Luminescent properties of R^{+} doped $Sr_2MgSi_2O_7: Eu^{2+}, Dy^{3+}$ ($R^{+} = Li^{+}, Ag^{+}$) phosphors

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Abstract: Long afterglow phosphor $Sr_2MgSi_2O_7: Eu^{2+}, Dy^{3+}$ doped with R^{+} ($R^{+} = Li^{+}, Ag^{+}$, respectively) was synthesized by the high temperature solid-state reaction method. Crystal structure, morphological and luminescent properties were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), photoluminescence (PL), decay curves and thermoluminescence (TL) curves. The results indicate that the incorporation of these metal ions have no influence on the position of the emission peak which is determined by the $4f^7 \rightarrow 4f^6 5d^1$ Eu^{2+} ions, but have influence on the intensity of the emission and the afterglow. The highest phosphorescent intensity was observed with 2.5 mol% of Li^{+} , and 0.4 mol% of Ag^{+} doping in respectively. Compared with the undoped sample, the optimum incorporation of Li^{+} ions could induce a remarkable increase of phosphorescent intensity and the decay constant by about 1.5 times and 1.6 times, respectively. Doping Ag^{+} ions can also improve the luminescence properties, but the performance is not good as Li^{+} ions. The mechanism of $Sr_2MgSi_2O_7: Eu^{2+}, Dy^{3+}, R^{+}$ ($R^{+} = Li^{+}, Ag^{+}$, respectively) enhancement has been discussed.

Keywords: $Sr_2MgSi_2O_7: Eu^{2+}, Dy^{3+}$; lithium ion; silver ion; luminescent properties

1 Introduction

Long afterglow phosphor refers to the material that can store the energy from the irradiation such as the sunlight or artificial light, and the luminescence can last for seconds, minutes, or even hours after the removal of excitation source at room temperature [1]. Phosphors with persistent luminescence are environment friendly and energy economized materials. They have wide potential applications in many areas including security signs, traffic signs, displays, and self-luminous crafts [2,3]. The silicates phosphors have drawn many research interests since they were first developed by Z.G. Xiao et al [4]. Compared with previously developed aluminates materials, such as the aluminates and the sulphides, the silicate base phosphor has more advantages on chemical stability, heat stability, lower cost and excellent weather resistance [5]. However, its long-lasting phosphorescence property was inferior to that of aluminates materials. Therefore, one of the research focuses is to enhance the duration of the afterglow.

$\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} is silicate-based phosphor with broad emission bands. The emission should be attributed to the transition from $4f^65d^1$ excited state to $4f^7$ ground state configuration of Eu^{2+} ions [6,7]. It is known that co-doping is one of the common methods to enhance the luminescent properties of long afterglow phosphors. Many studies have examined the optical properties of rare earth (RE) doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$, for example, RE^{3+} in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , the RE ions include Ce^{3+} [8], Er^{3+} [9], Nd^{3+} [10], Tb^{3+} [11], La^{3+} [12], et al. Another example is RE^{3+} in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , the RE ions include Ce^{3+} [13], Nd^{3+} [14], Ho^{3+} [15], et al and the results indicate that with proper RE ion doping can enhance the luminescent properties of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} .

However, only a few studies have investigated the co-doping of non-rare earth elements. As evidenced from literature, incorporation of smaller size atoms into R site enhances the luminescence properties to an interesting extent. Even in very small quantities, incorporation of Li^+ ions as sensitizers into the host matrix frequently plays an important role in the enhancement of the luminescent efficiency of phosphors [16-19]. Incorporation of Li^+ ions into the network cannot only enhance the luminescence efficiency but also control the morphology and grain size of the phosphors. As for Ag^+ , it has the similar radius of Sr^{2+} and can easily substitute Sr^{2+} sites [20], this will arouse the lattice distortion, and trigger more defects, which makes

the matrix contain shallow and deep traps [21]. However, there is no report on improvement of phosphorescence with Li^+ or Ag^+ ion incorporation in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} phosphors.

This work will discuss the influence the two kinds of monovalent ions, Li^+ or Ag^+ , on the crystal structure and luminescence properties by doping experiment, respectively. Based on the thermoluminescence curves changes between $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ ($\text{R}^+ = \text{Li}^+$, Ag^+ , respectively) phosphors and some other experiments, the mechanism of long afterglow was discussed.

