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Ceramics International 36 (2010) 1233–1238

CERAMICS INTERNATIONAL

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Characteristics of α′- and β-Sr_2SiO_4:Eu^{2+} phosphor powders prepared by spray pyrolysis

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Received 28 October 2009; received in revised form 11 November 2009; accepted 17 December 2009
Available online 28 January 2010

Abstract

α′- and β-Sr_2SiO_4:Eu^{2+} phosphor powders were prepared by spray pyrolysis from the spray solutions with and without NH_4Cl flux. The phosphor powders prepared from the spray solutions with the addition amount of NH_4Cl flux between 2 and 5 wt% of phosphor had regular polyhedron structures and main crystal structure of β-Sr_2SiO_4. On the other hand, the phosphor powders prepared from the spray solution with high addition amount of NH_4Cl flux as 6 wt% of phosphor had irregular morphology and crystal structure of α′-Sr_2SiO_4. The mean size of the β-Sr_2SiO_4 phosphor powders with regular polyhedron structure was 5.2 μm. The β-Sr_2SiO_4:Eu^{2+} phosphor powders had higher photoluminescence intensities than the α′-Sr_2SiO_4:Eu^{2+} phosphor powders. The β-Sr_2SiO_4:Eu^{2+} phosphor powders prepared from the spray solution with 5 wt% NH_4Cl flux of phosphor had the maximum photoluminescence intensity. The wavelengths of the emission spectra showing the maximum peak intensities changed from 543.2 to 561.8 nm when the addition amount of NH_4Cl flux was increased from 2 to 6 wt% of phosphor.

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

1. Introduction

Phosphor-combined light emitting diode (LED) is widely studied as backlight of the liquid crystal display (LCD) and lamp for lighting [1,2]. In order to successfully apply phosphor-combined LED to the lighting, fluorescent materials emitting yellow light should have high emission efficiency. $Y_3Al_5O_{12}$:Ce (YAG:Ce), $Tb_3Al_5O_{12}$:Ce (TAG:Ce), and Sr_2SiO_4:Eu^{2+} phosphors were mainly used as yellow-emitting phosphor for white LEDs [3–13].

Sr_2SiO_4:Eu^{2+} phosphor has two phases of α′ and β. The phases and morphologies of Sr_2SiO_4:Eu^{2+} phosphor powders were affected by the preparation conditions and the doping concentration of Eu dopant. The increase of Eu^{2+} concentration led to the phase transformation from β to α′-Sr_2SiO_4 [11,12]. Sr_2SiO_4:Eu^{2+} were mainly prepared by solid-state reaction method at high temperatures above 1280 °C [11–13]. A flux method is well-known to accelerate the kinetics of the formation of the desired compounds by enhancing diffusion coefficients. NH_4Cl flux was effective in the preparation of Sr_2SiO_4:Eu^{2+} phosphor powders by solid-state reaction method. However, the Sr_2SiO_4:Eu^{2+} phosphor powders post-treated at 1300 °C had the maximum photoluminescence intensity.

Spray pyrolysis has been applied to the preparation of green light emitting $(Ba,Sr)_2SiO_4$:Eu^{2+} phosphor powders with high brightness under ultraviolet [14,15]. Flux materials added to the spray solutions improved the morphological and optical properties of the $(Ba,Sr)_2SiO_4$:Eu^{2+} phosphor powders.

In this study, Sr_2SiO_4:Eu^{2+} phosphor powders with regular morphology and high photoluminescence intensity under ultraviolet and blue light irradiation were prepared by spray pyrolysis. NH_4Cl flux dissolved into the spray solutions affected the crystal structures, morphologies and photoluminescence spectra of the Sr_2SiO_4:Eu^{2+} phosphor powders.

