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Photoluminescence properties of Eu^{2+} and Mg^{2+} co-doped $CaSi_2O_2N_2$ phosphor for white light LEDs

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Abstract

$CaSi_2O_2N_2$:Eu, Mg phosphors have been synthesized through the conventional high temperature solid-state reaction method. The effect of Mg^{2+} doping on the structure and photoluminescence (PL) properties of $CaSi_2O_2N_2$:Eu, Mg was investigated systematically. The results reveal that the phosphor retains the $CaSi_2O_2N_2$ single phase, with the lattice expanding upon increasing the Mg^{2+} concentration, in an appropriate range. The average size of $CaSi_2O_2N_2$:Eu, Mg phosphor is 3–8 μm. At a certain concentration, doping Mg^{2+} ions can greatly enhance the absorption and PL intensity of $CaSi_2O_2N_2$:Eu, Mg phosphors. The temperature dependent luminescence measurements show that the thermal quenching remains small in the case of Mg^{2+} doping, in other word, Eu^{2+}/Mg^{2+} co-doped phosphor has a good thermal stability. Furthermore, the quenching concentration of Eu^{2+} in phosphors can also be increased by doping Mg^{2+}. Therefore, this novel $CaSi_2O_2N_2$:Eu, Mg phosphor is promising for white light emitting diodes (white-LEDs).

Keywords: Phosphor; Luminescence; Co-doping; Concentration quenching

1. Introduction

Nowadays, white light-emitting diodes (LEDs) are attracting extensive attention due to their inconceivable properties, such as the energy savings, positive environmental effects, controllability of their spectral, spatial, temporal, and so on [1,2]. White-LEDs are usually prepared through combining LED chips with phosphors. The efficient of white-LEDs depends heavily on the luminescence properties and thermal stability of phosphors. Phosphors are key material for white-LEDs. The traditional phosphor material, YAG:Ce^{3+} shows a poor color rendition [3]. Therefore, it is significant to develop novel phosphors.

Recently, $MSi_2O_2N_2$:Eu^{2+} (M = Ca, Sr, Ba) phosphors have been proved to be excellent phosphors for white-LED lighting application because of their outstanding luminescent properties, high thermal and chemistry stability, and relatively lower synthesized temperatures and atmospheric pressure [4–8]. However, the PL intensities of these phosphors still need to be further improved for practical applications.

According to reports, the emission intensity of phosphors can be improved through the following techniques: optimizing the preparation process, and incorporating rare-earth ions or non-rare-earth ions into phosphors. The former method is effectively but complex and costly [9]. Comparatively, the latter method is a very attractive means to develop high-efficiency phosphors. It has reported that the emission intensity of phosphors could be efficiently enhanced through co-doping rare-earth ions. The roles of co-doped rare-earth ions have been extensively studied. They are generally related to the processes of energy transfer, up-conversion or cross relaxation between different rare-earth ions [10–12]. On the other hand, doping non-rare-earth ions into phosphors can also improve the emission intensity of phosphors either. However, the roles of non-rare-earth ions in phosphors still need further studies. To the best of our knowledge, the studies mainly focus on the alkali metals ions (Li^+, Na^+, K^+) doping. The increase of emission intensity is attributed to the charge compensation resulting from

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the substitution effect of alkali metals ions to rare-earth ions [13–15]. In addition, it is found that the doping of Mg^{2+} is beneficial to reduce the impurity phase and the defect in γ-AlON phosphors, and subsequently improve the luminescence intensity of phosphors [16,17]. Phosphors with a limited amount of Mg^{2+} ions have been pointed out to be promising in terms of PL intensity [18]. However, the influence of Mg^{2+} ions on the PL properties of $MSi_2O_2N_2$:Eu (M = Ca, Sr, Ba) phosphors has not been investigated.

