



$\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ Green-emitting Nano Phosphor for Ultraviolet Light Emitting Diodes

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The aim of this work is to investigate the effect of $\text{Ca}_x\text{Sr}_{2-x}$ and activator on the structural and luminescent properties of green-emitting $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ nano phosphor. Using urea as fuel and ammonium nitrate as oxidizer, $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ has been successfully synthesized, using a combustion method. The particles were found to be small, spherical and of round surface. SEM imagery showed that the phosphors particles are of nanosize. The $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ emission spectrum for 360 nm excitation showed a single band, with a peak at 490 nm, which is a green emission. The highest luminous intensity was at 1,000 °C, which was obtained when the Eu^{2+} content (y) was 0.05. The results support the application of $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphor as a fluorescent material for ultraviolet light-emitting diodes (UV-LEDs). Characteristics of the synthesized $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphor were investigated by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and photoluminescence (PL) detection.

Keywords: CaSrSiO_4 , Phosphor, Combustion method, Light-emitting diode

1. INTRODUCTION

Recently, the generation of white light through a combination of an ultraviolet or blue-emitting chip and phosphors as a solid-state lighting source has attracted considerable interest [1,2]. These phosphors and chip-based light-emitting diodes (LEDs) have several advantages over conventional incandescent and fluorescent lamps, in terms of power efficiency, long lifetime, absence of pollution, and design flexibility [2,3]. White light-emitting diodes (W-LEDs) have been the subject of increasing interest, due to their advantages of low energy consumption, long life span, and lack of pollutants such as Hg, and to their potential applications in indicators, backlights, automobile headlights and general illumination [4]. White light-emitting diodes (LEDs) are in high demand in solid-state lighting (SSL) technology, because of their most challenging application as a replacement for conventional incandescent and fluorescent lamps. Therefore, they are considered the next generation of solid-state lighting. With-

out doubt, SSL is a pivotal emerging technology that promises to alter lighting in the future. With the development of materials science and technology, soft-chemical synthesis methods such as sol-gel [5], co-precipitation [6] and hydrothermal synthesis [7,8] have been successfully applied to synthesize phosphate-white LED phosphors. All of these methods use liquid components, which can be accurately controlled, and thoroughly mixed. Combustion synthesis is characterized by more complete reaction, increased reaction efficiency, fast reaction, and convenience.

The aim of this work is to investigate the effect of $\text{Ca}_x\text{Sr}_{2-x}$ and activator on the structural and luminescent properties of green-emitting $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ nano phosphor. For small spherical particles with smooth and round surfaces, $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphors were synthesized. Using urea as fuel, and ammonium nitrate as oxidizer, $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ was successfully synthesized, using a combustion method. The influence of X($\text{Ca}_x\text{Sr}_{2-x}$) content on the crystalline structure of the produced powders of $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphors was investigated. The results of characterization showed that the phosphors particles are nanosize. The phosphors exhibit a green emission spectrum for near uv excitation. The material has application as a fluorescent material for ultraviolet light-emitting diodes (UV-LEDs).

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In this work, we synthesize a $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ nano phosphor by a combustion method. Also, we investigate the effect of $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}_y$ on the structural transformation and luminescent properties of green-emitting $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ nano phosphor.

2. EXPERIMENT

In this study, $\text{CaSrSiO}_4:\text{Eu}^{2+}$ phosphors were prepared using a combustion method. $\text{Ca}(\text{NO}_3)_2$ (99.997%, Aldrich), $\text{Sr}(\text{NO}_3)_2$ (99.995%, Aldrich), SiO_2 (99.9%, Aldrich), and Eu_2O_3 (99.999%, Aldrich) were used as the starting materials. The CaSrSiO_4 phosphors were doped by Eu^{2+} , with the molecular formula of $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}_y^{2+}$. $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, SiO_2 and Eu_2O_3 were mixed together by mol ratio, and then distilled water was added. Urea was used as fuel, and ammonium nitrate served as the oxidizer. The parameters were measured, and are shown in Table 1. A flowchart of the preparation of the phosphor powders is shown in Fig. 1. The urea and ammonium nitrate solution was heated to 80°C , and continuously stirred, using a magnetic bar. The metal solution was dropped into the fuel, and the heating was continued for 30 minutes at 80°C . The solution was then transferred to a pre-heated furnace set to 500°C . After heating, different samples of the mixture were sintered in a furnace for 3 hours, at 600°C – $1,400^\circ\text{C}$. Crystalline development of the resulting samples was checked by X-ray diffraction (XRD, model D/MAX-2200), using $\text{CuK}\alpha$ -radiation in the range of $2\theta = 20$ – 80° . Measurement of the photoluminescence (PL) spectra was carried out by 150 W Xe lamp (spectrofluorometer, FP-6200, JASCO). The morphology and size of the prepared particles were investigated by field-emission scanning electron microscopy (FE-SEM, model S-4700, HITACHI).

