

$(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ Phosphor Particles by Spray Pyrolysis Process

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Abstract

$(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor particles with high brightness were prepared by spray pyrolysis. The changes in the photoluminescence intensity and morphology of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ were investigated by changing the posttreatment temperature and the concentration of dopant. The prepared $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ particles has a dense structure, but irregular shape after the posttreatment. When they were excited by the ultraviolet light of 410 nm, a broad emission band with a peak at 508 nm was observed. The photoluminescence intensity of the prepared $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ particles was enhanced by increasing the posttreatment temperature up to 1300 °C and further improved by adding several rear-earth codopants. The $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ particles prepared by spray pyrolysis had a good excitation spectrum in the wavelength longer than 350 nm. Therefore, it was concluded that the $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ prepared by spray pyrolysis is a good green-emitting phosphor for LED application.

1. Introduction

The development of a new illuminator to replace conventional incandescent electric lamp or fluorescent lighting is one of great research topics. In special, the illuminators working with light emitting diode (LED) has been received many researcher's attention because they have high brightness, long life time, small size, and low power consumption. In order to apply LED for a light source instead of the conventional lamp, it is essential to develop LED chip which emits white light. There are several processes for manufacturing LED emitting white light, which are achieved by pasting fluorescent materials above UV (ultra violet) LED, yellow phosphor material above blue LED, and combining two or three different-color semiconductor chips. Among those processes, it is considered that pasting fluorescent materials over UV LED chip is the most efficient process because the process is simple and can produce full color. In the case of combining two or three different-color semiconductor chips, the intrinsic efficiency,

working voltage, and life time of LED chips involved are lost. When pasting yellow phosphor material above blue LED, the working process is simple but only white color is achieved. However, in the case of pasting yellow phosphor material above blue LED and fluorescent materials above UV LED chip a full-color light can be obtained. In other to successfully apply phosphor-combined UV LED to the lighting, fluorescent materials must work under long-wavelength UV and have high emission efficiency[1]. Therefore, it is necessary to develop efficient fluorescent materials, which can be excited by long-wavelength UV light.

Eu-doped $(\text{Ba,Sr})_2\text{SiO}_4$, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{Y}_2\text{SiO}_5:\text{Tb}$ and $\text{BaAl}_{12}\text{O}_{19}:\text{Mn}$ phosphor are known as green emitting phosphor[2-8]. Among these green phosphor materials, $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor is suitable for LED phosphor because it has shorter decay time or higher luminescence characteristics than those of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ or $\text{Y}_2\text{SiO}_5:\text{Tb}$ phosphors

In the work, $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles were prepared by a pilot-scale spray pyrolysis process and their luminescence characteristics were investigated by changing the post-treatment temperature and the content of activator. Also, in order to improve the brightness of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor, several rare-earth materials were employed as a codopant.

2. Experimental

The spray pyrolysis system used is schematically shown in Figure. 1. A ultrasonic spray generator with six vibrators that has frequency of 1.7MHz was used to produce large amount of droplets. The length and inside diameter of quartz reactor were 1200 mm and 50 mm, respectively. The temperature of the reactor was fixed at 900 °C. The flow rate of air used as carrier gas was controlled at 45 L/min and the residence time of the particles inside the reactor was 0.65 sec.

The precursor solutions were prepared from barium, strontium nitrate and TEOS. The overall solution concentration was 0.3M and the doping concentration of europium was varied from 0.1 to 1 mol % with respect to total precursor concentration.

Rare-earth materials as a co-dopant were also changed from 0.1 to 1 mol % in order to optimize the photoluminescence intensity of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$. The as-prepared particles were post-treated between 900°C and 1400°C for 3 h under 10% H_2/N_2 mixture gas.

The crystal structure of the particles obtained was investigated by X-ray diffraction (XRD) and the morphology of the particles was monitored by scanning electron microscopy (SEM). Photoluminescence characteristics of the particles prepared by the spray pyrolysis were measured by photoluminescence spectroscopy [USHIO UER20H-146V].