In this study, we have introduced Mg^{2+} in $CaSi_2O_2N_2$:Eu phosphors to study the role of Mg^{2+} in phosphors and expect to improve the emission intensity of phosphors. The results indicate that doping a certain amount of Mg^{2+} ions into $CaSi_2O_2N_2$:Eu phosphor can efficiently enhance the luminescent intensity of this phosphor. There are two explanations for this enhancement. One is that the incorporation of Mg^{2+} ions cause some change in the field strength surrounding the Eu^{2+} ions. The other explanation is that partial Mg^{2+} ions may enter into the interstitial sites of crystal lattice, increasing the distance between Eu^{2+} ions and subsequently minimizing the Eu^{2+}–Eu^{2+} interaction, and then the PL intensity of phosphor improves. These help us to understand the roles of Mg^{2+} in phosphors and are beneficial for us to find more effective co-doping ions.

2. Experimental

All powder samples $Ca_{1-x-y}Si_2O_2N_2$:Eu_y, Mg_x were synthesized through high-temperature solid-state reaction. The raw materials were Si_3N_4, SiO_2, $CaCO_3$, $(MgCO_3)_4Mg(OH)_2\cdot 5H_2O$, and Eu_2O_3. They were mixed homogeneously in an agate mortar, and then the mixtures were dried, put into a high purity alumina crucible and subsequently placed in a horizontal alumina tube furnace to fire at 1400 °C for 5 h under N_2 atmosphere. After firing, the products obtained were ground in an agate mortar to be powder and then were washed with hydrochloric acid, water and alcohol.

Phase identification of the final products was done using X-ray powder diffraction (D/max 2550V, Rigaku, Japan) with Cu Kα irradiation (λ = 1.5406 Å). The particle size of phosphors was analyzed using scanning electron microscopy (SEM). The diffuse reflection spectra were measured with a UV-visible spectrophotometer (Lambda 950, Perkin Elmer, USA). The PL spectra were measured at room temperature using a fluorescent spectrophotometer (FP-6600, JASCO, Japan). To study the thermal quenching, the sample was heated in an oven for 10 min, and then it was quickly placed into the fluorescent spectrophotometer to obtain the emission intensity under the 400 nm excitation. The whole time of this measure process was kept within 5 s to ensure that the reduction in the temperature of the sample was limited. The decay time of phosphor was measured using a fluorescent spectrophotometer (FLS920, Edinburgh).

3. Results and discussion

3.1. $Ca_{0.95-x}Mg_xEu_{0.05}Si_2O_2N_2$ ($0 \leq x \leq 0.30$)

3.1.1. Crystal structure

Fig. 1(a) depicts the XRD patterns for $Ca_{0.95-x}Mg_xEu_{0.05}$-$Eu_{0.05}Si_2O_2N_2$ (x = 0.05, 0.08, 0.10, 0.12, 0.15, 0.20, 0.30) and JCPDs Card of $CaSi_2O_2N_2$ phase (No. 40-0117). The XRD patterns of the samples are consistent with that of $CaSi_2O_2N_2$ until the concentration of Mg^{2+} up to x = 0.10. The results indicate that the small amount of Mg^{2+} doping ions do not change the general structure of $CaSi_2O_2N_2$. However, when the concentration of Mg^{2+} is more than x = 0.10, the composition of these phosphors would constitute a mixture of $Ca_2MgSi_2O_7$ (No. 35-0592) and Si_3N_4 (No. 79-2011) impurity. With increasing the Mg^{2+} concentration, an obviously increase of the main peak intensity of these impurity phases is observed, indicating that the content of these impurity phases increase.