3. RESULTS AND DISCUSSIONS

Figure 2 shows XRD patterns of the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ ($X=0$) sintered at different temperatures. At the different temperatures, the XRD patterns show pure Sr_2SiO_4 phase. In this structure, Sr^{2+} ions locate at two kinds of nonequivalent lattice sites, and their coordination numbers are nine and ten, respectively. When the Eu is introduced into the Sr_2SiO_4 structure, it takes the place of the Sr^{2+} . In the case of precursor, not only the Sr_2SiO_4 phase was observed, but also impurities peaks, due to material not having been synthesized. At $1,000^\circ\text{C}$, the diffraction peaks became sharper and stronger. The Sr_2SiO_4 phase crystallized with results that are in good agreement. However, at $1,200^\circ\text{C}$, the Sr_2SiO_4 peaks were markedly weakened. Figure 3 shows XRD patterns of the $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphors ($x = 0.2, 0.5, 1.0, \text{ and } 1.5$) produced by the combustion method at $1,000^\circ\text{C}$. The structure of Ca_2SiO_4 is monoclinic, which is different from that of Sr_2SiO_4 (orthorhombic structure). Therefore, substitution of the Ca sites with Sr^{2+} ions might cause a monoclinic to orthorhombic structural transformation [9]. According to JCPDS card 72-2260, pure CaSrSiO_4 has a orthorhombic crystal structure with $\text{Pna}2_1(33)$ space group, and lattice parameters of $a = 20.87 \text{ \AA}$, $b = 9.496 \text{ \AA}$, and $c = 5.6 \text{ \AA}$. In the case of Sr substitution with Ca at a concentration ratio of 1.5, a single phase was identified by XRD, without any extraneous phase. Moreover, the Ca doped ions had a slight influence on the CaSrSiO_4 orthorhombic crystal structure. A comparison of JCPDS No. 72-2260 with the phosphor with Sr concentration ratio of 1.5 showed that the main diffraction peaks were shifted to a lower angle. Therefore, the addition of Sr increased the lattice parameters of the phosphor, because the ionic radius of Ca^{2+} (0.10 nm) is slightly lower

Table 1. Mol ratios of the $\text{CaSrSiO}_4:\text{Eu}^{2+}$ used by the combustion method at various temperatures

Various mol ratios of the materials		Temp.
$\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4$	$X = 0.2 / 0.5 / 1.0 / 1.5$	600°C
$y\text{Eu}^{2+}$	$Y = 0.01 / 0.02 / 0.03 / 0.05 / 0.1$	
SiO_2	1	~
Urea	20	$1,400^\circ\text{C}$
Ammonium nitrate	20	

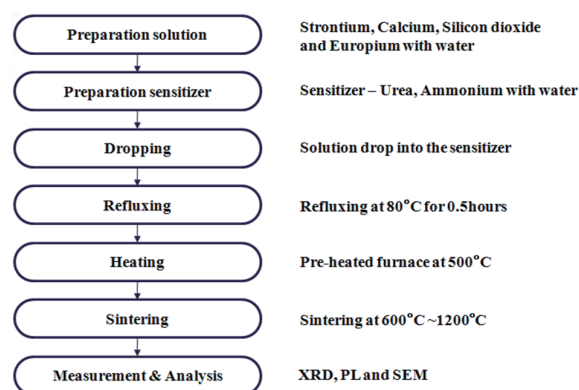


Fig. 1. Flowchart of the preparation of the phosphor powders.

