

Preparation of Eu-activated strontium orthosilicate ($\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$) phosphor by a sol–gel method and its luminescent properties

Wei-Hsiang Hsu^a, Meng-Huei Sheng^b, Ming-Shyong Tsai^{a,*}

^a Department of Chemical and Materials Engineering, Southern Taiwan University, Taiwan

^b Department of Information Management, Chia Nan University of Pharmacy and Science, Tainan, Taiwan

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Abstract

Eu^{2+} -activated Sr_2SiO_4 phosphor was successfully synthesized by a sol–gel method using sodium silicate and SrO as the starting materials. The wavelength of the emission peak and the emission intensity of the phosphor powders were influenced by the pre-treating temperature. The maximum emission intensity of the phosphor was found as pre-treated at 1200 °C in air and then heated at 1300 °C in the reducing atmosphere (10% H_2 + 90% He). As the pre-treating temperature was <1200 °C, the composition of the phosphor powder was not uniform, which leads to decrease of the emission intensity, whereas >1200 °C, the decrease of the emission intensity may be caused from the reversible phase transformation of $\text{Sr}_3\text{SiO}_5 \rightarrow \text{Sr}_2\text{SiO}_4$ at 1300 °C, which also shows the red-shift behavior.

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1. Introduction

Light-emitting diode (LED) with the phosphor material to generate white light is the present focus of research in the lighting industry [1]. White light LED shows many excellent properties such as low energy consumption, small size, light weight and long lifetime [1,2]. There are several technologies that combined UV LED and phosphor to general white light [3]: $\text{Sr}_2\text{SiO}_4:\text{Eu}$ and $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}$ excited with a UV LED ($\lambda_{\text{em}} = 430$ nm) [4]; $\text{Sr}_2\text{SiO}_4:\text{Eu}$ excited with a blue GaN chip ($\lambda_{\text{em}} = 400$ nm) [5]; $\text{X}_3\text{MgSi}_2\text{O}_8:\text{Eu}$, Mn (X = Ba, Sr, Ca) excited with a UV LED ($\lambda_{\text{em}} = 375$ nm) [6]. Eu-activated silicate phosphor ($\text{Sr}_2\text{SiO}_4:\text{Eu}$) is suitable for the application of the white light LED, which has a broaden emission band through 4f–5d energy transition of Eu activator ion. There are promising prospects as white light by UV LED [7]. Recently, $\text{Sr}_2\text{SiO}_4:\text{Eu}$ combined with the GaN blue LED to produce white light, which can compete with the commercially available InGaN-based YAG:Ce powder [5,8].

In the SrO–SiO₂ binary system, there are three transition compounds including: SrSiO_3 , Sr_2SiO_4 and Sr_3SiO_5 . The melting temperature of the Sr_2SiO_4 compound is 2325 ± 15 °C. The eutectic temperature between Sr_2SiO_4 and Sr_3SiO_5 is 2150 ± 15 °C at ~27 mol% SiO₂ [9]. The photoluminescence spectrums of these phosphors depend on the formation temperature. As the formation temperature increases, the emission peak of phosphor is shifted to the lower energy, the emission band broadens, and the emission intensity is increased [7]. In the present work, Eu^{2+} -activated Sr_2SiO_4 phosphor was synthesized by a sol–gel method using sodium silicate as the starting material. The wavelength of emission peak and the emission intensity of phosphor powders were influenced by the pre-treating temperature.

2. Experimental

$\text{Sr}_2\text{SiO}_4:\text{Eu}$ phosphor was synthesized through a sol–gel technique. The starting materials were sodium silicate (commercial grade, 30% SiO₂, 13% Na₂O), strontium oxide (SrO) and europium oxide (Eu₂O₃). 78.8 g sodium silicate was diluted with water to 500 ml, and the sodium ion in this diluted sodium silicate solution was then removed by the ion-exchange resin (amberlite 120). About 500 ml of the active silicic acid was collected after ion exchanging. The solid content of silica in the active silicate acid was about 3.24 wt%, which could be estimated by the density measurement of the solution. The detail descrip-

* Corresponding author. Tel.: +886 6 2533131x6946; fax: +886 6 2425741.
E-mail address: tsaims@mail.stut.edu.tw (M.-S. Tsai).