Fig. 1(b) shows the XRD peaks between 25.5° and 27.5°. Up to a concentration of x = 0.08, the positions of the peaks shift to smaller angles as the Mg^{2+} content increases, which means that the crystal lattice expands after doping Mg^{2+}. Mg^{2+} and Ca^{2+} are the same group elements and they have similar properties,

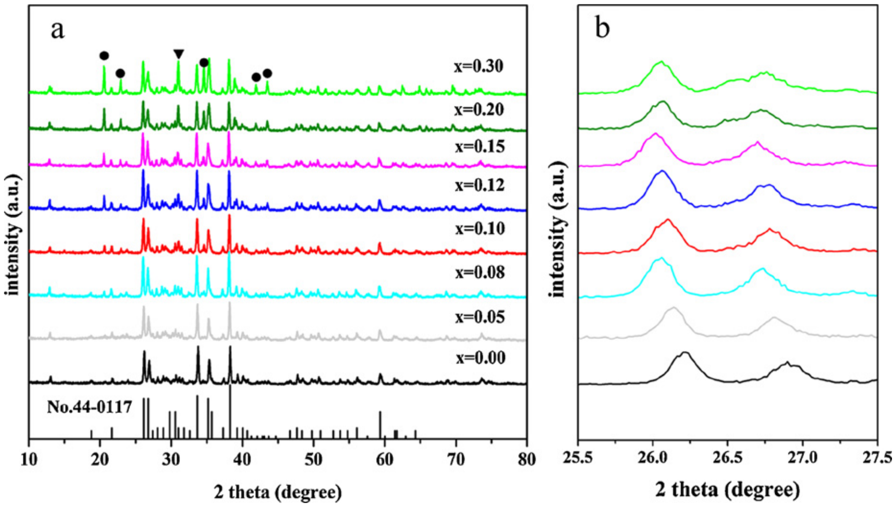

Fig. 1. (a) XRD patterns of $Ca_{0.95-x}Si_2O_2N_2$:$Eu_{0.05}$, Mg_x. Circles (●) indicate Si_3N_4 (No. 79-2011) and down triangle (▼) indicates $Ca_2MgSi_2O_7$ (No. 35-0592); (b) local regain of XRD patterns between 25.5° and 27.5°.

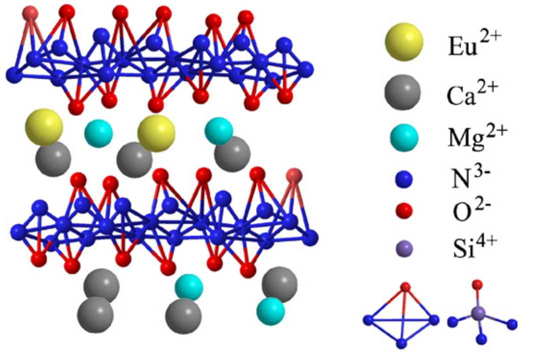

Fig. 2. Schematic diagram of the $CaSi_2O_2N_2$:Eu, Mg crystal structure.

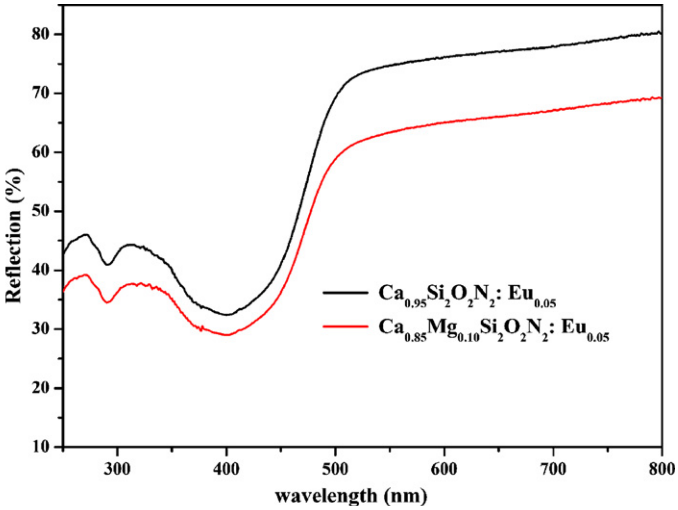

Fig. 4. Diffuse reflection spectra of $Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$ and $Ca_{0.85}Mg_{0.10}$-$Si_2O_2N_2$:$Eu_{0.05}$ phosphors.

