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Ceramics International 36 (2010) 339–343

CERAMICS INTERNATIONAL

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Effect of BaF_2 as the source of Ba component and flux material in the preparation of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor by spray pyrolysis

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Received 18 May 2009; received in revised form 13 July 2009; accepted 15 August 2009

Available online 23 September 2009

Abstract

The phosphor powders with the composition of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ were prepared by spray pyrolysis. Barium fluoride and barium nitrate were used as the source materials of Ba component. $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders had broad excitation wavelength ranging from 220 to 460 nm irrespective of mole ratios of barium fluoride and barium nitrate. $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders had broad emission spectrum between 470 and 600 nm and had the maximum peak intensity at 522 nm. Substitution of BaF_2 instead of some amount of barium nitrate improved the photoluminescence intensities of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders. The maximum photoluminescence intensity of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with barium fluoride and barium nitrate was about 595% of the phosphor powders prepared from spray solution without barium fluoride. The sky blue light emitting LED with prepared phosphor powders showed (0.1958 and 0.2719) on the CIE chromaticity diagram and luminous intensity of 1.68 cd.

Keywords: A. Powders: gas phase reaction; A. Powders: chemical preparation; C. Optical materials

1. Introduction

Green-emitting $(Ba,Sr)_2SiO_4:Eu$ phosphor was known to be suitable for blue and ultraviolet light emitting diodes (LEDs) phosphor because it has short decay time and high luminescence characteristics under long wavelength ultraviolet and blue light [1–5]. The $(Ba,Sr)_2SiO_4:Eu$ phosphor powders were prepared by various ceramic processing processes including solid-state, liquid solution and gas phase reaction methods [1–5].

Spray pyrolysis, which is one of the gas phase reaction methods, has been applied to the preparation of phosphor powders [6–14]. Spray pyrolysis was also applied to the preparation of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor powders [4,5]. In the spray pyrolysis, NH_4Cl as the flux material improved the morphological and optical properties of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor powders [4]. The maximum photoluminescence intensity of $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor powders prepared from spray solution with NH_4Cl flux was 156% of the phosphor powders prepared from spray solution without flux material. However, the types of flux material affect the properties of the phosphor powders prepared by spray pyrolysis. Europium-doped $Ba_xSr_{2-x}SiO_4$ phosphor powders have various emission spectra according to the ratio (x) of barium to strontium component. Green-emitting $Ba_xSr_{2-x}SiO_4:Eu$ phosphor powders showing the maximum peak intensity higher than 520 nm are good to the preparation of sky blue light emitting LED applying the blue LED. The emission spectra of the $Ba_{1.488}Sr_{0.5}SiO_4:Eu_{0.012}$ phosphor powders prepared by spray pyrolysis had the maximum peak intensity at 508 nm [4,5].

In this study, the phosphor powders with the composition of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ were prepared by spray pyrolysis. Barium fluoride (BaF_2) and barium nitrate were used as the source materials of Ba component. Barium fluoride, which has low solubility in water, was used as the flux material as well as the source material of Ba component. The sky blue light emitting LED was prepared by combining the InGaN based blue LED and the prepared $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders.

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0272-8842/$36.00
doi:10.1016/j.ceramint.2009.09.012

2. Experimental

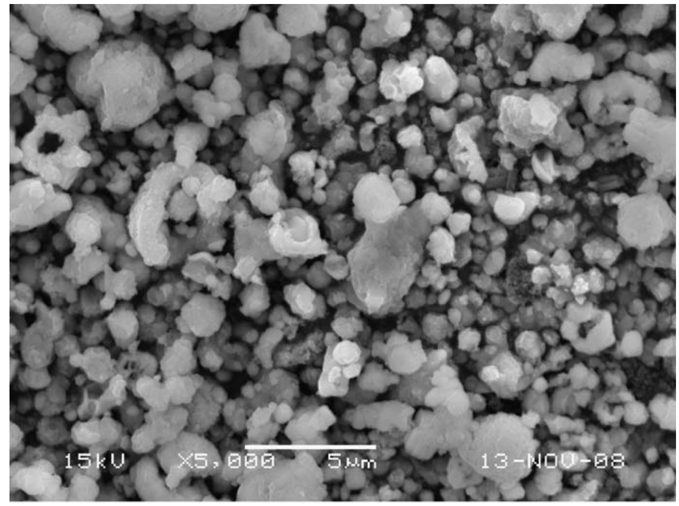
An ultrasonic spray generator with six vibrators that has frequency of 1.7 Hz was used to produce large amount of droplets. The length and inside diameter of quarts reactor were 1200 and 50 mm, respectively. The temperature of the reactor was fixed at 900 °C. The flow rate of air used as carrier gas was controlled at 45 l/min and the residence time of the powders inside the reactor was 0.6 s. The precursor solutions were prepared from barium fluoride, barium nitrate, strontium nitrate, europium oxide and tetraethyl orthosilicate (TEOS). The overall solution concentration was 0.3 M. The mole ratios of barium fluoride and barium nitrate were changed from 0.00/1.1 to 0.08/1.02. The as-prepared powders were post-treated between 1000 and 1275 °C for 3 h under 10% H_2/N_2 mixture gas.