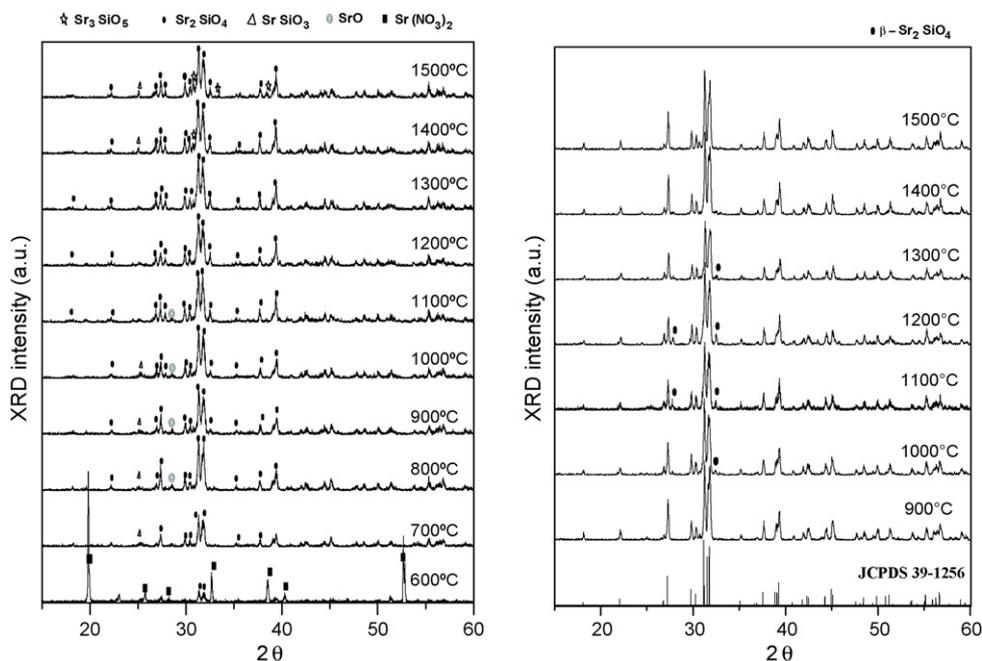


Fig. 1. X-ray diffraction patterns of the $\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$ phosphors for (a) pre-treated at the various temperatures, and then (b) calcined at 1300 °C in a reducing atmosphere.

tion about this ion-exchange process was reported in our previous study [10]. The silicate gel was obtained by heating the above solution at 60–80 °C for 10 h. $\text{Sr}(\text{NO}_3)_2$ and $\text{Eu}(\text{NO}_3)_3$ with the stoichiometric ratio of $\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$ were added to the silicate gel. The mixing gel was well stirred for 1 h. The foregoing sample was dried in an oven at 110 °C for several days and was then calcined at the desired temperature (600–1500 °C) for 1 h, respectively. Furthermore, all of the testing samples in this study were heat-treated in the reducing atmosphere (10% H_2 , 90% He) at 1300 °C for 1 h for the reducing reaction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$. The formation phase and the luminescent properties of $\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$ phosphor were characterized by X-ray diffraction (XRD, Rigaku, MultiFlex ZD3609N) with Cu K α radiation ($\lambda = 1.548 \text{ \AA}$). The scan range was from 15° to 60° with a scan step of 0.01° and the scan rate of

4°/min. The photoluminescence (PL) property was analyzed by MFS230 fluorescence spectrometer. The wavelength of the exciting light source was at 370 nm ($\lambda_{\text{ext}} = 370 \text{ nm}$). The morphologies of the calcined powder was observed by transmission electron microscope (TEM, Philips Tecnai G2 F20 FEG-TEM). The local compositions of the powders were identified by energy dispersive spectrometry system (EDS) in TEM.

