Synthesis and optical properties of red/blue-emitting Sr₂MgSi₂O₇:Eu³⁺/Eu²⁺ phosphors for white LED

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A B S T R A C T

Phosphor-converted white light emitting diodes (white LEDs) have received great attention in recent years since they have several excellent features such as high lumen output, low power consumption, long lifetime and environmentally friendly. In this work, we report the co-precipitation synthesis of red/blue Sr₂MgSi₂O₇:Eu³⁺/Eu²⁺ phosphors with various Eu doping concentration. The results show that the obtained Sr₂MgSi₂O₇:Eu³⁺/Eu²⁺ phosphors have good crystallinity and emit strong red (Sr₂MgSi₂O₇:Eu³⁺) and blue (Sr₂MgSi₂O₇:Eu²⁺) emissions under near UV light excitation. The sharp emission peaks at 577, 590, 612, 653, and 701 nm corresponded to the typical 5D₀ → 7Fₖ (j = 0,1,2,3,4) transitions of Eu³⁺, and the blue emission peaking at 460 nm is attributed to the typical 4F₉/₂ → 4I_{15/2} transition of Eu²⁺ in the same Sr₂MgSi₂O₇ host lattice. Both phosphors can be well excited in the wavelength range of 260–400 nm where the near UV-LED is well matched. The above results suggest that the Sr₂MgSi₂O₇:Eu³⁺/Eu²⁺ phosphors are promising red/blue-emitting phosphors for the application in near UV pumped phosphor-converted white LEDs.

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1. Introduction

Phosphors are widely used in solid-state lighting, especially for the phosphor-converted light emitting diode (white LED) in which yellow light-emitting phosphor (such as YAG:Ce³⁺) are pumped by GaN chips to generate white light [1]. On the one side, the current white LEDs show several advantages over incandescent and fluorescent lamps including low operating voltage, low energy consumption, long lifetime .... However, on the other side, this kind of white LED shows relatively low color-rendering index (CRI), and strongly in the infrared with broad band emitting luminescence on different host matrices since the involved 5d orbital of Eu²⁺ ion is external and strongly influenced by the crystal field [9,10].

Recently, the alkaline earth silicates based-phosphors (alkermanite phosphors) have been reported as one of the most essential luminescent materials due to their excellent thermal and chemical stability and high brightness. Particularly, Sr₂MgSi₂O₇ is a good candidate for UV-LED application since it has a rigid tetragonal structure and strong absorption band in UV region [7,8]. It is well known that Europium (Eu) is the most common rare earth to be used as an activator in phosphors. Eu³⁺ ion is a preferable activator for red phosphors with sharp emission peaks in the red region (from 570 to 700 nm) caused by the 5D₀ → 7Fₖ (J = 0, 1, 2, 3, 4) transitions of the trivalent state, while Eu²⁺ is the most frequently used activator in the blue phosphors and its emission usually consist of a broad band due to transitions from the 4F₉/₂ to the 4I_{15/2} ground state. Additionally, Eu²⁺ ion can emit light from the UV to the infrared with broad band emission luminescence on different host matrices since the involved 5d orbital of Eu²⁺ ion is external and strongly influenced by the crystal field [9,10].

Until now, the phosphors based on Sr₂MgSi₂O₇ host lattice were prepared by different methods such as solid-state reaction, hydrothermal, sol–gel methods or combustion processing with ultrasonic dispersion technique [11–14]. Among the various synthesis methods, the co-precipitation method is known to...
produce phosphor powders with uniform, narrow size distribution, and homogeneous distribution of the activator ions [15]. It is important to note that in most of the previous research, to synthesize the Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ phosphor, the precursor powders were normal sintered in reduced gas environment in a one-step synthesis process, therefore only the blue emitting phosphors can be obtained.