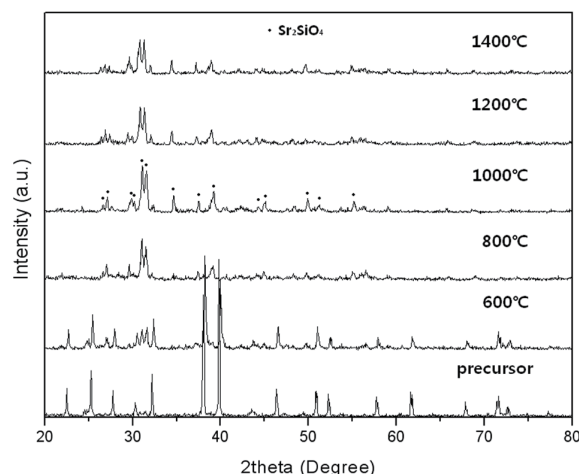


Fig. 2. XRD patterns of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:0.05\text{Eu}^{2+}$ sintered at different temperature.

than that of Sr^{2+} (0.118 nm) [6]. The main diffraction peaks were shifted to a smaller angle, as the concentration ratio of Ca^{2+} ions in the host lattice was increased from 0.2 to 1.5. Figure 4 shows SEM imagery of $\text{CaSrSiO}_4:\text{Eu}^{2+}$ synthesized at various firing temperatures. The surface morphologies of the phosphor at 600°C were rough. With increased sintering temperature, the phosphor particles became spherical, which occurred because the particles condense at higher temperatures [10]. But at $1,200^\circ\text{C}$, particles with agglomerates were observed. At over $1,200^\circ\text{C}$, the particles became cohesive and rough, due to the high sintering temperature. At this point, we determined that the characteristics of the phosphor powders were improved by increasing the sintering temperature; however, defects form in the phosphor, when it is heated beyond a critical temperature. Figure 5 shows the excitation and emission spectra of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:0.05\text{Eu}^{2+}$. The emission spectrum for 360nm excitation showed a single

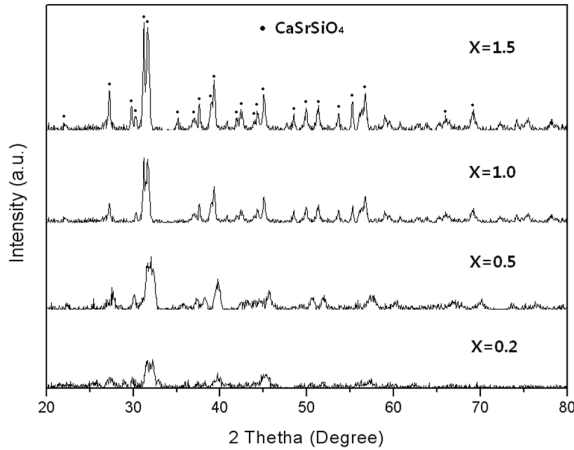


Fig. 3. XRD patterns of the $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:0.05\text{Eu}^{2+}$ phosphors at different concentrations of Ca molar ratio.

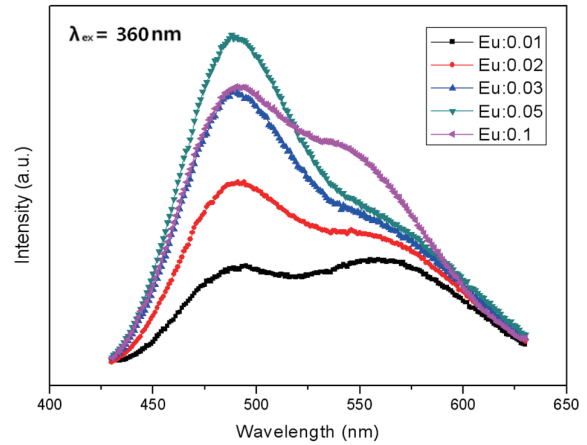


Fig. 6. PL Emission spectra of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:y\text{Eu}^{2+}$ phosphors at different concentrations of Eu molar ratio.

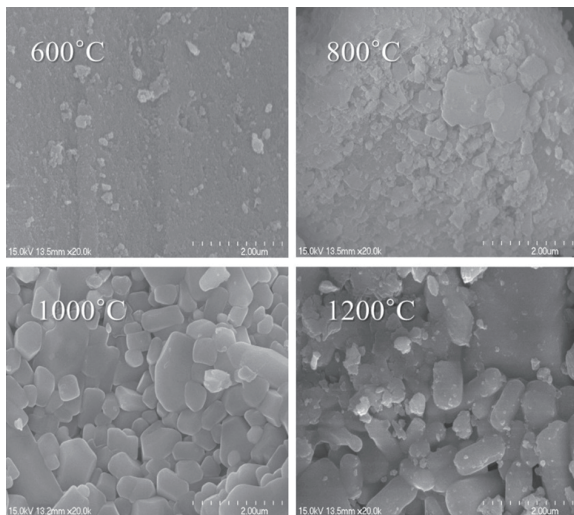


Fig. 4. SEM images of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:0.05\text{Eu}^{2+}$ phosphors at different temperatures.

