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The luminescence properties of $M_2MgSi_2O_7:Eu^{2+}$ (M = Sr, Ba) nano phosphor in ultraviolet light emitting diodes

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Abstract

The aim of this work is to investigate the effect of $(M = Sr, Ba)_2$ with an activator on the structural and luminescent properties of blue-emitting $M_2MgSi_2O_7:Eu^{2+}$ (M = Sr, Ba) nano phosphor. In order to achieve small spherical particles with smooth and round surface particles, $M_2MgSi_2O_7:Eu^{2+}$ phosphors were synthesized utilizing a combustion method. Using urea as a fuel and ammonium nitrate as an oxidizer, $M_2MgSi_2O_7:Eu^{2+}$ (M = Sr, Ba) was successfully synthesized. The influence of the $(M = Sr, Ba)_2$ content on the crystalline structure of the $M_2MgSi_2O_7:Eu^{2+}$ phosphors was investigated. The results of the characterization showed that both types of phosphor particles are nanosize. They exhibit the blue emission spectrum for near UV excitation. The material is applicable for use as the fluorescent material for ultraviolet light-emitting diodes (UV-LEDs).

Keywords: A. Powders: chemical preparation; B. Nanocomposites; D. Silicate

1. Introduction

Recently, a great amount of interest in phosphors has resulted in rapid developments in the promising display and illumination technologies. For general lighting purposes, photoluminescent materials, which include oxides, silicates, aluminates, aluminoborates, aluminosilicates, nitrides, borates, etc., play a very important role in potential applications for ultraviolet devices. For example, ultraviolet light emitting diodes (UV LEDs) are necessary in combining a UV chip with red, green, and blue (RGB) phosphors in order to generate white light [1,2]. Cold cathode fluorescent lamps (CCFLs) have attracted considerable interest in recent years as components for thin-film-transistor liquid-crystal-display (TFT-LCD) panels. It is also necessary to use R, G, and B phosphors to generate white light. Among the many things investigated, borates are good candidates for the host structure, due to their low synthetic temperature, easy preparation, and high luminescent brightness [3]. This type of white LED has the following advantages: a high color tolerance to variations in the UV chip and an excellent color rendering index due to white color generated by the phosphors. For this type of application, silicate-based phosphors activated with Eu^{2+} are very suitable [4]. These phosphors demonstrate broad emission colors through the transition of the Eu^{2+} activator strongly coupled to the host lattice. The absorption and the emission bands of the activators are also controlled by the host lattice crystal field [5]. The doped silicate-based phosphors with a maximum absorption of the near ultraviolet enable a wide range in the white spectrum [4,5]. Compared to the aluminate and the sulphides, the silicate base phosphors have many advantages, such as a chemical and physical stability, a varied luminescent color, and excellent water-resistance [6].

In this work, we investigated the effect of the activator on the structural and luminescent properties of Eu^{2+}-doped $M_2MgSi_2O_7$ (M = Sr, Ba) phosphor.

2. Experimental

In this study, $M_2MgSi_2O_7:Eu^{2+}$ (M = Sr, Ba) phosphors were prepared using the combustion method. $Sr(NO_3)_2$ (99.995%, Aldrich), $Ba(NO_3)_2$ (99.999%, Aldrich), SiO_2 (99.9%,

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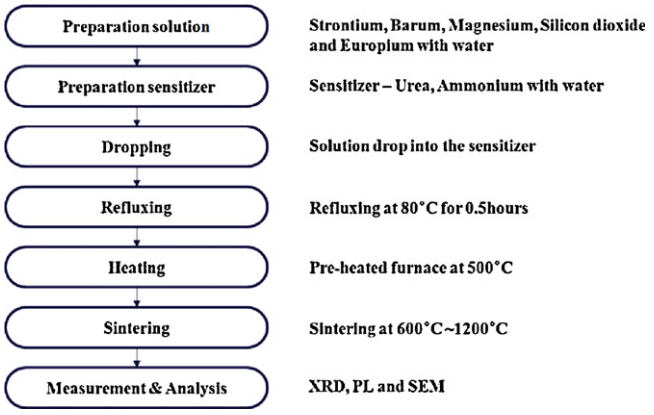

Fig. 1. Flowchart for the preparation of the phosphor powders.