In this work, we present the results of our study on red/blue phosphors based on Eu-doped Sr$_2$MgSi$_2$O$_7$ prepared by co-precipitation method. Initially, Eu$^{3+}$-doped phosphor was synthesized as a red emitting phosphor, and its structure and luminescent properties were investigated as a function of the sintering temperature. Lately, Eu$^{3+}$ doped phosphor was obtained by reducing the corresponding Eu$^{3+}$ phosphor in forming gas environment. Moreover, the influence of Eu$^{3+}$ doping concentration on the luminescent properties of the phosphors was also investigated.

2. Experimental

The Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ phosphor was synthesized by a co-precipitation reaction. In this reaction, nitrate salts Sr(NO$_3$)$_2$, Mg(NO$_3$)$_2$.6H$_2$O, tetraethylorthosilicate (C$_2$H$_5$O)$_4$Si (TEOS), and ethanol were used as precursors. All these chemicals were of analytic grade. The raw materials were weighed according to the nominal composition of Sr$_2$MgSi$_2$O$_7$.xEu$^{3+}$ (x = 0.02, 0.03, and 0.04). Sr(NO$_3$)$_2$.6H$_2$O and Mg(NO$_3$)$_2$.6H$_2$O were mixed in distilled water. A stoichiometric amount of TEOS and EtOH was also dissolved in ethanol and HNO$_3$, respectively. The solutions were stirred until the solution became transparent, after which they were mixed and continuously stirred for 3 h. Subsequently, an appropriate amount of NH$_4$OH was added to the solution to enable precipitation. The precipitate and solution were continuously stirred to obtain a white viscous gel. Then, centrifugal force was applied to allow the resulting precipitate to be separated. The separated precipitate was washed with DI water for several times. After drying at 200 °C for 24 h, the dry powder was calcined in air at various temperatures for 3 h to receive the Sr$_2$MgSi$_2$O$_7$.xEu$^{3+}$ phosphors. To produce the Sr$_2$MgSi$_2$O$_7$.xEu$^{3+}$ phosphors, the corresponding Sr$_2$MgSi$_2$O$_7$.xEu$^{3+}$ phosphor was subjected to ion reduction in the mixture of H$_2$/N$_2$ (10%/90%) gas at different temperatures for 2 h.

The phase purity of the phosphors was identified by X-ray diffraction (XRD) pattern. Measurements were carried out on a D8/Advance-Bruker diffractometer with CuKα radiation (λ = 1.5403 Å). The scan rate was kept at 1 s/step at a scattering angle range of 20–70. The Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR-800 spectrometer using He–Ne laser (632.8 nm) with a power density of 215 W/cm$^2$. A high-resolution mode of 1.2 cm$^{-1}$ was used. Morphology was taken with a JSM-7600F (Jeol Co., Japan) field emission scanning electron microscope (FESEM). PL and PLE spectra were measured on a NANO LOG spectrotiorimeter. PL and PLE spectra were obtained by using a 450 W xenon light source with a spectral resolution of about 1 nm.

3. Results and discussion

Fig. 1 shows XRD patterns of the product sintered at 900, 1100, 1200, and 1300 °C for 3 h.

It can be seen that until temperature of 1200 °C, the main crystalline phase in the powder is Si$_2$SiO$_4$, beside the Sr$_2$MgSi$_2$O$_7$ and Sr$_3$Mg$_2$SiO$_8$ phases with smaller portion. Contents of the desired Sr$_2$MgSi$_2$O$_7$ phase and the secondary Sr$_3$Mg$_2$Si$_3$O$_8$ phase increase with increasing the sintering temperature. At the temperature of 1300 °C, intensity of the diffraction peaks related to the Sr$_2$SiO$_4$ phase decreased abruptly, in contrast to the strong increase of the Sr$_2$MgSi$_2$O$_7$ phase. These results indicate that the presence and dominance of the Sr$_2$MgSi$_2$O$_7$ phase can only be obtained in the sample sintered at 1300 °C. Our results are similar to those reported by Kwon et al., in which the Sr$_3$SiO$_4$ phase in the Sr$_2$MgSi$_2$O$_7$ phosphor (synthesized by a conventional solid-state reaction method) disappeared only after sintering at 1300 °C or higher [16]. The XRD pattern Fig. 1 also confirms the tetragonal structure of the Sr$_2$MgSi$_2$O$_7$ host lattice. The main phase Sr$_2$MgSi$_2$O$_7$ has tetragonal crystal structure. Eu$^{3+}$ ion in this crystal structure occupies a unique position (position symmetry C1) with eight neighboring O$^{2-}$ ions and the Sr–O distance is 2.662 Å in average. When Eu is doped into Sr$_2$MgSi$_2$O$_7$, Eu ions are expected to replace the position of Sr$^{2+}$ in the crystal network because of the excellent compatibility ionic radius of Eu$^{3+}$ and Sr$^{2+}$, 1.25 and 1.26 Å, respectively [17–19].