The crystal structure and morphology of phosphor powders were investigated by X-ray diffractometry (RIGAKU DMAX-33 X-ray) and scanning electron microscopy (PHILIPS XL 30S FEG), respectively. The photoluminescence spectra of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders after post-treatment were measured using a spectrofluorophotometer (PERKIN-ELMER LS50-B) under the excitation of 455 nm blue light produced by an Xe flash lamp. The sky blue light emitting LED was prepared by combining the InGaN based blue LED and the prepared phosphor powders. The luminescence of the sky blue light emitting LED under operating condition of 20 mA at room temperature was measured.

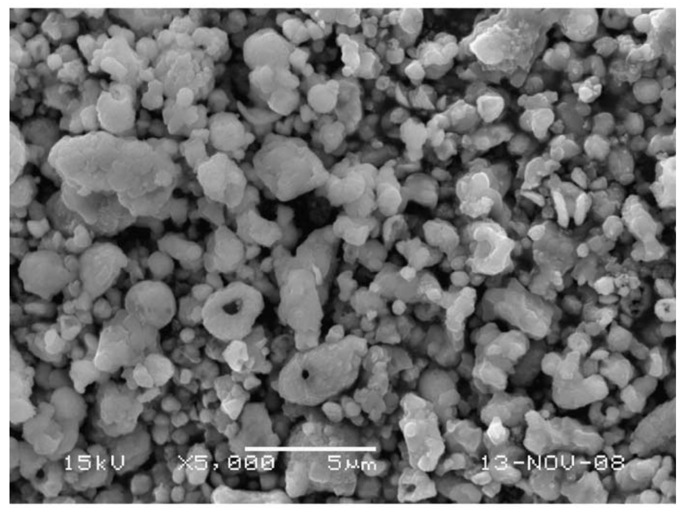
3. Results and discussions

The morphologies of the precursor powders prepared by spray pyrolysis from the spray solutions with various mole ratios of barium fluoride and barium nitrate were shown in Fig. 1. The precursor powders had spherical-like shape and micron size irrespective of mole ratios of barium fluoride and barium nitrate because of short residence time of the powders inside the hot wall reactor. The morphologies of the $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders post-treated at a temperature of 1150 °C were shown in Fig. 2. The morphologies of the precursor powders disappeared after post-treatment irrespective of the mole ratios of barium fluoride and barium nitrate. The morphologies and mean sizes of the $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders were affected by the mole ratios of barium fluoride and barium nitrate. The phosphor powders prepared from the spray solution without BaF_2 had polyhedral structure and unbroken morphology. On the other hand, the phosphor powders prepared from the spray solutions with BaF_2 had broken morphologies. The mean sizes of the phosphor powders increased with increasing the mole ratios of barium fluoride and barium nitrate. BaF_2 increased the mean sizes of the phosphor powders by acting as flux material.

Fig. 3 shows the excitation spectra of the phosphor powders prepared from spray solutions with different mole ratios of barium fluoride and barium nitrate. $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders post-treated at a temperature of 1150 °C had broad excitation wavelength ranging from 220 to 460 nm irrespective of mole ratios of barium fluoride and barium nitrate. The phosphor powders prepared from spray solution with BaF_2 had higher excitation spectrum than that of the powders prepared from spray solution without BaF_2.