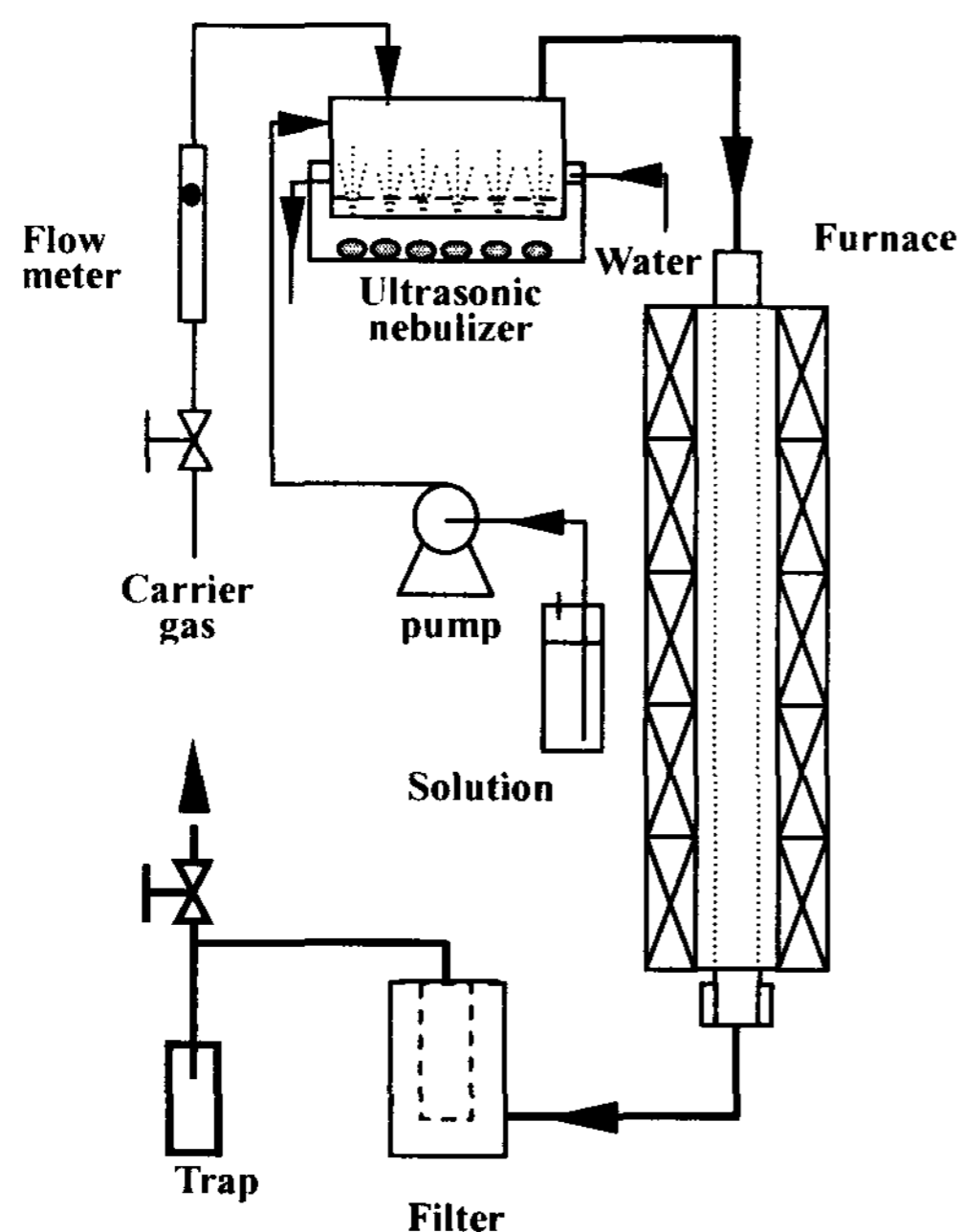


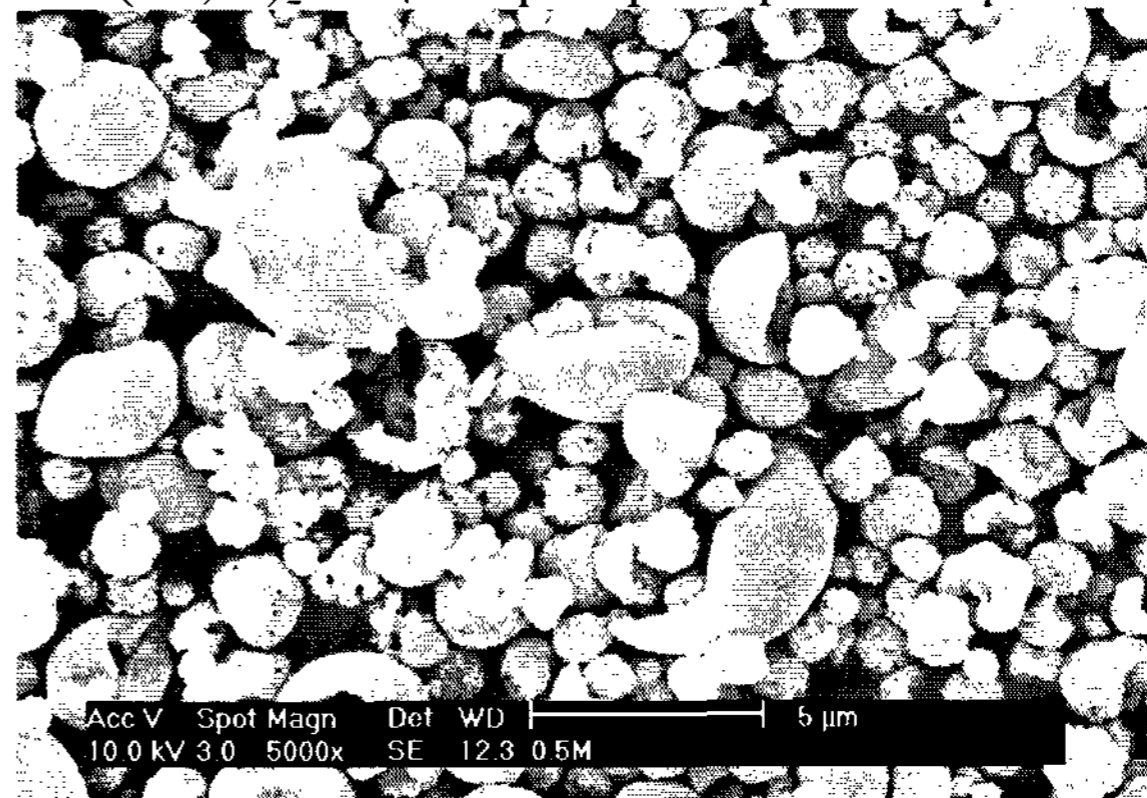
Figure 1. Schematic diagram of the spray pyrolysis system.

3. Results and Discussions

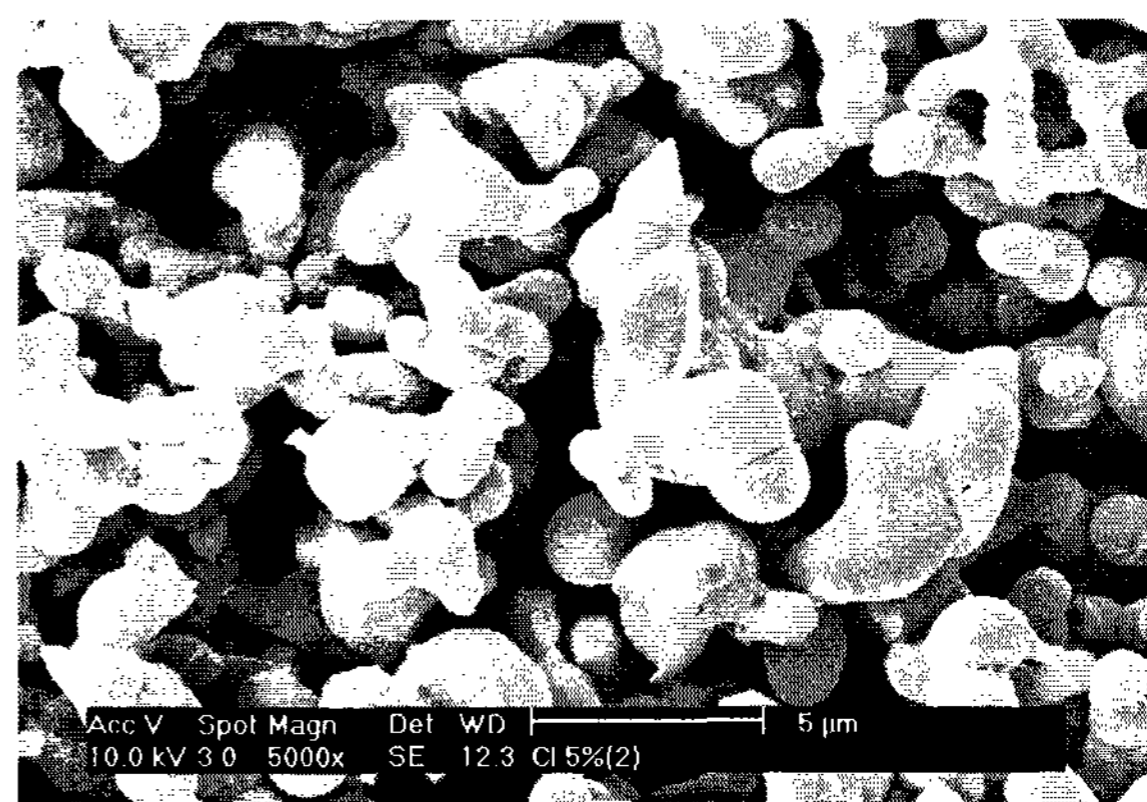
The SEM photographs of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles prepared from the aqueous solution in the spray pyrolysis were shown in Figure 2. Before the post-treatment, the as-prepared $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ particles have hollow and porous morphology. However, after the post-treatment at 1200°C , the prepared $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ particles turned to dense one, but they have irregular and agglomerated structure.