Mg^{2+} ions are expected to occupy the sites of Ca^{2+}. If Mg^{2+} ions occupy the sites of Ca^{2+}, the lattice would shrink due to the smaller ionic radius of Mg^{2+} compared with Ca^{2+}. This is inconsistent with the experimental result. Thus, we make an assumption that a large portion of Mg^{2+} ions enter into the interstitial sites of crystal lattice with a small percentage of Mg^{2+} ions replacing the Ca^{2+} sites in the low doping concentration of Mg^{2+}. The schematic diagram of the $CaSi_2O_2N_2$:Eu, Mg crystal structure is depicted in Fig. 2. In the higher concentration of Mg^{2+}, more Mg^{2+} ions would substitute Ca^{2+} sites and the crystal lattice shrunk.

3.1.2. Phosphor morphology

Fig. 3 shows the typical SEM images of $CaSi_2O_2N_2$:Eu, Mg powders. It is observed that some of the powders are agglomerated into irregular morphologies. The average size of the powders is in the range of 3–8 μm.

3.1.3. The diffuse reflection spectra

Fig. 4 shows the diffuse reflection spectra of $Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$ and $Ca_{0.85}Mg_{0.10}Si_2O_2N_2$:$Eu_{0.05}$ phosphors. The results indicate that the absorption intensity of $Ca_{0.85}Mg_{0.10}Si_2O_2N_2$:$Eu_{0.05}$ over the entire wavelength range is larger than that of $Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$. This implies doping Mg^{2+} ions could enhance the absorption of $Ca_{0.85}Mg_{0.10}Si_2O_2N_2$:$Eu_{0.05}$ phosphors.

3.1.4. Photoluminescence characterization

The excitation and emission spectra of $Ca_{0.95-x}Si_2O_2N_2$:$Eu_{0.05}$, Mg_x are shown in Fig. 5(a). The results indicate that the profile of excitation and emission spectra are analogically for all the compositions. There is no notably red-shift or blue-shift. The excitation spectra measured by monitoring the emission at the 545 nm expand from UV to blue spectral region. The emission spectra recorded under the 400 nm excitation exhibit a single symmetrical band at about 545 nm stemming from the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} [19]. More importantly, the concentration of Mg^{2+} obviously affects the PL intensity of phosphors. Fig. 5(b) shows that the PL intensity decrease at first, which may be result from the

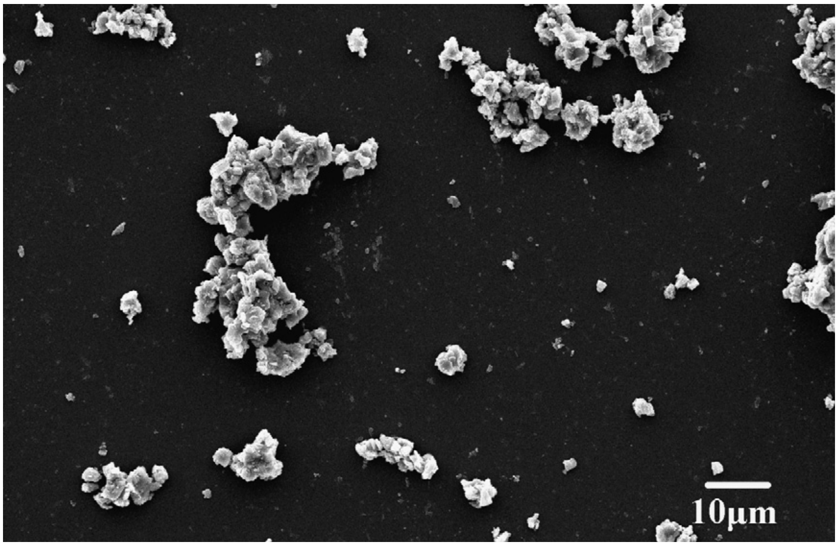

Fig. 3. Typical SEM image of $CaSi_2O_2N_2$:Eu, Mg phosphors.