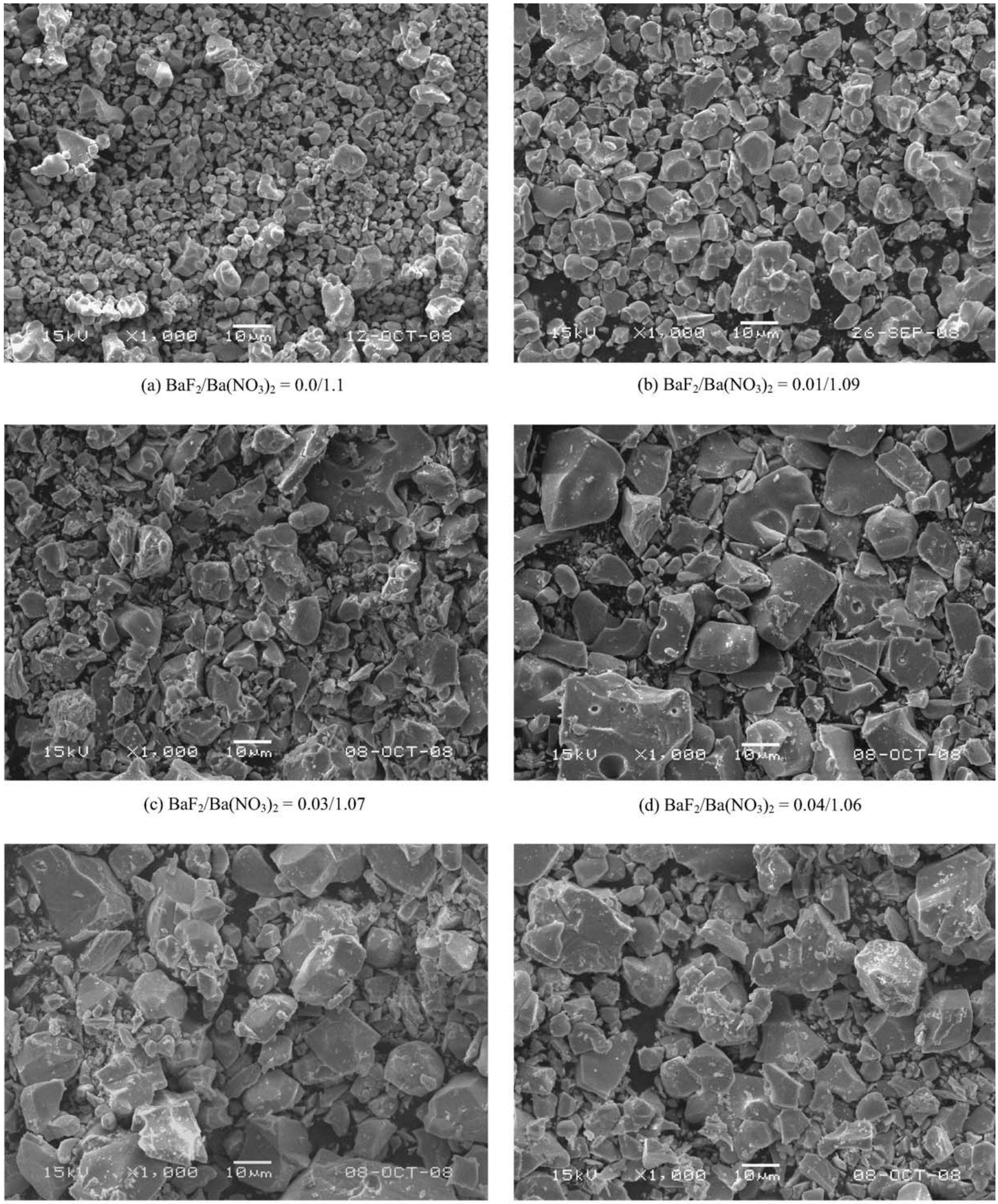
(a) $BaF_2/Ba(NO_3)_2$ = 0.0/1.1



(b) $BaF_2/Ba(NO_3)_2$ = 0.04/1.06

Fig. 1. SEM photographs of as-prepared $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ powders.

The emission spectra of the $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from the spray solutions with various mole ratios of barium fluoride and barium nitrate under excitation wavelength of 455 nm were shown in Fig. 4. The $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders had broad emission spectrum between 470 and 600 nm and had the maximum peak intensity at 522 nm. Substitution of BaF_2 instead of some amount of barium nitrate improved the photoluminescence intensities of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders. The $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with mole ratio of barium fluoride and barium nitrate of 0.04/1.06 had the maximum photoluminescence intensity. The maximum photoluminescence intensity of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with barium fluoride and barium nitrate was about 595% of the



(a) $BaF_2/Ba(NO_3)_2$ = 0.0/1.1

(b) $BaF_2/Ba(NO_3)_2$ = 0.01/1.09

(c) $BaF_2/Ba(NO_3)_2$ = 0.03/1.07

(d) $BaF_2/Ba(NO_3)_2$ = 0.04/1.06

(e) $BaF_2/Ba(NO_3)_2$ = 0.06/1.04

(f) $BaF_2/Ba(NO_3)_2$ = 0.08/1.02

Fig. 2. SEM photographs of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders post-treated at 1150 °C.

phosphor powders prepared from spray solution without barium fluoride.