The effect of posttreatment temperature on the crystal structure of prepared particles was shown in Figure 3. The $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles post-treated below 1100°C had low crystallinity but

the $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles post-treated



(a) Before post-treatment



(b) After post-treatment

Figure 2. SEM photographs of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles.

above 1200°C had high crystallinity.

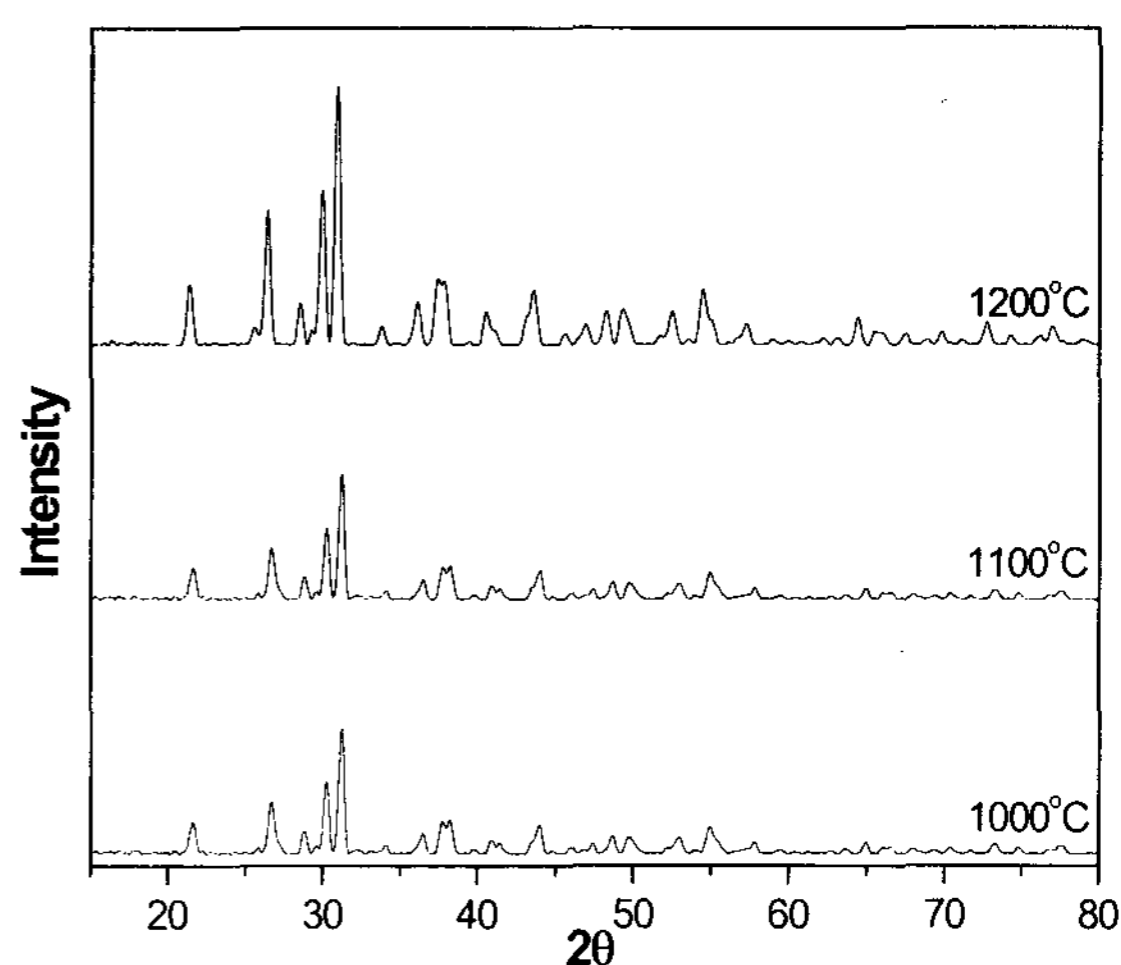


Figure 3. XRD spectra of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles.

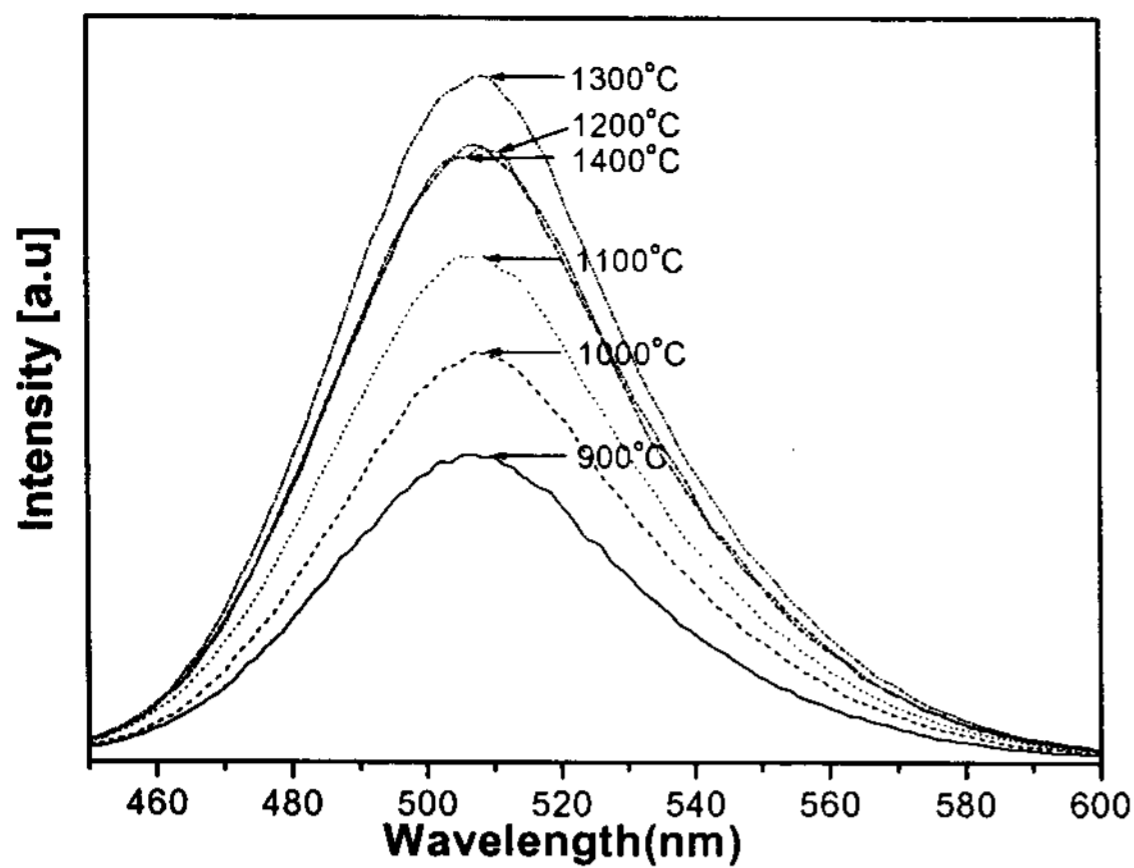


Figure 4. Emission spectra of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles annealed at different temperatures.

