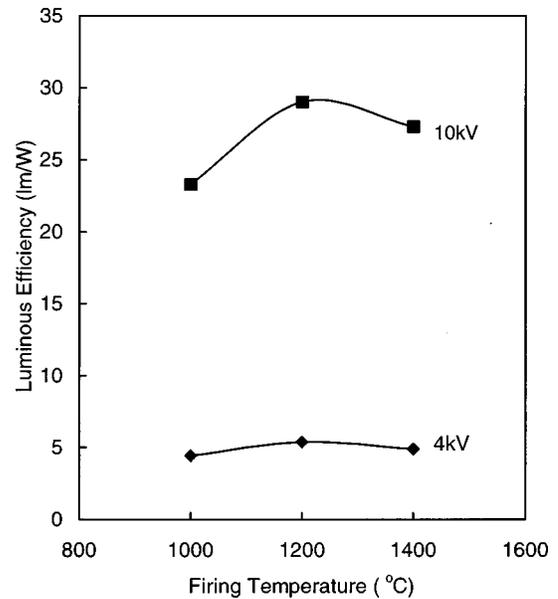


FIG. 3. Luminous efficiency of $2\text{SrO}\cdot\text{CeO}_2$ via firing temperature at different acceleration voltages, showing that the powder fired at 1200 °C for 2 h has the highest efficiency at all excitation voltages.

The luminous efficiency of $2\text{SrO}\cdot\text{CeO}_2$ is lower than that of $3\text{SrO}\cdot\text{CeO}_2$ at lower acceleration voltages (below 5 kV) and is higher at higher excitation voltages (above 5 kV). The exact reason remains to be further investigated.

For field emission displays, in addition to the two criterions of high efficiency at low excitation voltage and high current density, the chromaticity is also a very important property, because it affects the ratios of the three basic colors.¹¹ Figure 5 presents the emission spectrum and CIE 1931 chromaticity of the $2\text{SrO}\cdot\text{CeO}_2$ powder fired at 1200 °C for 2 h. The peak is located at ~ 470 nm, different from the 485 nm reported for thin films.⁹ The emission spec-

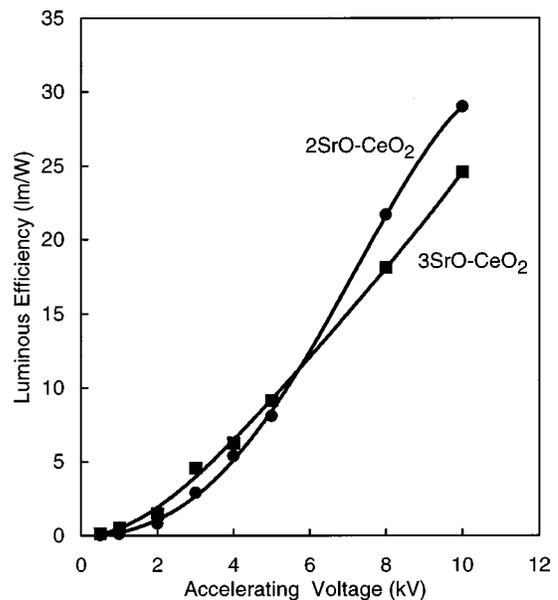


FIG. 4. Luminous efficiency of powder with different Sr:Ce ratios as a function of acceleration voltage, showing that $2\text{SrO}\cdot\text{CeO}_2$ has higher efficiency at high voltages (above 5 kV), while $3\text{SrO}\cdot\text{CeO}_2$ has higher efficiency at lower voltages (below 5 kV).

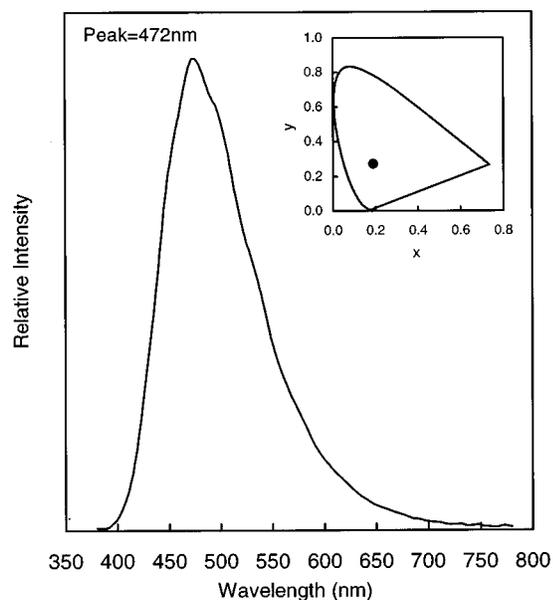


FIG. 5. Emission spectrum and chromaticity of $2\text{SrO}\cdot\text{CeO}_2$ fired at 1200°C for 2 h, showing that the emission peak is at ~ 470 nm, and chromaticity coordinates are $x=0.19$, $y=0.26$.

trum is wider, slightly spreading into the green region. So the CIE chromaticity index are $x\cong 0.19$ and $y\cong 0.26$, which is better than what was reported by E. Danielson, etc.⁹ Doping the compound with other alkaline earth elements (such as Ca or Ba) might improve the emission and shift the CIE chromaticity index to lower values.

In this letter we have reported a new blue powder phosphor Sr_2CeO_4 . Its luminous efficiency, chromaticity, and particle morphologies are presented. The phosphor powder fired at 1200°C for 2 h has higher luminous efficiency at both 4 and 10 kV. Experimental results show this phosphor has potential application in field emission displays.

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