The effects of mole ratio of barium fluoride and barium nitrate on the crystal structures of the $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders post-treated at 1150 °C were shown in Fig. 5. The phosphor powders prepared by spray pyrolysis had similar crystal structure regardless of the mole ratio of barium fluoride and barium nitrate. However, the substitution of barium fluoride instead of some amount of barium nitrate decreased the mean crystallite sizes of the phosphor powders calculated by Scherrer's equation. The mean crystallite sizes of the phosphor powders as shown in Fig. 2(a) and (d) were 57 and 41 nm, respectively. The effect of excess addition of barium fluoride instead of substitution of barium nitrate on the photoluminescence intensities of the $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders was also investigated. Addition of barium fluoride

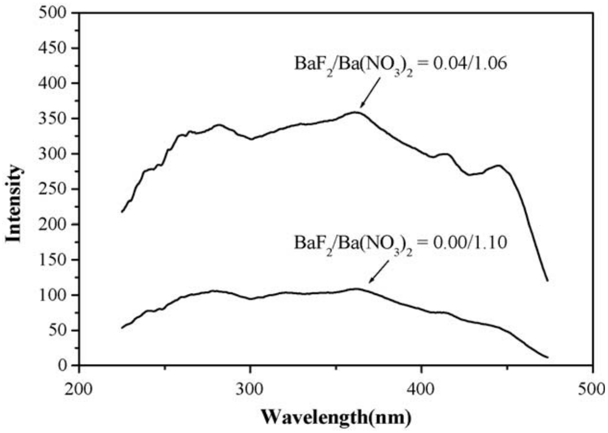


Fig. 3. Excitation spectra of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders at $\lambda_{em} = 522$ nm.

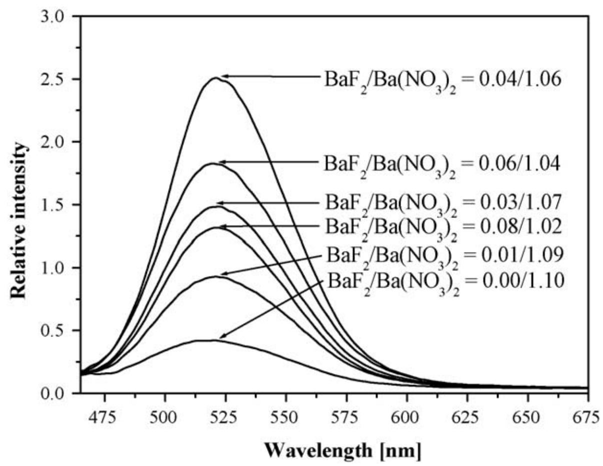


Fig. 4. Emission spectra of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders at $\lambda_{ex} = 455$ nm.

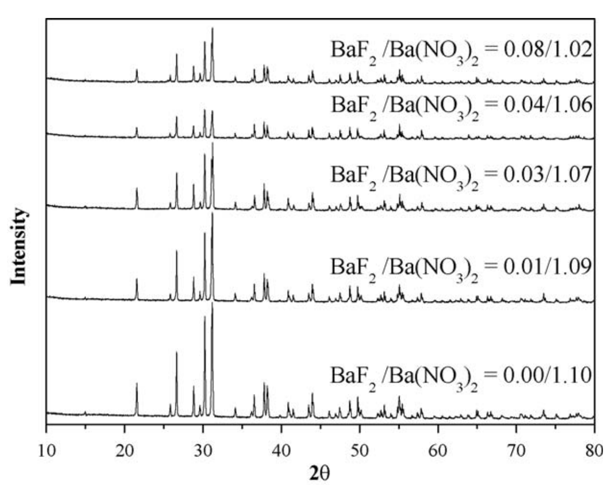


Fig. 5. XRD patterns of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders post-treated at 1150 °C.

as the flux material improved the photoluminescence intensities of the phosphor powders. The maximum photoluminescence intensity of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with excess amount of barium component applying barium fluoride was 330% of the phosphor powders prepared from spray solution with stoichiometric amount of barium component as nitrate form. However, $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solutions with stoichiometric amount of barium component applying barium fluoride and barium nitrate had higher photoluminescence intensities than those prepared from spray solutions with excess amount of barium component applying barium fluoride as flux material.