3. Results and discussion

The XRD pattern of the phosphors pre-treated at the desired temperature is exhibited in Fig. 1(a). The crystal structure of

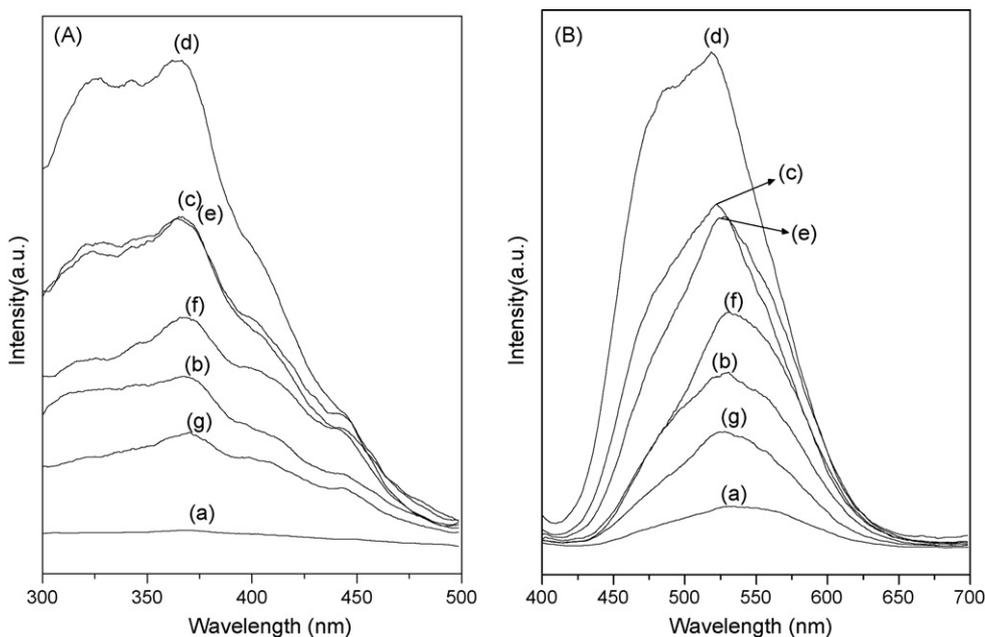


Fig. 2. (A) Excitation and (B) emission spectra of $\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$ pre-treated at various temperatures, and then calcined at 1300 °C in a reducing atmosphere.

the formed powder is major α - Sr_2SiO_4 (JCPDS #39-1256) and β - Sr_2SiO_4 (JCPDS #38-0271) with minor SrSiO_3 (JCPDS #36-0018) as pre-treated at 700–1000 °C. The pure Sr_2SiO_4 is found in the pre-treating temperature between 1100 and 1300 °C. However, as the pre-treating temperature is at the higher temperature (above 1400 °C), the formed phases are Sr_2SiO_4 with minor Sr_3SiO_5 (JCPDS #26-0984) and minor SrSiO_3 . Furthermore, all the samples were completely converted to pure Sr_2SiO_4 phase after calcining at 1300 °C for 1 h in the reducing atmosphere (10% H_2 , 90% He), as shown in Fig. 1(b). The formed phosphors have the wide exciting band 300–500 nm with the stronger excitation peak at ~ 370 nm, as shown in Fig. 2(A). The emission spectra of the products are in broad band 450–600 nm, as shown in Fig. 2(B). Fig. 3 shows the relative emission intensity and the emission peak of the phosphors versus the pre-treating temperature. By increasing the pre-treating temperature, the emission intensity is increased first and is then decreased. In addition, the emission wavelength was slightly blue-shifted as the emission intensity was increased, as shown in Fig. 2(B). The maximum emission intensity was found at 1200 °C (the pre-treating temperature). To discuss the decrease of the emis-