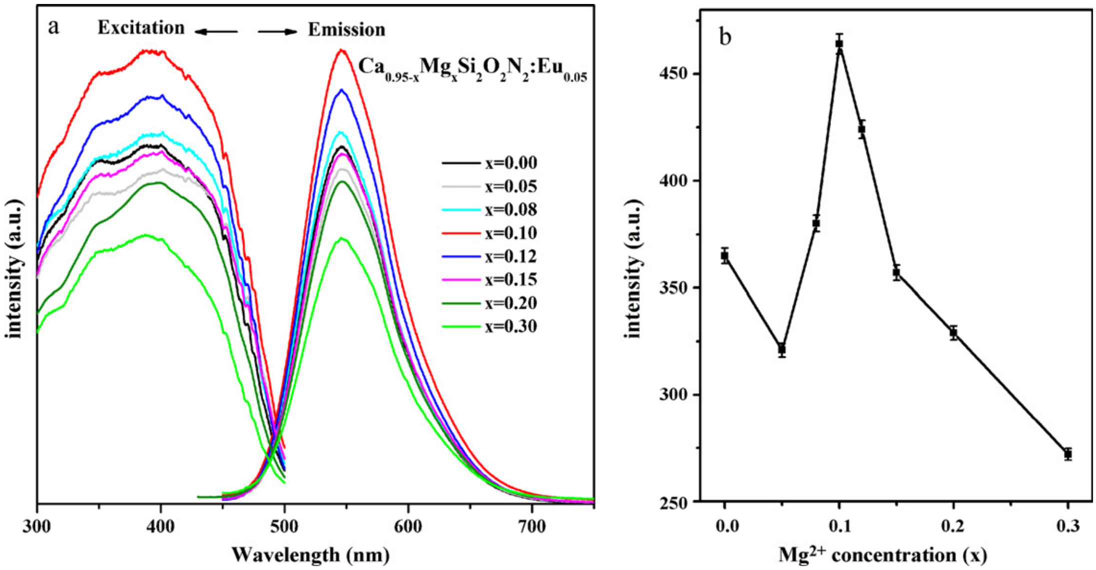

Fig. 5. (a) Excitation and emission spectra of $Ca_{0.95-x}Si_2O_2N_2$:$Eu_{0.05}$, Mg_x phosphors and (b) dependence of the emission intensity on the concentration of Mg^{2+} in phosphors.

imperfect atomic arrangement originally in the host lattice by doping Mg^{2+}. Upon increasing the concentration of Mg^{2+}, the intensity is improved. The phosphor has the highest intensity when the concentration comes up to $x = 0.10$. The emission intensity of Mg^{2+} at $x = 0.10$ is about 1.3 times that of the sample without Mg^{2+}. The enhancement of the PL intensity is probably due to the smaller radius of doping Mg^{2+} (0.072 nm) compared with Ca^{2+} (0.100 nm) and the larger Pauling's electronegativity of the Mg^{2+} (1.31) compared with the Ca^{2+} (1.00). The Mg^{2+} ions with smaller size and larger mismatch electronegativity cause some changes in the field strength surrounding the Eu^{2+} ions, which strongly enhances the PL intensity [13,20]. On the other hand, based on the assumption that we made in 3.1.1, Mg^{2+} ions may located in the interstitial sites and Eu^{2+} ions were separated by Mg^{2+} ion as shown in Fig. 2. It is known that there is no energy transfer from Mg^{2+} to Eu^{2+} [21]. Thus, the increase of distance between Eu^{2+} ions induces a decrease of the interactions among Eu^{2+} [22], which results the improvement of the emission intensity. When the concentration of Mg^{2+} is further increased in excess of $x = 0.10$, the emission intensity would be reduced. The decrease in emission intensity of phosphors at high Mg^{2+} concentration may be derived from those by-products shown in Fig. 1(a).