To evaluate the possibility of replacing the Eu$^{3+}$ ions on the position of Sr ions in the host lattice, Raman spectra measurement of the doped 4% Eu$^{3+}$ and undoped Sr$_2$MgSi$_2$O$_7$ host were carried out. The Raman spectra taken at room temperature are shown in Fig. 2. For the host lattice (curve a), Raman peaks are observed at 901, 652, 220, 201 and 153 cm$^{-1}$. The peaks correspond to the stretching vibrations of the Si–O and Si–Si bonds of the Si$_2$O$_4$ group [20]. For the doped Sr$_2$MgSi$_2$O$_7$:4%Eu$^{3+}$ sample, the Raman spectrum (curve b) is similar to that of the undoped Sr$_2$MgSi$_2$O$_7$ sample, no other peaks were found. This result implies that the Eu$^{3+}$ dopant ion was not substituted on the Sr$^{2+}$ site, and did not change the unite cell volume and SiO$_2$Si angle, instead they were incorporated in to host lattice by replacing the Sr$^{2+}$ sites.

The morphology of the phosphors was characterized by FESEM. Fig. 3 show FESEM images of the as-received phosphor (dry powder) (a) and the Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ phosphor sintered at 1300 °C for 3 h (b). The dry powder show clusters of particles with variety shapes and sizes, whereas the Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ phosphor exhibits needle-like shape particles with an average length of about 1 micron. The chemical composition of the Sr$_2$MgSi$_2$O$_7$:3%Eu$^{3+}$ phosphor has been measured using energy dispersive X-ray spectroscopy (EDS). The result of the EDS analysis is shown in Fig. 3(c) which is representing the composition of the phosphor powder studies.

Fig. 4 illustrates the photoluminescence (PL) spectra of Sr$_2$MgSi$_2$O$_7$:4%Eu$^{3+}$ phosphor samples sintered at different temperatures in the range of 900–1300 °C. Under the near UV excitation of 360 nm, a broad blue emission band centered around 430–470 nm and several sharp lines in the orange–red region...
peaking at about 577, 590, 612, 653, and 701 nm. The sharp red emission lines should be ascribed to the transitions within the 4f6 configuration of Eu3+. These lines correspond to the 5D0 → 7F0, 5D0 → 7F1, 5D0 → 7F2, 5D0 → 7F3, and 5D0 → 7F4 transitions of Eu3+, respectively [21]. Here, the emission line at 612 nm is attributed to the electric dipole transition (5D0 → 7F2), while the emission around 590 nm is assigned to the magnetic dipole transition (5D0 → 7F1), which is sensitive to site symmetry. According to the parity selection rule, when the Eu3+ ions are located at the site with an inversion symmetric center, the 5D0 → 7F1 magnetic dipole transition is permitted, which results in orange-red emission around 590 nm. In the other case, if the Eu3+ ions located at the site without an inversion symmetric center, because the opposite parity 5d configuration is mixed into 4f configuration, the parity selection rule is able to lifted, and forbidden transition is partially allowed, the hypersensitive 5D0 → 7F2 electric dipole transition will be permitted, which results in red emission around 612 nm [13,21,22]. Thus, the observation of the strongest emission peak at 612 nm in our phosphor may indicate that Eu3+ ions mainly occupy non-inversion symmetric center in the host lattice. For the broad blue emission band, it is known that Eu2+ presents a broad emission band peaking at around 460 nm due to the 4f5d1 to 4f7 transition of Eu2+ (4S7/2, J = 0, 1, 2, 3, and 4). Since no reduction process has been carried out with the phosphor, it is quite possible that during the high temperature sintering, a small amount of Eu3+ ions were reduced to Eu2+ ions that leads to the blue emission [23–26]. Longer sintering time and higher temperature can enhance this ion transformation. It can also be seen from Fig. 4 that while the PL intensity of the red emissions increased with increasing sintering temperature, the peak position and the shape of the blue band change arbitrary with increasing temperature. Since the blue emission bands related to Eu2+ ions is sensitive to the host lattice environment, the change of the blue emission band with sintering temperature may indicate the change of the crystalline phases in the sample as observed from XRD results. In our opinion, the increase of the PL intensity of the red emission is related to the higher content of the Sr2MgSi2O7 phase upon increasing temperature from 900 to 1300 °C.

