Enhanced afterglow properties of Nd³⁺ co-doped Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ synthesized by sol-gel method

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Abstract

In this study, Sr_{1.94}MgSi₂O₇: 0.02Eu²⁺, 0.04Dy³⁺ and Sr_{1.928}MgSi₂O₇: 0.02Eu²⁺, 0.04Dy³⁺, 0.012Nd³⁺ long afterglow luminescent materials were successfully synthesized **via** the sol-gel method **under reducing atmosphere** at 1100 °C for 3 h. **No** phase structure **effect** of Sr₂MgSi₂O₇, **or** significant lattice distortion occurred while **a** small amount of rare earth ions **were** doped. Moreover, co-doping Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ **with** Nd³⁺ has virtually no effect on the morphology of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺. **Co-doping** Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ **with** Nd³⁺ has **also** no **evident** effect on the position of the fluorescence emission peak. **However, the applied concentration of** Nd³⁺ co-doping **created** deeper traps and **enhanced** the afterglow properties of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺.

Keywords: Luminescence ; **co-dope**; sol-gel preparation; **afterglow properties**; traps

1 Introduction

In recent years, Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ luminescent materials have **become the focus of extensive investigation** for **their** afterglow **properties**^[1-5]. Zhang *et al.*^[6] synthesized Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ particles **via** the sol-gel method and modified **them** with 3-aminopropyltriethoxysilane to improve dispersibility and compatibility in the polylactic acid matrix. **Their** results indicated the decay curves of the composite films **to** have a similar tendency **to** the pure Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ particles. Yoshimura *et al.*^[7] successfully prepared a novel Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ **nanoparticle solution** with afterglow properties **via** laser ablation in liquid. Ye *et al.*^[8] reported novel one-dimensional PLA/ Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ composite fibers composed of long-persistent luminescence nanoparticles. **Preparation** and properties of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ have been widely studied, **however**, how to enhance the afterglow **properties** of Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ **via co-doping** has been rarely reported.

Not only the species of rare earth ions can influence afterglow characteristics^[9, 10], **but also the preparation method**^[11], doping concentration and the relative molar ratio of earth ions^[12, 13]. Wu *et al.*^[14] prepared long afterglow phosphors Sr_{1.97}MgSi₂O₇: Eu_{0.01}²⁺, Dy_{0.02-x}³⁺, Nd_x³⁺ (x=0, 0.01, 0.02) and Sr_{1.99}MgSi₂O₇: Eu_{0.01}²⁺ **via** high-temperature solid state reaction. They found decreasing decay constants of the afterglow with increasing Nd³⁺ for Dy³⁺ substitution. Wako *et al.*^[12] prepared CaAl₂O₄: Eu²⁺, Nd³⁺, and found increasing photoluminescence (PL) intensity with an increase in Nd³⁺ concentration from 0.25 mol% to 1 mol%, while PL intensity decreased for 2 mol% to 4 mol% of Nd³⁺.

In this study, Sr_{1.94}MgSi₂O₇: 0.02Eu²⁺, 0.04Dy³⁺ and Sr_{1.928}MgSi₂O₇: 0.02Eu²⁺, 0.04Dy³⁺, 0.012Nd³⁺ long afterglow luminescent materials were successfully synthesized **via** the sol-gel method **under reducing atmosphere** at 1100 °C for 3 h. The **augmentation** of afterglow **properties** **attained by the applied concentration of** Nd³⁺ **for the co-doping of** Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ have been discussed.

2 Material and methods

2.1 Synthesis of SMS and SMSN luminescent materials

A series of SMS and SMSN samples were synthesized using the sol-gel method. **Here, a typical preparation process is described:** First, H₃BO₃ was dissolved in distilled water to form **the**

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homogeneous solution A; $\text{Sr}(\text{NO}_3)_2$ was dissolved in 3.6 M HNO_3 to form solution B; Under mechanical stirring, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 3.6 M HNO_3 until it was completely dissolved to form the homogeneous solution C; Dy_2O_3 was dissolved in 3.6 M HNO_3 to form solution D; Eu_2O_3 was dissolved in 3.6 M HNO_3 to form solution E; Nd_2O_3 was dissolved in 3.6 M HNO_3 to form solution F; $\text{Si}(\text{OCH})_5$ and absolute ethyl alcohol were completely mixed to form the homogeneous solution G. Solutions B, C, D, E, F were added to solution A in sequence under mechanical stirring to form a mixture. Then, solution G was slowly added to the mixture and stirred at 70 °C for 2 h.

The resulting sol was aged at 70 °C for 24 h, dried at 70 °C for 72 h, and then sintered under reducing atmosphere at 1100 °C for 3 h. The samples were obtained after cooling to room temperature in the furnace. Nominal compositions of the samples were $\text{Sr}_{1.94-z}\text{MgSi}_2\text{O}_7$: 0.02Eu^{2+} , 0.04Dy^{3+} , $z\text{Nd}^{3+}$ ($z = 0$ and 0.012), named SMS ($z = 0$) and SMSN ($z = 0.012$), respectively.