The decay times of $Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$ and $Ca_{0.85}Mg_{0.10}$-$Si_2O_2N_2$:$Eu_{0.05}$ phosphors have been calculated using a curve fitting technique. The decay times of these phosphors are listed in Table 1. Both of them have two lifetimes: a fast one and a slow one. That is because there are four Ca^{2+} crystallographic sites that can be occupied by Eu^{2+} in $CaSi_2O_2N_2$, two sets of two have a similar surrounding [23]. The slow decay component exceeds 90%, which reflects that one type of site may be preferentially occupied [23]. The decay times of Eu^{2+} decreases after doping Mg^{2+} ions, which indicates the existence of energy transfer from matrix to Eu^{2+}, and subsequently the emission intensity of phosphor is enhanced.

The thermal quenching of the luminescence is an important parameter for LED phosphors. Fig. 6 represents the temperature dependence of the luminescence of Mg^{2+}–Eu^{2+} co-doped $CaSi_2O_2N_2$. Doping Mg^{2+} has little influence on the thermal

Table 1
Decay time (τ) and intensity proportion (P) of $Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$ and $Ca_{0.85}Mg_{0.10}Si_2O_2N_2$:$Eu_{0.05}$ phosphor.

Sample	τ_1/ns	P/%	τ_1/ns	P/%
$Ca_{0.95}Si_2O_2N_2$:$Eu_{0.05}$	960.92	92.67	252.29	7.33
$Ca_{0.85}Mg_{0.10}Si_2O_2N_2$:$Eu_{0.05}$	952.32	93.58	226.22	6.42

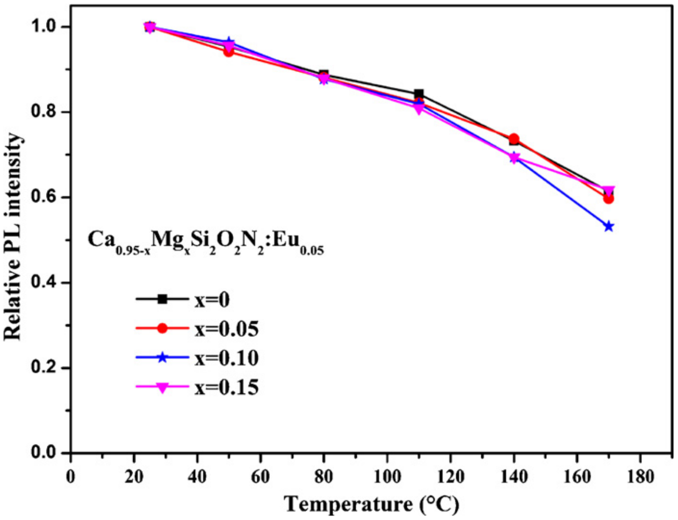

Fig. 6. Temperature dependence of the integrated luminescence intensity on the concentration of Mg^{2+} in $Ca_{0.95-x}Mg_xSi_2O_2N_2$:$Eu_{0.05}$ ($x = 0$, 0.05, 0.10, 0.15; $\lambda_{ex} = 400$ nm).

quenching. The temperature quenching remains small after doping Mg^{2+} and the PL intensity measured at 140 °C maintains about 75% of that at room temperature. This kind of phosphors has high thermal stability.

3.2. $Ca_{1-y}Si_2O_2N_2$:Eu_y and $Ca_{0.90-y}Mg_{0.10}Si_2O_2N_2$:$Eu_y$ ($0.005 \leq y \leq 0.15$)

To investigate the influence of Mg^{2+} doping on the interactions among Eu^{2+} ions in phosphors, we used $Ca_{1-y}Si_2O_2N_2$:Eu_y and $Ca_{0.90-y}Mg_{0.10}Si_2O_2N_2$:$Eu_y$ as examples and studied the quenching concentration of Eu^{2+} in these phosphors. To reduce the deviation caused by experimental conditions, such as of the light intensity of the exciting sources, the reflectance of the samples, and the sensitivity of the detection [24], each experiment was repeated at least five times. Fig. 7(a) shows the excitation and emission spectra at room temperature of $Ca_{1-y}Si_2O_2N_2$:Eu_y phosphors, the excitation spectra locate in the UV to blue spectral region and the emission spectra for 400 nm excitation show the typical broad band of