2. Experimental

$Sr_{1.93}SiO_4$:$Eu_{0.07}$ (Sr_2SiO_4:Eu^{2+}) phosphor powders were prepared by post-treatment of the precursor powders obtained by spray pyrolysis. An ultrasonic spray generator with six vibrators that has frequency of 1.7 MHz was used to produce large amount of droplets. The length and inside diameter of

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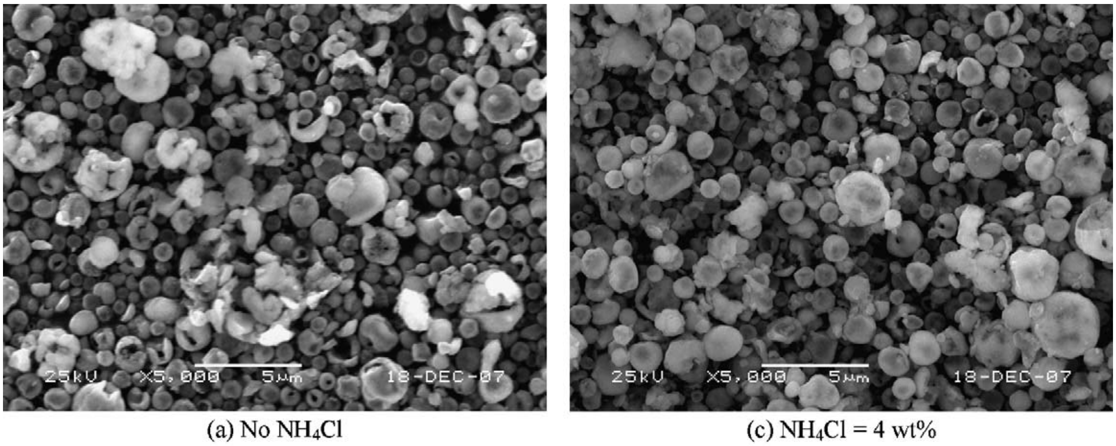
doi:10.1016/j.ceramint.2010.01.007

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 fixed at 45 L min^{-1} and the residence time of the powders inside the reactor was 0.6 s. The precursor solutions were prepared from strontium nitrate, europium oxide and fumed silica (aerosil 300, Degussa). The overall solution concentration was 0.5 M. The addition amount of NH_4Cl used as flux material was changed from 2 to 6 wt% of phosphor. The precursor powders obtained by spray pyrolysis were post-treated at a temperature of 1040 °C for 3 h under 10% H_2/N_2 mixture gas.

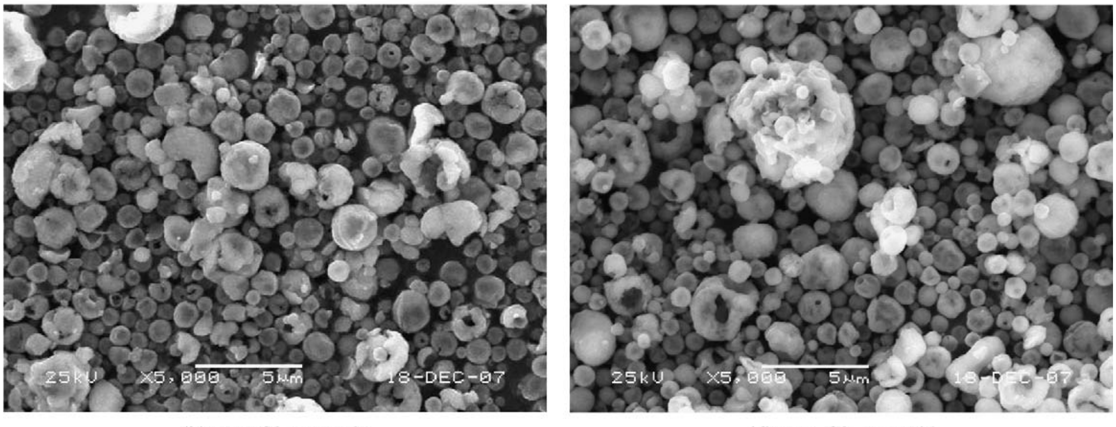
The morphological characteristics of the powders were analyzed using scanning electron microscopy (SEM). The crystal structures of the post-treated phosphor powders were investigated using X-ray diffractometry (XRD) using Cu Kα radiation ($\lambda = 1.5418$ Å). The compositions of the powders were analyzed using energy dispersive X-ray (EDX). The photoluminescence spectra of phosphor powders were measured using a spectrofluorophotometer under the excitation of a 455 nm blue light produced by an Xe flash lamp.