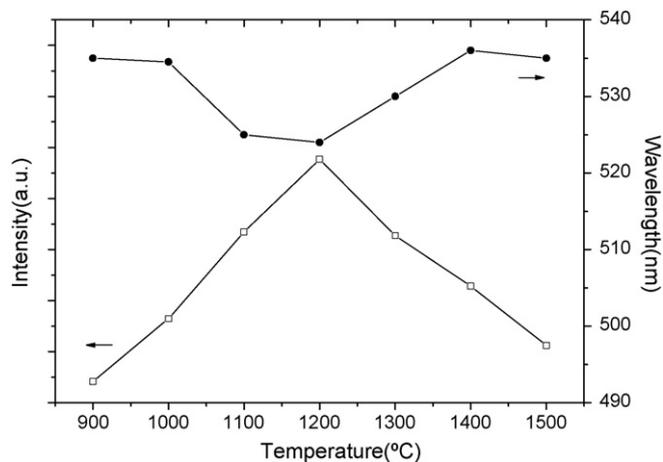


Fig. 3. Relationship between the luminescence intensity and wavelength of $\text{Sr}_{1.95}\text{SiO}_4:\text{Eu}_{0.05}$ phosphors at different pre-treating temperatures.

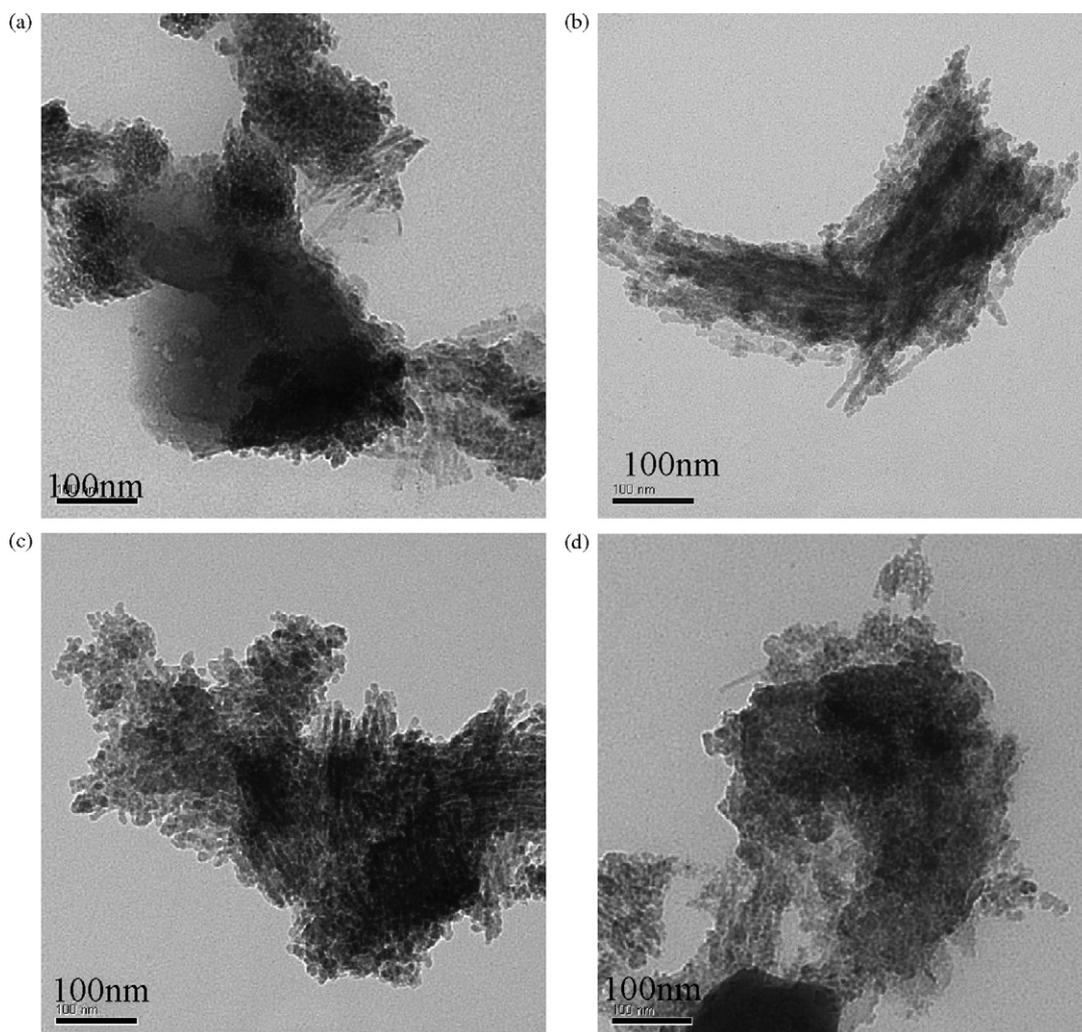


Fig. 4. TEM photographs of $\text{Sr}_2\text{SiO}_4:\text{Eu}$ phosphors as pre-treating temperatures at (a) 900 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C, then calcined at 1300 °C in a reducing atmosphere.

sion intensity at the high pre-treating temperature, the focus should be on the formation phase after different pre-treating temperature. A little Sr_3SiO_5 is presented in the high pre-treated temperature phosphor (above 1400°C); however, it is phase transferred to the Sr_2SiO_4 phase after re-heating at 1300°C in the reducing atmosphere. Therefore, some of Sr_2SiO_4 was formed by the reaction path of $\text{Sr}_3\text{SiO}_5 \rightarrow \text{Sr}_2\text{SiO}_4$. The structure of Sr_2SiO_4 has two different Sr^{2+} sites in the host lattice: $\text{Sr}^{2+}(\text{I})$ and $\text{Sr}^{2+}(\text{II})$ (coordination number = 9 and 10, respectively). When Eu^{2+} ion substituted Sr^{2+} sites in Sr_2SiO_4 , the emission spectra has two different emission wavelengths, which were caused from these two different substitution sites [4,11]: blue-green band and yellow band. It was known that strontium is located at (0.181, 0.181, 0.25) in the Sr_3SiO_5 structure [12]. On the other hand, in the Sr_2SiO_4 structure, strontium is distributed at $\text{Sr}^{2+}(\text{I})$ (0.25, -0.0014, 0.5798) and $\text{Sr}^{2+}(\text{II})$ (0.25, 0.3403, 0.3022) [13]. When pre-treated at 1500°C , the Sr_3SiO_5 phase was formed first. After re-heating at 1300°C in a reducing atmosphere, the phase transformation of $\text{Sr}_3\text{SiO}_5 \rightarrow \text{Sr}_2\text{SiO}_4$ occurred, and the location of strontium atoms should be changed from (0.181, 0.181, 0.25) to (0.25, 0.3403, 0.5798) and (0.25, -0.0014, 0.3022). However, the diffusion distance of (0.181, 0.181, 0.25) \rightarrow (0.25, 0.3403, 0.5798) is shorter than that of (0.181, 0.181, 0.25) \rightarrow (0.25, 0.3403, 0.3022). It revealed that strontium is rather moved