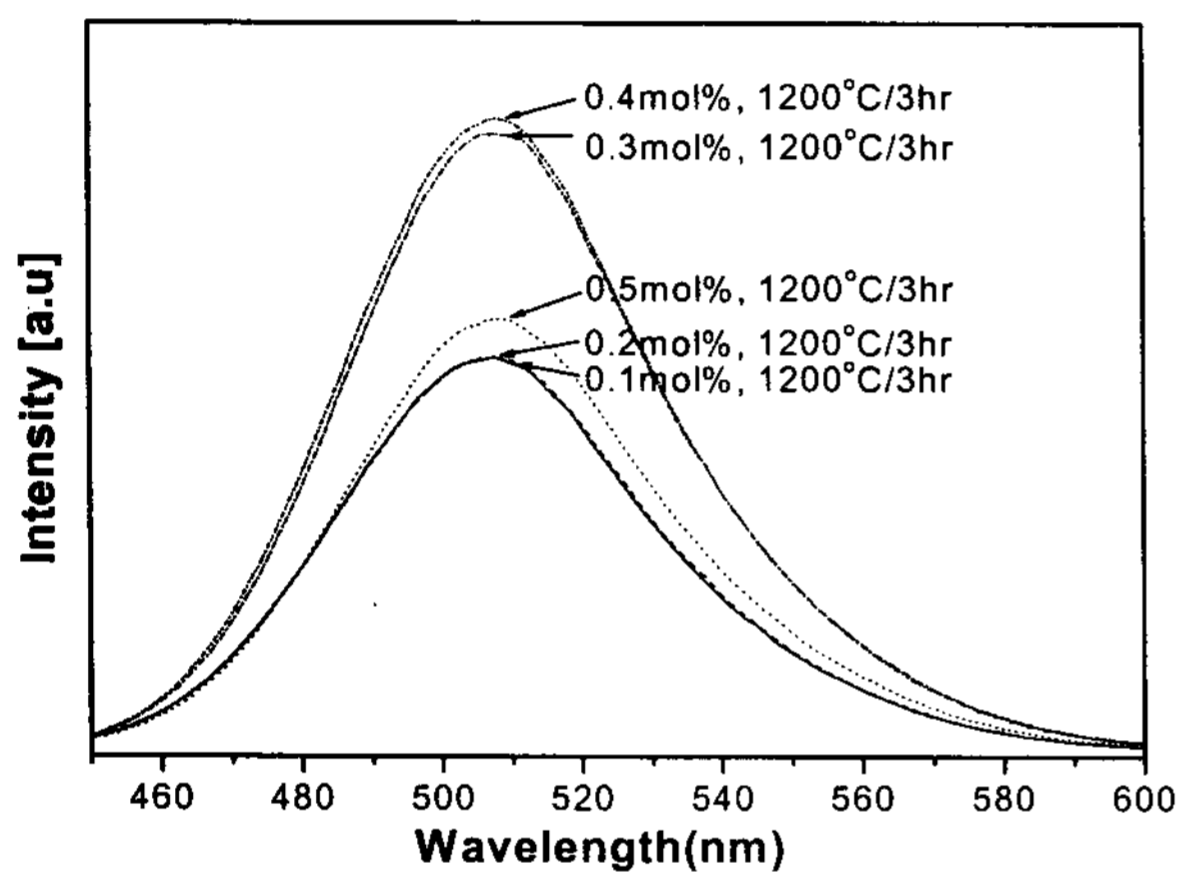
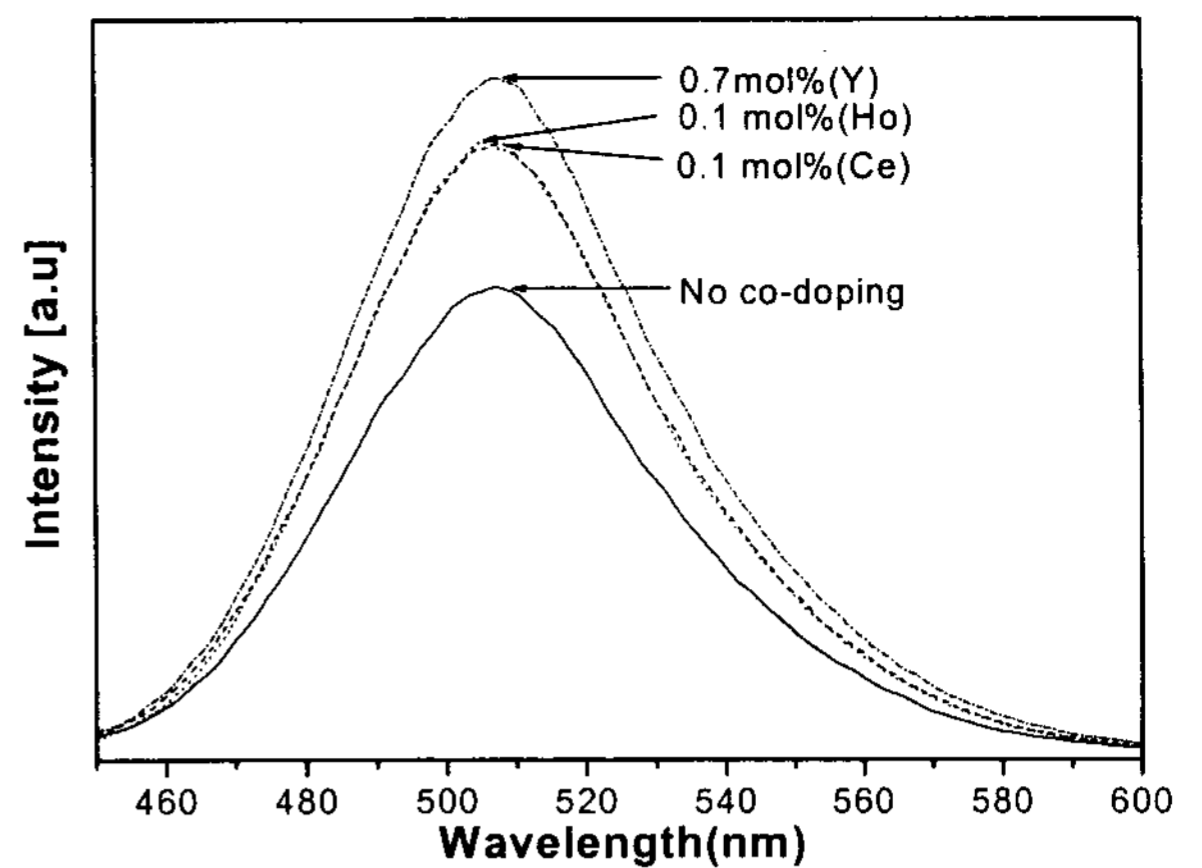