3. Results and discussions

The morphologies of the precursor powders prepared by spray pyrolysis from the spray solutions with different addition amount of NH_4Cl flux are shown in Fig. 1. The precursor powders had hollow and porous morphologies irrespective of the addition amount of NH_4Cl flux because of high drying and decomposition rates of the droplets or powders. Fig. 2 shows the SEM images of the $Sr_2SiO_4:Eu^{2+}$ phosphor powders post-treated at a temperature of 1040 °C. The $Sr_2SiO_4:Eu^{2+}$ phosphor powders prepared by spray pyrolysis from the spray solutions with NH_4Cl flux had the maximum photoluminescence intensity at a low post-treatment temperature of 1040 °C. NH_4Cl flux and high mixing degree of the components inside the precursor powders obtained by spray pyrolysis decreased the preparation temperature of the $Sr_2SiO_4:Eu^{2+}$ phosphor powders. The morphologies of the phosphor powders were affected by the addition amount of NH_4Cl flux dissolved into the spray solutions. The phosphor powders prepared from the spray solution without flux material had maintained the spherical shape of the precursor powders after post-treatment. On the other hand, the spherical shape of the precursor powders prepared from the spray solutions with NH_4Cl flux disappeared after post-treatment. The phosphor powders prepared from the spray solution with 2 wt% flux had irregular morphology with large size above 10 μm. However, the phosphor powders prepared from the spray solutions with 4 and 5 wt% flux had regular polyhedron structures. The mean sizes of the phosphor powders as shown in Fig. 2(c) and (d) were 8.2 and 5.2 μm, respectively. Fig. 3 shows the XRD patterns of the phosphor powders prepared from the spray solutions with different