Fig. 2. Raman spectra of the Sr2MgSi2O7 (a) and Eu3+-doped Sr2MgSi2O7 (b) phosphors sintered at 1300 °C in air ambient for 3 h.

Fig. 3. FESEM images of the as-received powder (dry powder) (a) and the Sr2MgSi2O7:3%Eu3+ phosphor powder sintered at 1300 °C in air ambient for 3 h (b) and EDS spectrum (c) of the Sr2MgSi2O7:3%Eu3+ phosphor after sintering.

Fig. 5 shows the excitation spectrum (PLE monitored at 612 nm) of the Sr2MgSi2O7:Eu3+ phosphor. The PLE spectrum covers a wide region between 350 and 600 nm revealing that the phosphor can be excited by near UV at 360, 381, 393 and 463 nm. Such excitation wavelengths are well matched with near UV-LED excitation wavelength, indicating a great potential for white LED application. Furthermore, the strong excitation peak at 463 nm points out that the Sr2MgSi2O7:Eu3+ phosphor can also be used in the blue LED pumped white LED.

To investigate the effect of Eu3+ doping concentration on PL intensity of Sr2MgSi2O7 phosphors synthesized by co-precipitation method, the emission spectra of the phosphors at various Eu3+ concentrations (x = 0.02, 0.03, and 0.04) are presented in Fig. 6. The emission intensity increases until x = 0.03 and then decreases as a result of enhanced dipole–dipole interaction. This optimal Eu3+ concentration is lower than that reported in the literature [17].
The PL and PLE spectra of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ phosphors sintered at 1300 $^\circ$C for 3 h and reduced at 1300 $^\circ$C for 2 h are shown in Fig. 7. The PL spectra show a broad emission band in the blue peaking at 462 nm under the excitation wavelength of 360 nm. This emission is due to the 4f$^6$5d$^1$e$^4$f$^7$ transition of Eu$^{2+}$ ions in the host lattice. Also, the PLE spectrum monitored at 460 nm is shown in Fig. 7. It is shown that the blue emission band can be efficiently excited by both UV and near UV excitation source from 260 to 415 nm. Thus, the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ phosphor obtained in this work matches well the excitation wavelength of the near UV LED chip.

4. Conclusions

Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$/Eu$^{2+}$ phosphors were prepared by the co-precipitation method followed by sintering at 1300 $^\circ$C for 3 h in air ambient (Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$) and reduced at 1300 $^\circ$C for 2 h in forming gas environment (Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$). The Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ phosphor shows strong red emission peaking at 612 nm that can be excited by both near UV (360, 381, 393 nm) and blue (463 nm) LED.

The Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ phosphor emits strong blue light peaking at 462 nm and can be excited by both UV and near UV-LED. These results suggested that the Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$/Eu$^{2+}$ phosphors have high potential for phosphor-converted white LED application.

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