2.2 Characterization

The PL and decay curves were obtained via a Hitachi F-7000 fluorescence spectrophotometer (Japan) equipped with a 450 W Xe lamp as the excitation light-source. The X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Rigaku D/Max-2500) with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), and diffraction angles ranging from 10° to 80°. Microstructural aspects of the samples were analyzed via scanning electron microscopy (SEM, Hitachi Limited, Japan). Thermoluminescence (TL) spectra of the samples were obtained using a FJ427A1 thermoluminescence measurement instrument (Beijing, China).

3 Results and discussion

Fig. 1 shows XRD patterns of SMS and SMSN calcined at 1100 °C for 180 min. The XRD peak positions and relative intensities of SMS and SMSN matched those of the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ standard powder XRD (JCPDF No. 75-1736) with tetragonal crystal system. Eu^{2+} , Dy^{3+} and Nd^{3+} ions substituted Sr^{2+} ions in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ lattice due to similar electronegativity and ionic radius. No additional peaks were detected for other phases, indicating that the phase structure of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ had no effect, nor did significant lattice distortion occur, while a small amount of rare earth ions are doped^[8].

Figs. 2a and 2b show the SEM images of SMS powder and SMSN. As shown in Figure 2a, the SMS powder possessed an indefinite shape, and particle sizes ranged from 0 to 10 μm . Similarly, Figure 2b shows the morphology and particle size of the SMSN powder to almost exactly equal that of SMS. Nd^{3+} co-doping $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} virtually has no effect on the morphology of the $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} .

Fig. 3 shows the corresponding excitation spectra (a) and emission spectra (b). Figure 3a reveals no significant change of the positions of the fluorescence excitation peaks due to Nd^{3+} co-doping, and broad bands appeared in the range of 250-330 nm and 335-450 nm. The peaks were located at 275 nm and 360 nm, respectively. The emission spectra of SMS and SMSN are shown in Figure 3b. The samples were illuminated with light at a wavelength of 360 nm. Only one broadband emission peak is centered at 469 nm and broadband appeared in the range of 420-550 nm. This emission corresponds to the transition between the excited state and the ground state ($4f^65d \rightarrow 4f^7$) of Eu^{2+} ions^[15]. As a consequence, it can be concluded that Nd^{3+} co-doping of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} has no evident effect on the position of the fluorescence emission peak.

Fig. 4 shows decay curves of SMS and SMSN (a) and TL curves of SMS and SMSN (b). The

luminescent decay curves of SMS and SMSN under UV excitation for 5 min are shown in Figure 4a. Both SMS and SMSN exhibit good afterglow performances, indicating the existence of traps in SMS and SMSN, which induce the afterglow. Furthermore, the afterglow performance of SMSN is superior to that of SMS. Both SMS and SMSN comprised rapid decay and subsequently long lasting phosphorescence^[16, 17]. The luminous intensities of the SMS and SMSN decayed exponentially, so their decay curves can also be evaluated by fitting a second-order exponential equation. The form of this equation can be expressed as follows:

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (1)$$

where I is the phosphorescence intensity; t is the decay time; I_1 , I_2 , τ_1 , and τ_2 are constants that determine the trend of the decay. Both SMS and SMSN were excited for 5 min with a 360 nm light source. After this excitation, the SMSN showed increased decay time. For SMSN, the values for I_1 and I_2 were 1014.78 and 44.79, while those for τ_1 and τ_2 were 2.20 and 239.19. For SMS, the values for I_1 and I_2 were 941.91 and 41.90, while those for τ_1 and τ_2 were 1.23 and 197.22. These results indicate that SMSN shows a higher phosphorescence intensity and increased decay time compared to SMS. The TL curves of SMS and SMSN are shown in Figure 4b. SMS has a broad band peaking at 98 °C, while SMSN has a broad band peaking at 101 °C. Since temperature corresponds to the energy for detrapping, the trap of SMSN is deeper than that of SMS. These results indicate that Nd^{3+} co-doping creates deeper traps and thus enhances the afterglow properties of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$.

4. Conclusions

The applied doping concentration of Nd^{3+} co-doping significantly enhances afterglow properties of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$. The TL indicates that these improved afterglow properties result from a deeper trap of the sample.

Acknowledgements

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Figure captions:

Fig. 1 XRD patterns of SMS and SMSN

Fig. 2 SEM images of SMS (a) and SMSN (b)

Fig. 3 (a) Excitation spectra of SMS and SMSN. (b) Emission spectra of SMS and SMSN

Fig. 4 (a) Decay curves of SMS and SMSN. (b) TL curves of SMS and SMSN