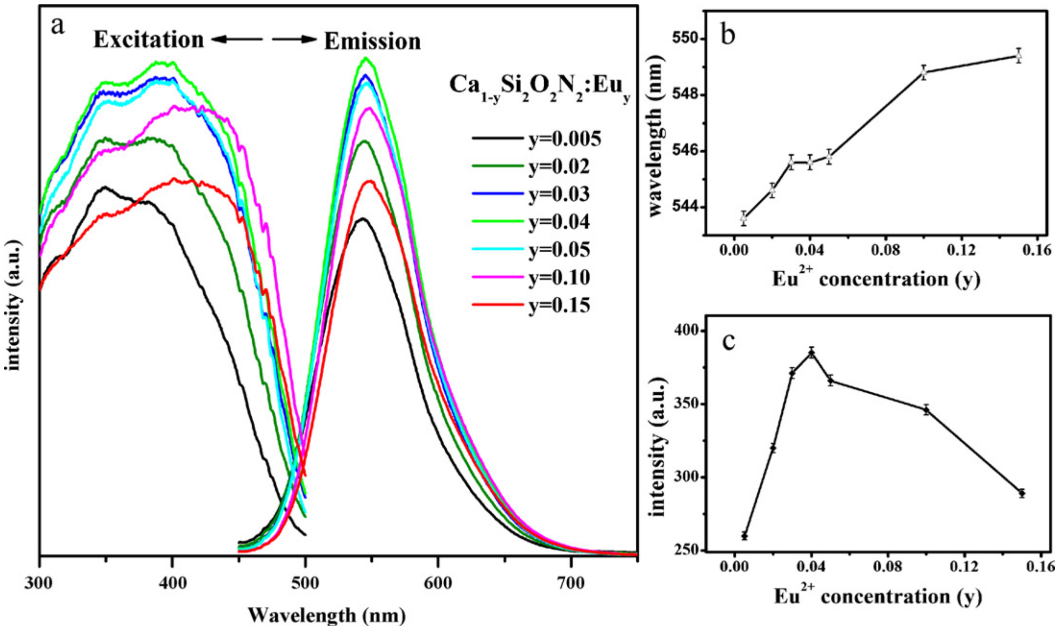

Fig. 7. (a) Excitation and emission spectra of $Ca_{1-y}Si_2O_2N_2$:Eu_y phosphors; (b) dependence of the emission wavelength and (c) the emission intensity on the concentration of Eu^{2+} in $CaSi_2O_2N_2$:Eu.

