Effect of strontium nitride on the properties of $Sr_2Si_5N_8:Eu^{2+}$ red phosphor

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Abstract: The nitride phosphor $Sr_2Si_5N_8:Eu^{2+}$ was synthesized by the high temperature solid-state method. The properties of $Sr_2Si_5N_8:Eu^{2+}$ were discussed by X-ray diffraction (XRD) scanning electron microscope (SEM) and spectra analysis. The XRD pattern shows that the single phase produces when strontium nitride is a bit excessive. The SEM photo implies that the excessive strontium nitride works as a flux in the reaction system. The position of emission peak is also located at about 612 nm as strontium nitride is excessive. The luminescent intensity of the phosphor adding excessive strontium nitride is higher than that of the phosphor introducing stoichiometric strontium nitride. The optimized content of nitride strontium was 2.05 mol/mol for the obtained phosphor with excellent properties.

Key words: luminescence; strontium nitride; alkaline earth; white LEDs; rare earth

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1. Introduction

White light-emitting diodes (LEDs) have drawn much attention due to their valuable application, such as a backlight source for liquid crystal displays and power descent lamps[1, 2]. Phosphor-converted LED (pc-LED) is the popular white light device[3, 4], wherein $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) is the superior commercial yellow phosphor[5–7]. However, there is a lack of perfect red phosphors for white LED application at present[8]. Recently, the nitride phosphors have been intensively studied as a host lattice in exploration of LED conversion phosphors, which exhibit unusual, interesting luminescent properties when activated by rare earth ions, such as Eu^{2+}, Ce^{3+}[9,10]. Most importantly, the nitride phosphors emit visible light efficiently under near-ultraviolet or blue light irradiation and have outstanding thermal, chemical and mechanical stability[11–13] compared with those conventional phosphors.

In previous work, we reported the influence of Eu^{2+} ion on the properties of $Sr_2Si_5N_8:Eu^{2+}$ phosphors[14] and the Sr/Ca ratio on the properties of $(Sr_{1-x}Ca_x)_2Si_5N_8:Eu^{2+}$ phosphors[15]. With respect to the above mentioned investigations, there still remain a number of questions, for example, how to improve the luminescent intensity and the morphology of the nitride phosphor. In this paper, the nitride phosphor was synthesized by the high temperature solid-state method. The motivation of the paper is to study the effect of strontium nitride on the properties of $Sr_2Si_5N_8:Eu^{2+}$ phosphors. The structure, morphology and luminescent properties are characterised by XRD, SEM and spectra analysis, respectively.

2. Experimental

$Sr_2Si_5N_8:Eu^{2+}$ phosphors were synthesized by high temperature solid-state method. The raw materials Si_3N_4 (99%) and Eu_2O_3(4N) were stoichiometrically weighted out, and then strontium nitride was added. Subsequently they were mixed and ground together in an agate mortar homogeneously in a purified argon glove box. The mixtures were then transferred into an alumina crucible positioned in a tube furnace to fire at 1400 ℃ for 9 h under nitrogen/hydrogen atmosphere with volume ratio 95 : 5. The sintered cake was grinded and sieved, and then the $Sr_2Si_5N_8:Eu^{2+}$ samples were obtained.

The crystal structure of the phosphors was checked using a D8 DISCOVER X-ray diffractometer that was manufactured by BRUKER in Germany. The SEM analysis was conducted on SIRION scanning electron microscope made in Japan. The emission spectra were detected by RF-5301PC spectrofluorometer made in Japan.