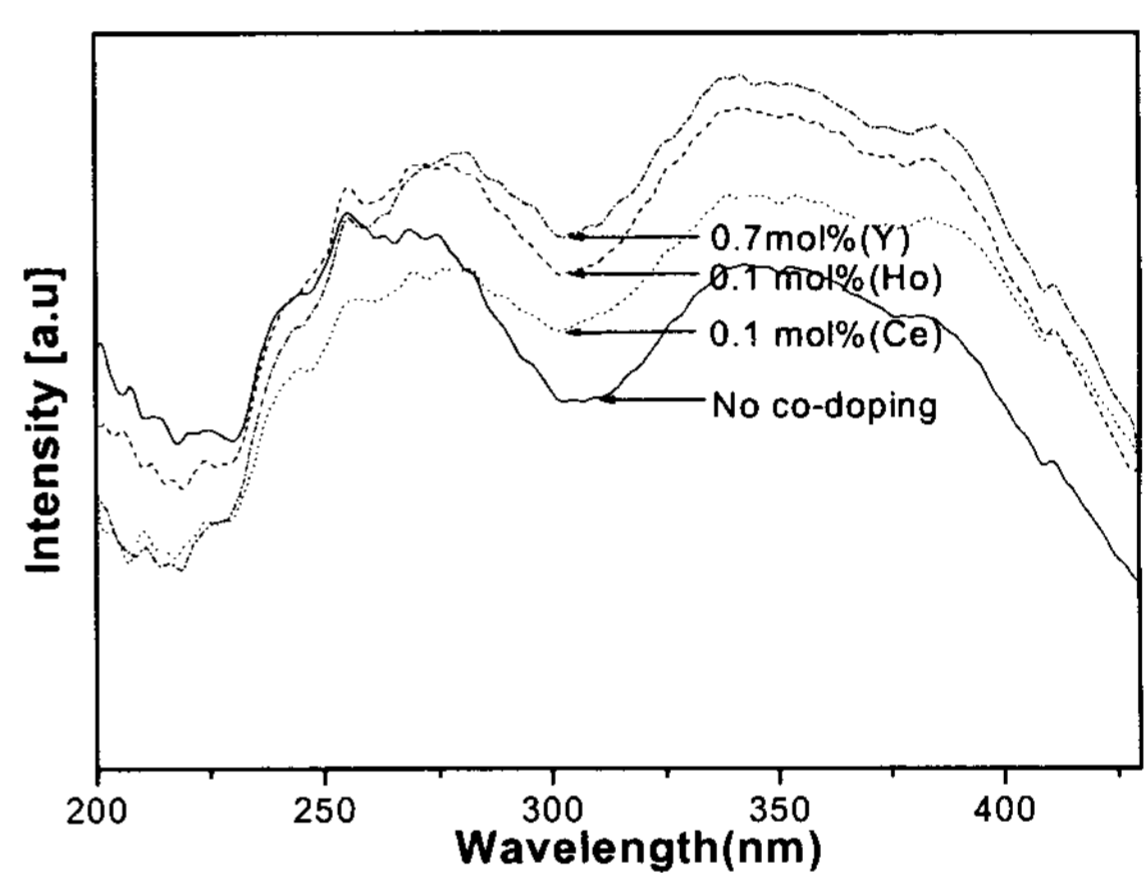