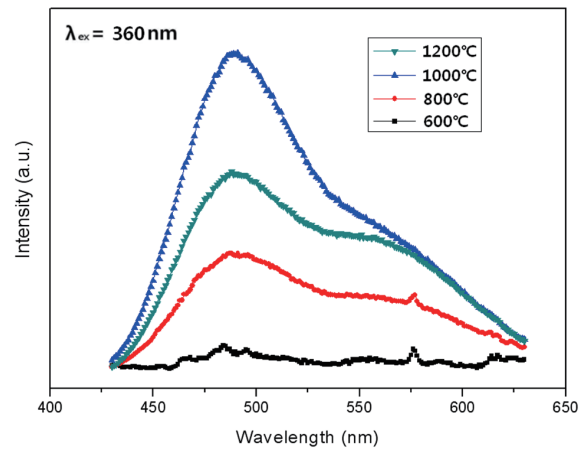


Fig. 7. PL emission spectra of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:0.05\text{Eu}^{2+}$ phosphors at different temperatures.

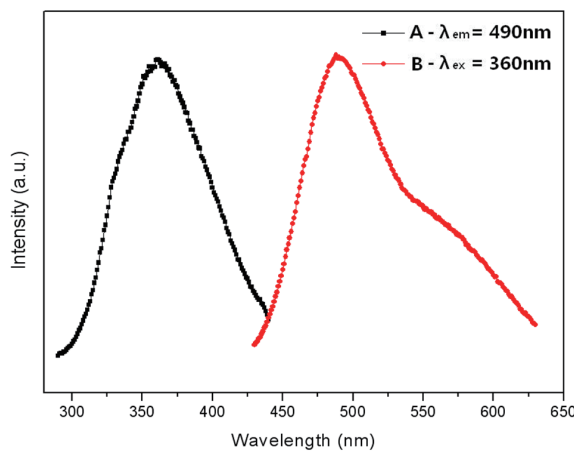


Fig. 5. (a) Excitation and (b) emission spectra of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:0.05\text{Eu}^{2+}$.

band, with a peak at 490 nm, which is a green emission. The main emission peak is at about 490 nm, which is ascribed to the transition between 5d and 4f of Eu^{2+} . The 5d state of Eu^{2+} is greatly affected by the crystal field, and it can be spitted by different crystal fields. This makes Eu^{2+} emit different light when the crystal fields change [11]. Figure 6 shows the PL emission spectra of the $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} . The emission intensity of green emission increased with increasing Eu^{2+} concentration to 0.05. Moreover, when the concentration of Eu^{2+} was above 0.05, a decrease in the emission intensity was observed and this may be attributed to non-radiative energy transfer between the Eu^{2+} ions. This non-radiative energy transfer may be attributed to the distance dependent multipole-multipole interaction between Eu^{2+} ions [12,13]. As the concentration increases, the distance between dopant ions decreases, and this may lead to non-radiative energy transition. The emission spectra showed the presence of a broad band, whose broadness indicates the existence of an interaction between the host and activator. This was attributed to the presence of excited electrons in the outer shell of the Eu^{2+} ions. The probability of energy transfer between Eu^{2+} ions increased with increasing Eu^{2+} concentration. Figure 7 shows the PL emission spectra of the $\text{CaSrSiO}_4:\text{Eu}^{2+}$ phosphor synthesized at various firing temperatures under 360 nm excitation. The excitation band must originate from the 4f → 5d transition of doped Eu^{2+}

ions, because the host $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4:\text{Eu}^{2+}$ barely showed any absorption between 250 and 450 nm [14].

4. CONCLUSIONS

In the present research, the $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphors with different concentrations of Eu^{2+} were prepared by a combustion method. The particles were found to be small and spherical with round surfaces. With increased sintering temperature, the phosphor particles became spherical, which occurs because the particles condense at higher temperatures. We determined that the characteristics of the phosphor powders were improved by increasing the sintering temperature. The $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ emission spectrum for 360 nm excitation showed a single band, with a peak at 490 nm, which is a green emission. The luminescent properties of the $\text{Ca}_x\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}^{2+}$ phosphor were optimized by changing the Eu^{2+} content. As a result, the highest luminous intensity was at 1,000 °C, which was obtained when the Eu^{2+} content (y) was 0.05. Increase of the Eu^{2+} concentration played a key role in enhancing the luminous intensity. In conclusion, these optimized phosphors are expected to have potential application in ultraviolet light-emitting diodes (UV-LEDs) as fluorescent material.

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