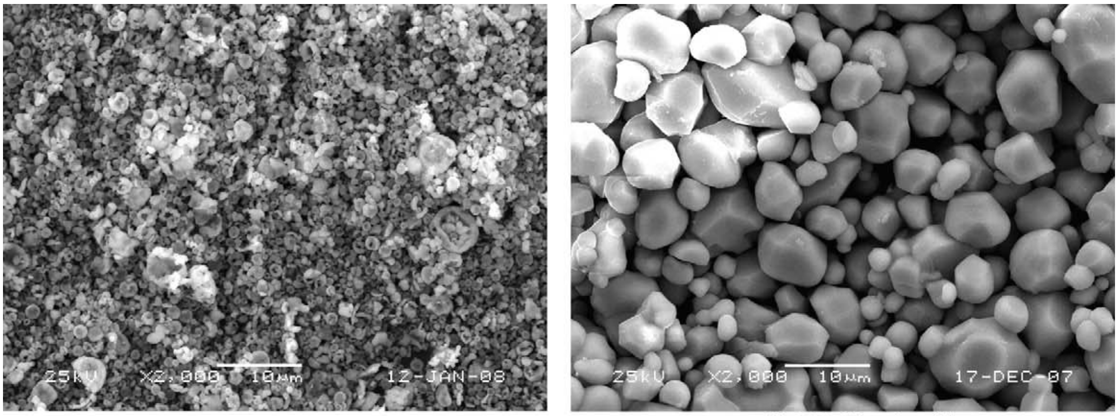


(a) No NH_4Cl (c) NH_4Cl = 4 wt%



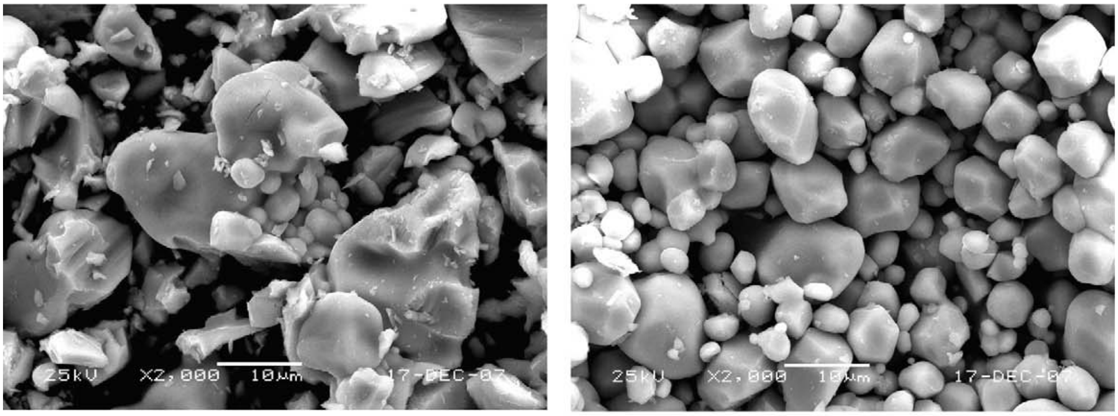
(b) NH_4Cl = 2 wt% (d) NH_4Cl = 6 wt%

Fig. 1. SEM images of the precursor powders prepared by spray pyrolysis.



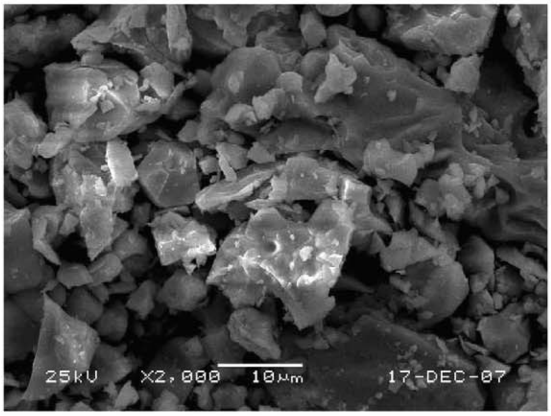
(a) No NH_4Cl

(c) NH_4Cl = 4 wt%



(b) NH_4Cl = 2 wt%

(d) NH_4Cl = 5 wt%



(e) NH_4Cl = 6 wt%

Fig. 2. SEM images of the $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor powders post-treated at 1040 °C.

addition amount of NH_4Cl flux. The phosphor powders prepared from the spray solution without flux material had pure crystal structure of α'-Sr_2SiO_4. NH_4Cl flux changed the crystal structure of the $Sr_2SiO_4:Eu^{2+}$ phosphor powders post-treated at the same temperature. The phosphor powders prepared from the spray solutions with the addition amount of NH_4Cl flux between 1 and 5 wt% of phosphor had main crystal structure of β-Sr_2SiO_4. On the other hand, the phosphor powders prepared from the spray solution with high addition amount of NH_4Cl flux as 6 wt% of phosphor had pure crystal structure of α'-Sr_2SiO_4. The change of the crystal structure of the phosphor powders changed the morphologies of the $Sr_2SiO_4:Eu^{2+}$ phosphor powders. The change of the crystal structure of the phosphor from β to α' phase changed the morphologies of the powders from regular polyhedron shape to irregular shape. Fig. 4 shows the EDX spectra of the phosphor powders prepared from the spray solutions without and with NH_4Cl flux. The compositions of the phosphor powders were shown in Table 1. The spectrum of the phosphor powders prepared from the spray solution with NH_4Cl flux had a small peak of Cl. Elimination of Cl component by post-treatment at a high temperature was not completed. However, the phosphor powders had similar compositions to that of the spray solution irrespective of addition of NH_4Cl flux.