Aldrich), $Mg(NO_3)_2$, Eu_2O_3 (99.999%, Aldrich) were used as the starting materials. The $M_2MgSi_4O_7$ phosphors were doped by Eu^{2+} with a molecular formula of $M_{2-x}MgSi_2O_7{:}xEu^{2+}$ (M = Sr, Ba). The M[M = $Ba(NO_3)_2$, $Sr(NO_3)_2$], $Mg(NO_3)_2$, SiO_2 and Eu_2O_3 were mixed together with a mole ratio and distilled water was added. Urea was used as the fuel and ammonium nitrate served as the oxidizer.

A flowchart of the preparation of the phosphor powders is shown in Fig. 1. The urea and ammonium nitrate solution were 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 min 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 then sintered in the furnace for 3 h at 600–1200 °C.

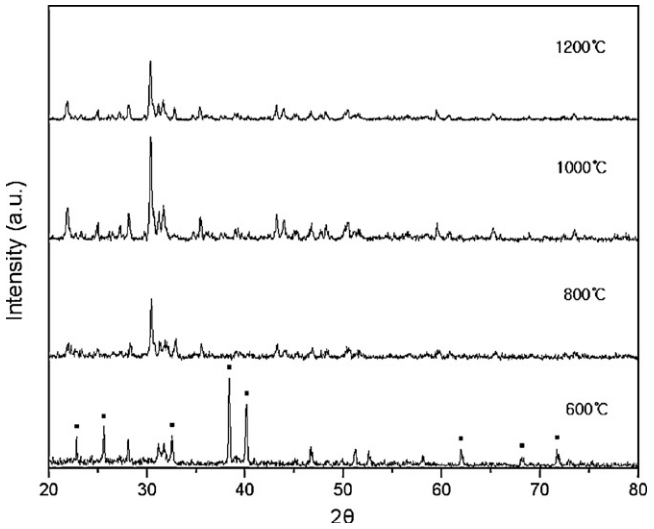

Fig. 2. XRD patterns of the $Sr_2MgSi_2O_7{:}Eu^{2+}$ sintered at different temperatures.

The crystalline development of the resulting samples was checked by X-ray diffraction (XRD, model D/MAX-2200) using Cu Kα-radiation in the range of $2\theta = 20–80°$. The measurement of the photoluminescence (PL) spectra was carried out with a 150 W Xe lamp (QM 3 PH QuantaMaster Luminescence). The morphology and the size of the prepared particles were investigated with a field-emission scanning electron microscope (FE-SEM, model S-4700, HITACHI).