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows the XRD pattern of $Sr_2Si_5N_8:Eu^{2+}$ added

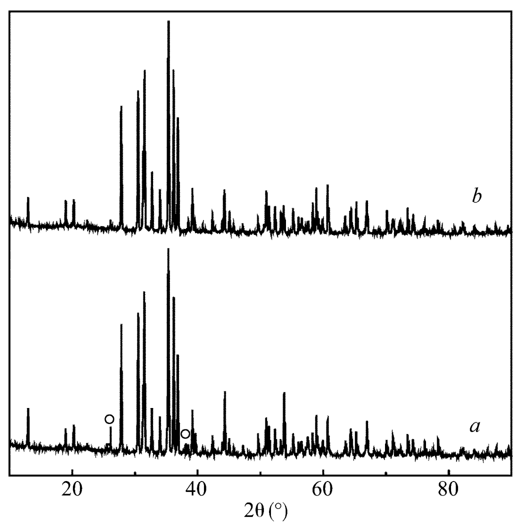

Fig. 1. XRD pattern of $Sr_2Si_5N_8:Eu^{2+}$ added with strontium nitride (*a*) stoichiometrically ratio and (*b*) excessively. ("○" belong to $SrSi_2N_2O_2$ impure phase)

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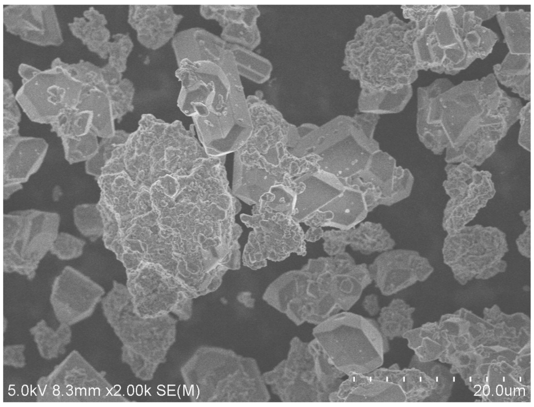
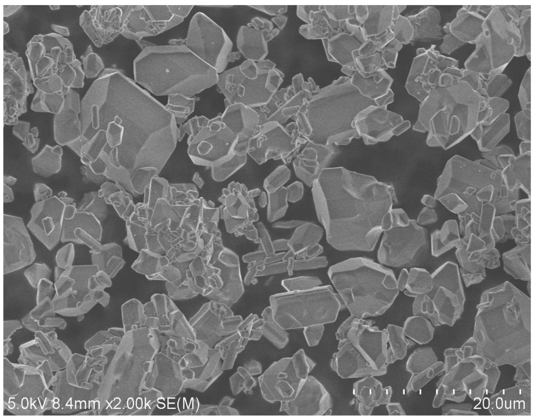


(a)



(b)

Fig. 2. SEM photo of $Sr_2Si_5N_8$:Eu^{2+} added with strontium nitride (a) stoichiometrically ratio and (b) excessively.

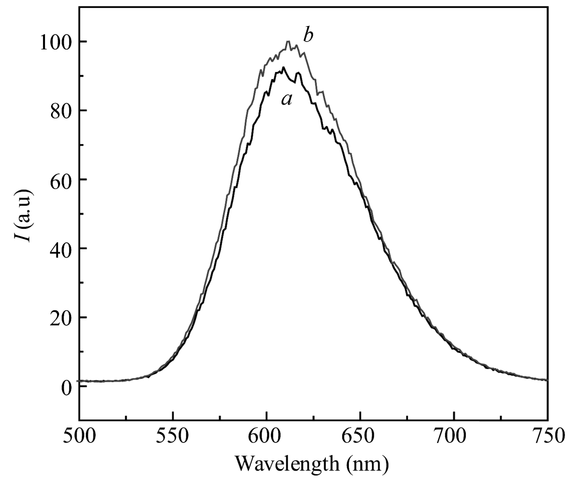


Fig. 3. Emission spectra of $Sr_2Si_5N_8$:Eu^{2+} added with strontium nitride (*a*) stoichiometrically and (*b*) excessively.