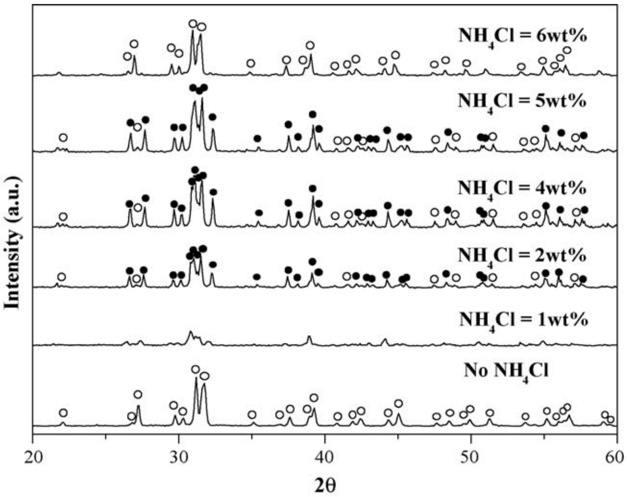
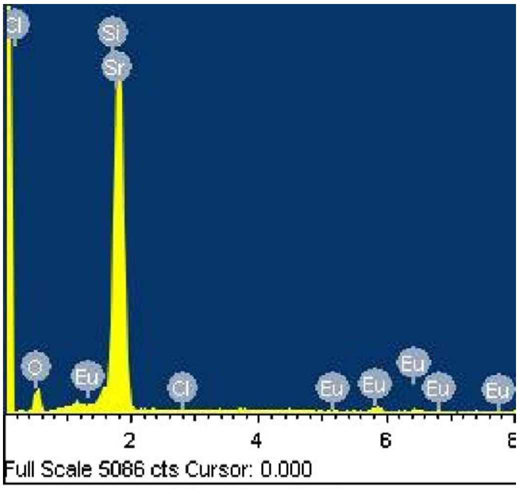
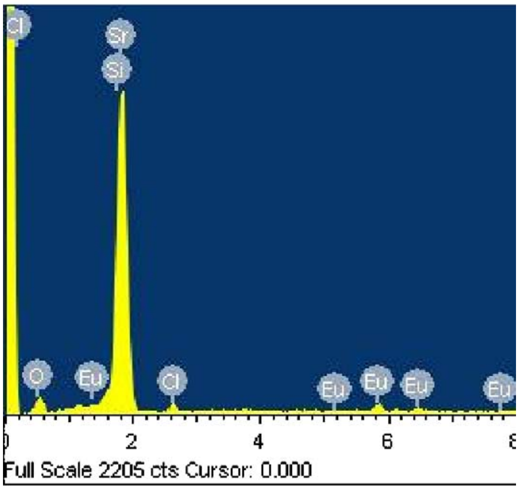


Fig. 3. XRD patterns of the $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor powders post-treated at 1040 °C.



(a) No NH_4Cl



(b) 5 wt% NH_4Cl

Fig. 4. EDX spectra of the $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor powders post-treated at 1040 °C.

Table 1
Compositions of the phosphor powders prepared from the spray solutions with and without NH_4Cl flux.

Sample	Element				
	Sr	Si	O	Eu	Cl
No flux	33.9	15.7	49.0	1.4	0
5 wt% NH_4Cl	31.8	17.0	48.1	1.4	1.7

Fig. 5 shows the excitation spectra of the prepared $Sr_2SiO_4:Eu^{2+}$ and the commercial $Y_3Al_5O_{12}:Ce^{3+}$ phosphor powders. The $Sr_2SiO_4:Eu^{2+}$ phosphor powders prepared from the spray solutions with and without NH_4Cl flux had broad excitation wavelength from 275 to 460 nm. Therefore, the $Sr_2SiO_4:Eu^{2+}$ phosphor powders could be applied to ultraviolet and blue light emitting diodes. The excitation spectra of the β-$Sr_2SiO_4:Eu^{2+}$ phosphor powders prepared from the spray solutions with 2, 4 and 5 wt% NH_4Cl flux had higher peak intensities than those of the α′-$Sr_2SiO_4:Eu^{2+}$ phosphor powders prepared from the spray solutions without flux and with 6 wt% NH_4Cl flux.