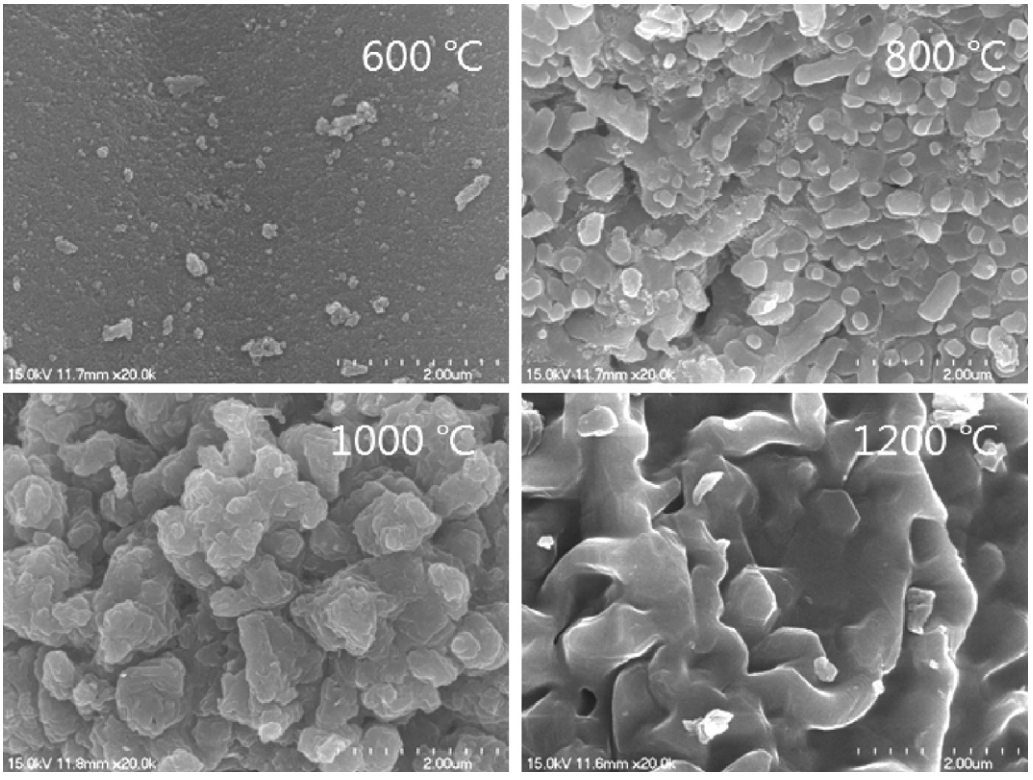

Fig. 3. SEM images of the $Sr_2MgSi_2O_7{:}Eu^{2+}$ sintered at different temperatures.

3. Results and discussion

The XRD patterns of the $Sr_2MgSi_2O_7$:Eu^{2+} powders at the different sintering temperatures from 600 °C to 1200 °C for 3 h are shown in Fig. 2. It was found that the XRD pattern of the precursor possessed mixed phases due to the fact that they were not synthesized. In general, the luminescent intensity is strongly affected by the phase purity and the crystallinity of the host compound. A high phase purity is needed to obtain a high luminescent intensity. When the temperature was at 1000 °C, the diffraction peaks became sharper and stronger. However at 1200 °C the $Sr_2MgSi_2O_7$:Eu^{2+} peaks were markedly weakened. In terms of phase purity, the sample prepared at 1000 °C should therefore show the highest luminescent intensity.

Fig. 3 shows the SEM images of the $Sr_2MgSi_2O_7$:Eu^{2+} sintered at different temperatures. The surface morphologies of the phosphor at 600 °C were rough. With an increased sintering temperature the phosphor particles became spherical, which occurs because the particles condense at higher temperatures [7]. But at 1200 °C, particles with agglomerates were observed. At over 1200 °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.

The emission spectra of the $Sr_2MgSi_2O_7$:Eu^{2+} with various concentrations of Eu^{2+} are shown in Fig. 4. The photoluminescence emission spectra were measured for the $Sr_2MgSi_2O_7$:Eu^{2+} powders under an excitation of 355 nm. It is shown that these phosphors show an intense and blue emission. The excitation spectra show a broad band from 250 to 450 nm when the emission wavelength was monitored at 460 nm. This emission, located at 460 nm (excited at 355 nm), is attributed to the typical $4f^65d^1$–$4f^7$ transition of Eu^{2+} [8]. However, no special Eu^{3+} emission peaks were observed in the spectra. This means that the Eu^{3+} in the crystal matrix has been completely reduced to Eu^{2+}. The main emission peak was 460 nm, resulting in a blue light emission.

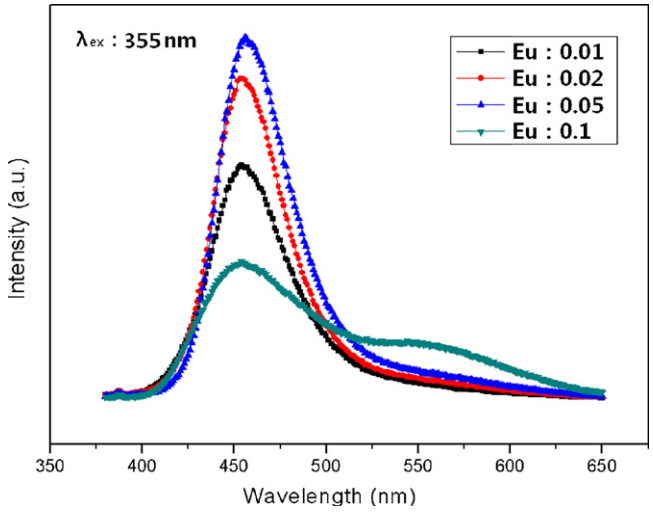

Fig. 4. PL emission spectra of the $Sr_2MgSi_2O_7$:Eu^{2+} powders at various concentrations of Eu^{2+}.