Figure 5. Emission spectra of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles at different activator concentration.



(b) Excitation spectra

Figure 6. PL spectra of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles.

The effect of post-treated temperature on the PL intensity of prepared particles was shown in Figure 4. The photoluminescence (PL) intensity of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles was increased by increasing posttreatment temperature because the phosphor particles post-treated at higher temperatures have higher crystallinity. Under long-wavelength UV excitation (410nm), the photoluminescence spectra were broad and have a peak at 508nm. The maximum PL intensity, which was obtained at 1300°C, was about 2 times higher than that at 900°C. On the other hand, the $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ particles post-treated at 1400°C had lower brightness than that at 1300°C.

The effect of activator concentration on the PL

intensity of prepared particles was shown in Fig. 5. The behavior of PL intensity with varying the concentration of activator was in the same manner to that with changing the post-treated temperature. The maximum PL intensity of particles was obtained when the Eu concentration was 0.4mol% and about 1.6 times higher than that obtained at 0.1mol%.

One way to improve the photoluminescence efficiency of phosphor is to use codopant. So, in this work, several codopants such as Y, Ce, and Ho were tested in order to enhance the photoluminescence intensity of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles. First, the concentration effect of codopant on the photoluminescence of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles was tested to determine an optimum

content of codopant. Figure 6 shows the effect of the codopants used on the PL intensity and excitation spectra of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles. The concentration of codopant labeled in Figure 6 is the optimum one found in advance. The $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles co-doped with Y, Ce, and Ho have higher photoluminescence intensity and better excitation spectrum in comparison with bare $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles. As shown in Figure 6, each codopant has different optimized concentration. Under fixed concentration of Eu, the maximum PL intensity of particles prepared by adding each codopant was about 40% enhanced in comparison with that without co-dopant. Among other things, yttrium co-doped $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor has the best PL intensity and yttrium concentration was 0.7mol % of overall concentration.

4. Conclusions

High efficient green-emitting $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles were prepared by the spray pyrolysis. The prepared $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles had high photoluminescence intensity and good excitation spectra under the wavelength longer than 350 nm. So, we concluded that the $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles are appropriate for the application as a LED green-phosphor. The photoluminescence intensity of $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ phosphor particles prepared by spray pyrolysis was also improved by using codopants and it was found that the best codopant is yttrium.

5. References

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