to $\text{Sr}^{2+}(\text{II})$ than to $\text{Sr}^{2+}(\text{I})$ during the phase transformation of $\text{Sr}_3\text{SiO}_5 \rightarrow \text{Sr}_2\text{SiO}_4$. The emission intensity caused from the $\text{Sr}^{2+}(\text{I})$ site at the 900–1200 $^\circ\text{C}$ range is higher than that at 1300–1500 $^\circ\text{C}$. The product pre-treated at high temperature shows the single emission band (the emission wavelength is red-shifted). With the pre-treated temperature at 1200°C , the Sr_2SiO_4 phase is formed directly, and Eu^{2+} ions are distributed normally at $\text{Sr}^{2+}(\text{I})$ and $\text{Sr}^{2+}(\text{II})$ sites in the Sr_2SiO_4 structure. So the powder shows two emission bands (the emission wavelength is blue-shifted). On the other hand, the relative emission intensity was decreased by decreasing the pre-treating temperature as the pre-treating temperature was $\leq 1200^\circ\text{C}$. It may be caused from the non-uniform composition of the powder at the lower pre-treating temperature. Although all of the products show the same Sr_2SiO_4 phase, the emission intensity and the emission peak are influenced by the uniformity of the powder composition. The effect maybe caused from the existence of the wide range defect structure in Sr_2SiO_4 structure. The detail works are in progress. Fig. 4 shows the TEM morphology of the phosphors pre-treated at $\leq 1200^\circ\text{C}$ and then treated in the reducing atmosphere at 1300°C . The morphologies of the powder do not change significantly by changing the pre-treating temperature. The small spherical particles (outside particles) with the rod-like particles were around the black and large agglomerate particle (inside particles). The compositions of the phosphors on the outside particles and the inside particles were analyzed by EDS. The results are shown in Fig. 5. The composition of the phosphors obtained by pre-treating at 900°C and treated in the reducing atmosphere at 1300°C was not uniform. The small particles were Sr rich and the black agglomerates were Si rich. By increasing the pre-treating temperature, the variation of the composition of these particles was decreased. The composition of the product pre-