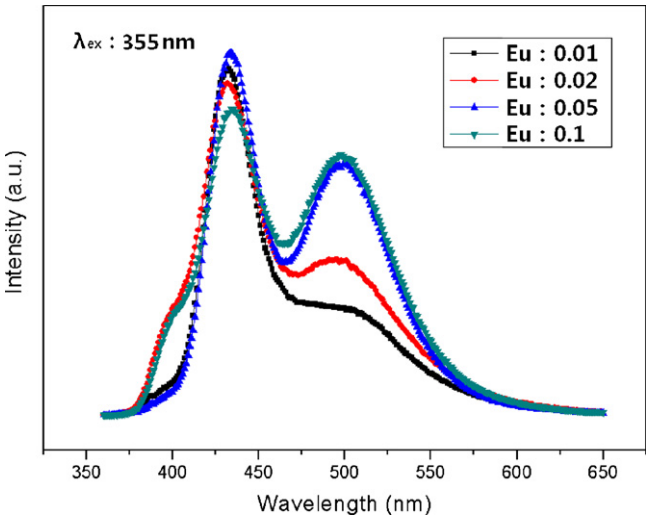

Fig. 5. PL emission spectra of the $Ba_2MgSi_2O_7$:Eu^{2+} powders at various concentrations of Eu^{2+}.

The emission spectra of $Ba_{2-x}MgSi_2O_7$ with different xEu^{2+} contents ($x = 0.01$–0.1) excited by 355 nm are shown in Fig. 5. The shape and position have no obvious changes with an increased Eu^{2+} concentration. However, the two emission intensities show different behaviors. When the concentration of the Eu^{2+} ions increases, the emission intensity at the longer wavelength (550 nm) increases whereas the emission intensity at the shorter wavelength (460 nm) is slightly different. It is obvious that an energy transfer between the two different luminescent centers occurs. Blasse has pointed out that the critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with the volume of the unit cell [9].

Fig. 6 shows the variation of the intensity to the Eu^{2+} concentration for the $M_2MgSi_2O_7$:Eu^{2+} (M = Sr, Ba). The intensity of the emission peak showed its highest intensity at $Sr_2MgSi_2O_7$: $Eu_{0.05}$ in Fig. 6(a). However, the $Sr_2MgSi_2O_7$:Eu_x phosphor was found to decrease over $x = 0.05$. The dependence of the emission intensity on the Eu^{2+} concentration for the $Ba_2MgSi_2O_7$:Eu_x (x varies from 0.01, 0.02, 0.05 and 0.1 mol) is shown in Fig. 6(b). With an increasing Eu^{2+} content x, the intensity of the emission band of the $Ba_2MgSi_2O_7$:Eu_x phosphor was slightly different at 435 nm, but at 500 nm, it increased the intensity up until $x = 0.1$.

The relative emission intensities and CIE chromaticity coordinates of the $Sr_{2-x}MgSi_2O_7$:Eu_x^{2+} ($x = 0.01$–0.1) are listed in Table 1 and Fig. 7. With an increase of the Eu^{2+} (over 0.05) concentrations, it is noted that the hues of the $Sr_{2-x}MgSi_2O_7$:Eu_x^{2+} phosphors range in color from blue to greenish blue.

From the results so far achieved, it can be concluded that the optimized $Sr_{1.95}MgSi_2O_7$:$Eu_{0.05}^{2+}$ (0.1514, 0.1093) phosphor is expected to be successfully used as the blue phosphor for UV LEDs.