Fig. 6 shows the emission spectra of the α′ and β-$Sr_2SiO_4:Eu^{2+}$ phosphor powders prepared by spray pyrolysis

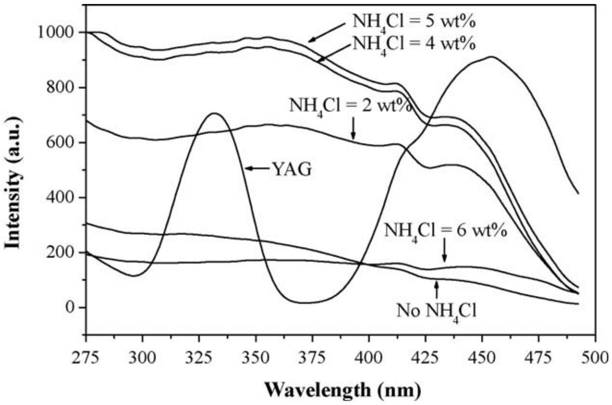


Fig. 5. Excitation spectra of the $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor powders post-treated at 1040 °C.

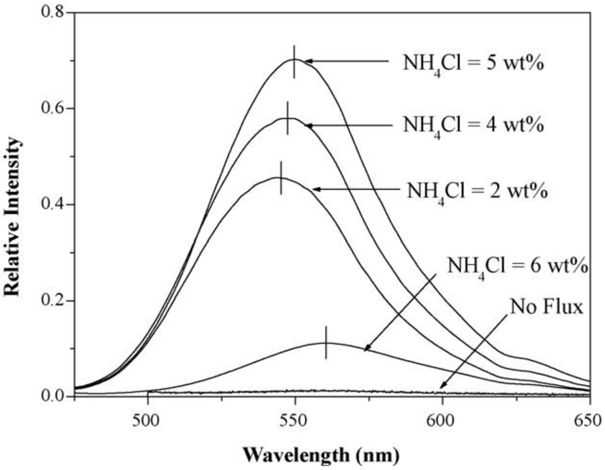


Fig. 6. Emission spectra of the $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor powders post-treated at 1040 °C under excitation wavelength of 455 nm.

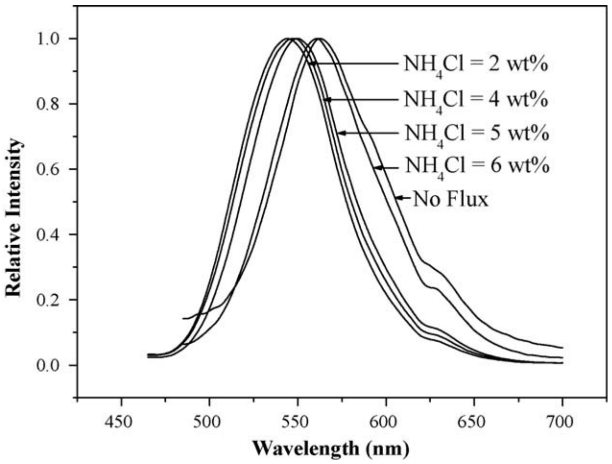


Fig. 7. Normalized emission spectra of the $Sr_{1.93}SiO_4$:$Eu_{0.07}$ phosphor powders post-treated at 1040 °C.