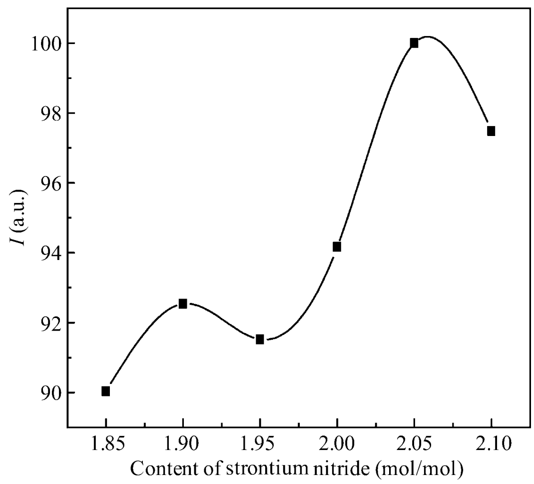


Fig. 4. Effect of the content of strontium nitride on the intensity of $Sr_2Si_5N_8$:Eu^{2+}.

with strontium nitride according to stoichiometric ratio and excessively, respectively. The examination of the diffraction peaks confirms that only $Sr_2Si_5N_8$ phase is prepared successfully when strontium nitride is a bit excessive. However, besides the main $Sr_2Si_5N_8$ phase, a few $SrSi_2N_2O_2$ diffraction peaks are generated when the raw materials were stoichiometrically weighted out. This suggests that it is helpful to produce pure phase as strontium nitride is excessive, which enhances the luminescent intensity of the phosphor.

3.2. SEM analysis

Figure 2 is the SEM photo of $Sr_2Si_5N_8$:Eu^{2+} added with strontium nitride according to stoichiometric ratio and excessively, respectively. It is obvious that the powders produce reunion and the morphology is not regular and smooth when strontium nitride was weighted out according to stoichiometric ratio. However, the powder consists of well-crystallized and well-dispersed grain with a mean size of 10 μm. It implies that the excessive strontium nitride promotes the crystallization action of pellets and works as the flux in the system.

3.3. Spectra analysis

Figure 3 is the emission spectra of $Sr_2Si_5N_8$:Eu^{2+} added with strontium nitride according to stoichiometric ratio and excessively, respectively (λ_{ex} = 460 nm). The emission spectra exhibit a broad emission band peaking at about 612 nm which is assigned to the $4f^6 5d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ion[16]. Compared with other Eu^{2+} ion doped phosphors, the emission band of $Sr_2Si_5N_8$:Eu^{2+} locates at a fairly long wavelength range. Furthermore, in the Eu^{2+} ion doped oxynitride or nitride hosts the emission occurs at longer wavelengths with increasing nitrogen content[9], which is attributed to the higher electronegativity of $N^{3-}$and the nephelauxetic effect which effectively lower the center of gravity of 5d orbital of Eu^{2+} ions[17].

Figure 4 is the different contents of strontium nitride on the intensity of $Sr_2Si_5N_8$:Eu^{2+}. Obviously, when the content of strontium nitride is a bit excessive (2.05 mol/mol), the luminescent intensity of the phosphor is the best. The distortion of crystal produces when strontium nitride is excessive. The width between the valence band and conduction band is much lower, which results in the easier 4f–5d transition of Eu^{2+}, and then the intensity of luminescence becomes stronger. At the same time, the excessive strontium nitride is helpful for forming the pure phase $Sr_2Si_5N_8$. Both behaviors enhance the emission intensity of the phosphor.

4. Conclusion

The $Sr_2Si_5N_8:Eu^{2+}$ red phosphor with different contents of strontium nitride added was prepared by a high temperature solid state method. The XRD shows that it is helpful to produce pure phase when strontium nitride is a bit excessive. The SEM photo exhibits that the excessive strontium nitride promotes the crystallization action of pellets and woks as a flux in the system. The emission spectra show a broad emission band at 612nm due to the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ion. The luminescent intensity of the phosphor adding excessive strontium nitride is higher than that of the phosphor introducing stoichiometric strontium nitride.

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