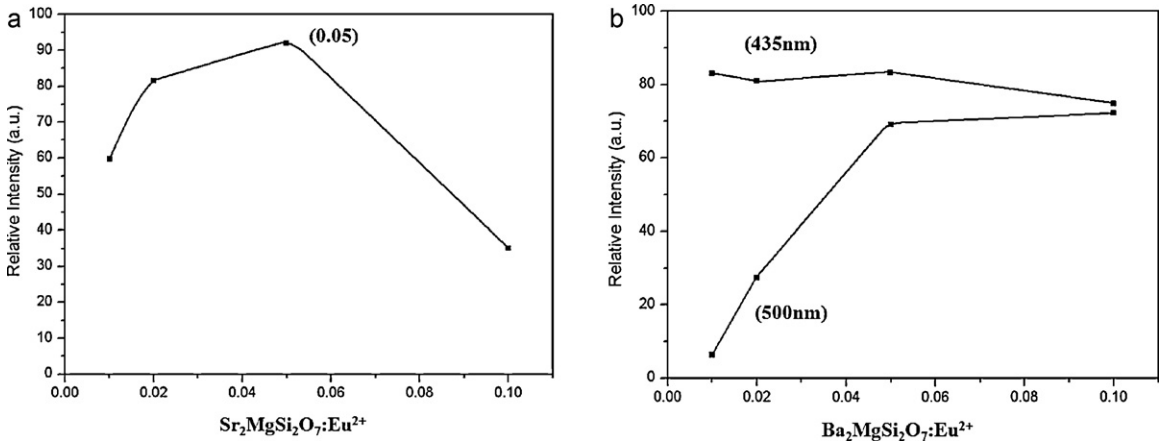

Fig. 6. Variation of the PL intensity of (a) the $Sr_{2-x}MgSi_2O_7:Eu_x^{2+}$ with different Eu^{2+} concentrations and (b) the $Ba_{2-x}MgSi_2O_7:Eu_x^{2+}$ with different Eu^{2+} concentrations.

Table 1
CIE chromaticity coordinates of the $Sr_{2-x}MgSi_2O_7:Eu_x^{2+}$ ($x = 0.01$–0.1).

	$Sr_{2-x}MgSi_2O_7:Eu_x^{2+}$	CIE x	CIE y
1	$Sr_{1.91}MgSi_2O_7:Eu_{0.01}^{2+}$	0.1472	0.0922
2	$Sr_{1.98}MgSi_2O_7:Eu_{0.02}^{2+}$	0.1502	0.0951
3	$Sr_{1.95}MgSi_2O_7:Eu_{0.05}^{2+}$	0.1514	0.1093
4	$Sr_{1.9}MgSi_2O_7:Eu_{0.1}^{2+}$	0.2323	0.2409

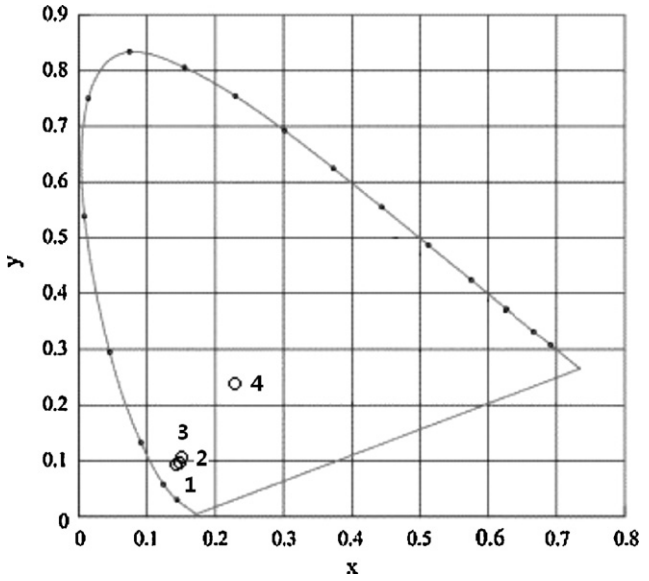

Fig. 7. CIE chromaticity coordinates of the $Sr_{2-x}MgSi_2O_7:Eu_x^{2+}$ ($x = 0.01$–0.1).

4. Conclusions

The combustion synthesis method for preparing Eu^{2+}-doped silicate phosphor particles $M_{2-x}MgSi_2O_7:Eu_x^{2+}$ (M = Sr, Ba), which is expected to be used for the blue phosphor in UV LEDs, was investigated. The phosphor has a blue Eu^{2+} emission with an emission peak at 446 nm. The luminescent properties of the $M_2MgSi_2O_7:Eu^{2+}$ phosphor were optimized by changing the Eu^{2+} content. It was found that the quenching concentration was changed by changing the Eu_x^{2+} concentration. The quenching concentration was $x = 0.1$. The highest luminescent intensity, which was obtained when the Eu^{2+} content (x) was 0.05, showed a pure-blue emission compared to the $BaMgSi_2O_7:_xEu^{2+}$ phosphor ($x = 0.01$).

As a result, an increase of the quenching concentration played a key role in enhancing the luminescent intensity. From the results so far achieved it can be concluded that the optimized $Sr_{1.95}MgSi_2O_7:Eu_{0.05}^{2+}$ (0.1514, 0.1093) phosphor is expected to be successfully used as the blue phosphor in UV LEDs.

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