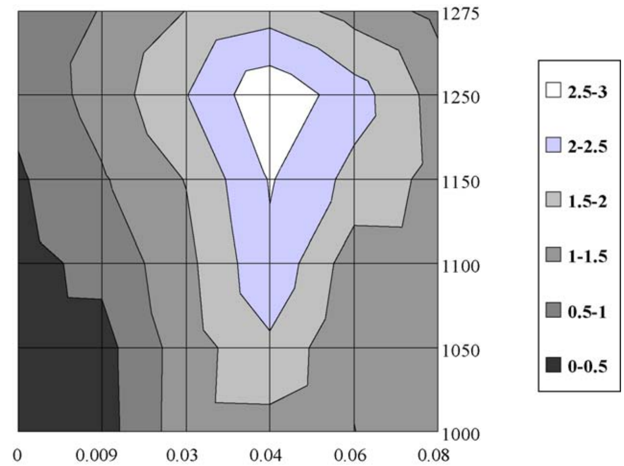


Fig. 6. The relative brightness of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders described as brightness of color.

The relative brightness of the phosphor powders prepared from spray solutions with stoichiometric amount of barium component applying barium fluoride and barium nitrate according to the post-treatment temperatures was described as brightness of color in Fig. 6. The $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with mole ratio of barium fluoride and barium nitrate of 0.04/1.06 had the maximum photoluminescence intensity at a post-treatment temperature of 1250 °C. Substitution of BaF_2 instead of some amount of barium nitrate improved the photoluminescence intensities of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders even at low post-treatment temperatures.

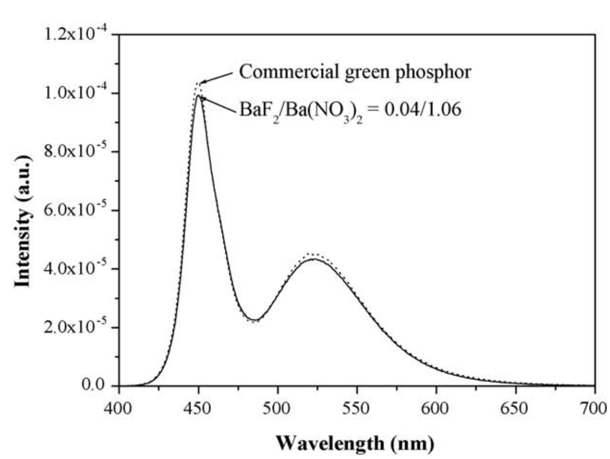


Fig. 7. Emission spectra of sky blue light emitting LEDs.

The sky blue light emitting LEDs were prepared by combining the InGaN based blue LED and green-emitting phosphors. The commercial green-emitting phosphor and the prepared $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders were applied. The luminescences of the sky blue light emitting LEDs under operating condition of 20 mA at room temperature were measured. Fig. 7 shows the emission spectra of the sky blue light emitting LEDs. Two distinct emission bands from blue LED and green-emitting phosphors are clearly resolved at 450 nm and at around 522 nm, respectively. The sky blue light emitting LED with commercial phosphor powders showed (0.1976 and 0.2722) on the CIE chromaticity diagram and luminous intensity of 1.74 cd. On the other hand, the sky blue light emitting LED with prepared phosphor powders showed (0.1958 and 0.2719) on the CIE chromaticity diagram and luminous intensity of 1.68 cd.

4. Conclusions

Green-emitting $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders were prepared by spray pyrolysis. The effects of mole ratio of barium fluoride and barium nitrate on the morphologies, crystal structures and optical properties of the prepared phosphor powders were investigated. The mean sizes of the phosphor powders increased with increasing the mole ratios of barium fluoride and barium nitrate. The phosphor powders prepared from spray solution with BaF_2 had higher excitation and emission spectra than those of the powders prepared from spray solution without BaF_2. BaF_2 improved the photoluminescence intensities of the phosphor powders by acting as flux material. $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solutions with stoichiometric amount of barium component applying barium fluoride and barium nitrate had higher photoluminescence intensities than those prepared from spray solutions with excess amount of barium component applying barium fluoride as flux material.

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