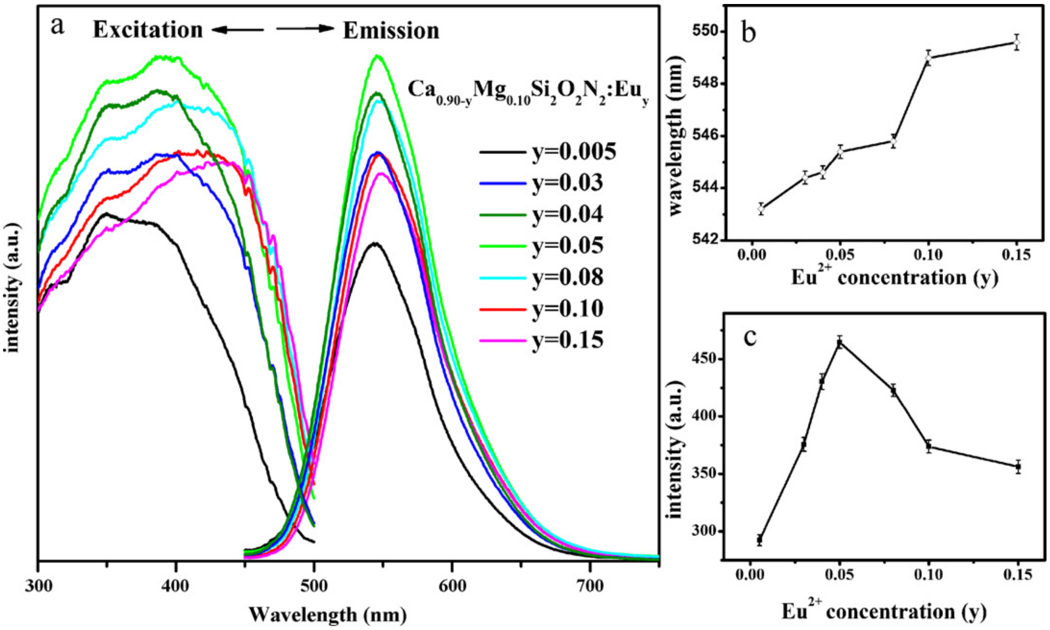

Fig. 8. (a) Excitation and emission spectra of $Ca_{0.90-y}Si_2O_2N_2$:Eu_y, $Mg_{0.10}$ phosphors; (b) dependence of the emission wavelength and (c) the emission intensity on the concentration of Eu^{2+} in $Ca_{0.90-y}Si_2O_2N_2$:Eu_y, $Mg_{0.10}$.

Eu^{2+}. In addition, the emission intensity become stronger with increasing the Eu^{2+} concentration and then the intensity decrease, which can be explained by concentration quenching [25]. As can be seen in Fig. 7(b), varying the concentration of Eu^{2+} from $y = 0.005$ to 0.15, the emission band maximum shifts from 543.6 to 549.4 nm for $Ca_{1-y}Si_2O_2N_2:Eu_y$. The regulation space by changing the Eu^{2+} concentration is greater than that of $Sr_2SiO_4:Eu^{2+}$ phosphor [26].The fact that the excitation and emission bands shift to the longer wavelength region with increasing Eu^{2+} concentration is ascribed to the possible reason that the higher Eu^{2+} concentration lowers the emission energy [27]. Fig. 7(c) shows that the emission intensity increase with increasing Eu^{2+} concentration and the maximum at $x = 0.04$. Concentration quenching occurs when the concentration of Eu^{2+} is more than $x = 0.04$.

The excitation and emission spectra of $Ca_{0.90-y}Si_2O_2N_2:Eu_y$, $Mg_{0.10}$ phosphors shown in Fig. 8(a) are general similar to that of $Ca_{1-y}Si_2O_2N_2:Eu_y$ phosphors. The emission band maximum shift from 543.2 nm to 549.6 nm when varying the concentration of Eu^{2+} from $y = 0.005$ to $y = 0.15$ as can be seen in Fig. 8(b). In addition, according to Fig. 8(c), the critical concentration of Eu^{2+} in this phosphor is at approximated 0.05. The critical concentration of Eu^{2+} in $CaSi_2O_2N_2$:Eu, Mg increases compared with that of $CaSi_2O_2N_2$:Eu. The result is critical and provides a new idea for future research.

The concentration quenching is caused by the interaction among Eu^{2+}, so the increase of the quenching concentration means that the interaction decreases. This result indicates that doping Mg^{2+} indeed can minimize the Eu^{2+}–Eu^{2+} interaction.

4. Conclusions

In conclusion, a series of $Ca_{1-x-y}Si_2O_2N_2:Eu_y$, Mg_x phosphors were synthesized using high temperature solid-state reaction. The average size of $CaSi_2O_2N_2$:Eu, Mg phosphor is 3–8 μm. The concentration of Mg^{2+} affects the structure and PL performance of these phosphors. Within an appropriate content, doping Mg^{2+} remarkably enhances the emission and the absorption intensity of phosphors. This novel phosphor also has high thermal stability and high quenching concentration. It is a very promising phosphor for white-LEDs applications.

Acknowledgments

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