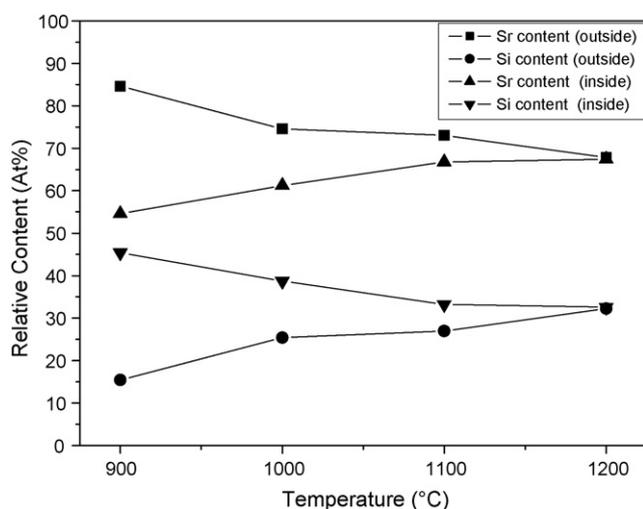


Fig. 5. EDS analysis of the inside and outside powders at various temperatures between 900 and 1200°C and then treated at 1300°C in the reducing atmosphere.

treated at 1200°C was uniform. It may be the reason that the product has the highest emission intensity when pre-treated at 1200°C .

4. Conclusions

Eu^{2+} -activated Sr_2SiO_4 phosphor was synthesized via a sol-gel method. The photo luminescent properties of the phosphor were investigated. The emission intensity and the emission peak of the phosphor were affected by the pre-treating temperature. The maximum emission intensity of Sr_2SiO_4 was obtained by pre-treating at 1200°C and reducing at 1300°C in 10% $\text{H}_2 + 90\%$ He atmosphere. If the pre-treating temperature is $>1200^\circ\text{C}$, some powder is formed as Sr_3SiO_5 first and is then phase transferred to Sr_2SiO_4 after being reduced in 10% $\text{H}_2 + 90\%$ He (the reaction of $\text{Sr}_3\text{SiO}_5 \rightarrow \text{Sr}_2\text{SiO}_4$ occurred). Due to Eu^{2+} ions substituting at $\text{Sr}^{2+}(\text{II})$ than $\text{Sr}^{2+}(\text{I})$, in the Sr_2SiO_4 host lattice, the formed phosphor showed the low emission intensity and the single emission band in the yellow range. On the other hand, if the pre-treating temperature is $<1200^\circ\text{C}$, the emission intensity is decreased by the non-uniform chemical composition of powder. The product pre-treated at 1200°C has the maximum emission intensity and two emission bands.

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