under excitation wavelength of 455 nm. The phosphor powders had a broad emission spectrum between 475 and 650 nm. The β-Sr_2SiO_4:Eu^{2+} phosphor powders had higher photoluminescence intensities than the α′-Sr_2SiO_4:Eu^{2+} phosphor powders. The β-Sr_2SiO_4:Eu^{2+} phosphor powders prepared from the spray solution with 5 wt% NH_4Cl flux of phosphor had the maximum photoluminescence intensity. NH_4Cl flux improved the photoluminescence intensities of the Sr_2SiO_4:Eu^{2+} phosphor by changing crystal structure, mean size and surface property of the powders. The β-Sr_2SiO_4:Eu^{2+} phosphor powders as shown in Fig. 2(d) had large size and clean surface. Phosphor powders with large size and clean surface had high photoluminescence intensity because of low surface defects.

Fig. 7 shows the normalized emission spectra of the $Sr_{1.93}SiO_4$:$Eu_{0.07}$ phosphor powders prepared from the spray solutions with and without NH_4Cl flux. The location of wavelength of the emission spectra showing the maximum peak intensities moved to the right when the phase of Sr_2SiO_4:Eu^{2+} phosphor powders was changed from α′ to β [11,12]. The wavelengths of the emission spectra showing the maximum peak intensities changed from 543.2 to 561.8 nm when the addition amount of NH_4Cl flux was increased from 2 to 6 wt% of phosphor. Fig. 8 shows the CIE chromaticity coordinates of the Sr_2SiO_4:Eu^{2+} phosphor powders. The colors of the Sr_2SiO_4:Eu^{2+} phosphor powders changed from yellow-green to yellow when the addition amount of NH_4Cl flux was increased from 2 to 6 wt% of phosphor.

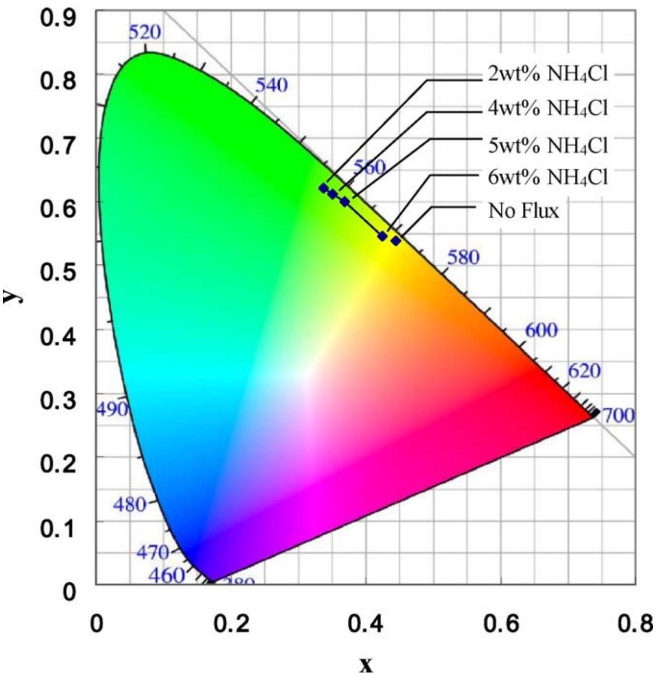


Fig. 8. CIE chromaticity coordinates of the $Sr_{1.93}SiO_4$:$Eu_{0.07}$ phosphor powders post-treated at 1040 °C.

4. Conclusions

Sr_2SiO_4:Eu^{2+} phosphor powders with high photoluminescence intensities under ultraviolet and blue light were prepared by spray pyrolysis at a low post-treatment temperature of 1040 °C. NH_4Cl flux dissolved into the spray solution improved the morphological and optical properties of the Sr_2SiO_4:Eu^{2+} phosphor powders. β-Sr_2SiO_4:Eu^{2+} phosphor powders prepared from the spray solution with 5 wt% NH_4Cl of phosphor had regular polyhedron shape and high photoluminescence intensity.

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