2 Experimental

2.1 Phosphor synthesis

The $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ ($\text{R}^+ = \text{Li}^+$, Ag^+ , respectively) phosphors were prepared by the high temperature solid state reaction method. The raw materials were SrCO_3 (AR), SiO_2 (AR), MgO (AR), H_3BO_3 (AR), Li_2CO_3 (AR), AgNO_3 (AR), Eu_2O_3 (99.99%) and Dy_2O_3 (99.99%). The contributions of Eu_2O_3 elements and Dy_2O_3 elements in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ phosphors were 1.0 mol% and 2.0 mol%. The small amounts of H_3BO_3 were added as flux. The raw materials were weighted in stoichiometric proportion for $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} (denoted as SED), $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , x mol% Li^+ ($x = 1.5, 2.0, 2.5$ and 3.0 , respectively) (denoted as SED- x Li), and $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , y mol% Ag^+ ($y = 0.2, 0.3, 0.4$ and 0.5 , respectively) (denoted as SED- y Ag), and then mixed thoroughly in an agate mortar for 4 h. The mixed powders were sintered at 1250°C for 2 h in a weak reducing atmosphere. The reducing atmosphere was generated with the help of activated carbon. At last the samples were cooled down to room temperature and ground into the particle size between 120 and 140 mesh before the measurement.

2.2 Measurement techniques

The crystal structure of the samples was examined by an X-ray diffractometer (XRD, PANalytical X'pert Pro type, Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) and a 2θ scan range of 10° to 80° . The surface morphology of the samples was

characterized by a scanning electron microscope (SEM, Carl zeiss, Germany). The excitation and emission spectra of the samples were obtained by a Hitachi F-7000 Fluorescence Spectrophotometer. The afterglow curves of phosphors were recorded by a long afterglow material optical test system with artificial light ($1000\pm 5lx$). The thermoluminescence (TL) curves were obtained by a ROSB TL/OSL3DP thermoluminescent dosimeter with a heating rate of 2 K/s. All the measurements are performed at room temperature.

3 Results and discussions

3.1 XRD analysis

Fig. 1 shows the XRD patterns of SED, SED- x Li and SED- y Ag phosphors. It can be seen that all the samples exhibit similar XRD patterns and all of the diffraction peaks are indexed to the tetragonal $Sr_2MgSi_2O_7$ structure (JCPDS No. 75-1736). No impurity phase has been observed in any of the compositions, this indicates that relatively low concentrations of Eu^{2+} , Dy^{3+} and R^+ in $Sr_2MgSi_2O_7$ host have no significant influence on the crystal structure in this work. Furthermore, as can be seen in Fig. 1(a), the peaks of the SED- x Li were sharper and stronger than those of bare SED, and the crystallinity of the phosphors was improved with increase in Li^+ concentration from 0.0 to 2.5 mol% and then decreased for higher concentrations. It indicates that the alkali metal can serve as flux and improve the crystallinity [22,23]. As can be seen in Fig. 1(b), compared with SED, the peaks of the SED- y Ag have no significant enhancement, which indicated that Ag^+ cannot serve as flux. Similar with Li^+ doping, the peak of the SED-0.4 mol% Ag was sharper and stronger than SED-0.5 mol% Ag. The results indicate that when the content of Li^+ or Ag^+ increases further beyond certain limits, the oxygen vacancies of host lattice increase accordingly, which may destroy the crystallization of $Sr_2MgSi_2O_7$ and lead to the decrease of luminescence intensity [24].

3.2 Photoluminescence (PL)

Fig. 2 shows the excitation spectra measured at 468 nm emission and emission spectra measured under 360 nm excitation wavelength of SED, SED- x Li and SED- y Ag phosphors. As shown in Fig. 2, under the 360 nm excitation, all samples exhibit a broad emission with a peak around 468 nm. This emission corresponds to the

transition between the excited state to the ground state ($4f^65d^1 \rightarrow 4f^7$) of Eu^{2+} ions [25,26]. No other emission band is observed. It indicates that the co-doping with Dy^{3+} ions, or R^+ ions has no influence on the position of the emission peak but the emission intensity. Furthermore, as can be seen in Fig. 2(a), the emission intensity of the SED- x Li phosphor linearly increased with increased Li^+ content and reached a maximum when the concentration was 2.5 mol% and decreased at higher concentrations. As can be seen from Fig. 2(b), the emission intensity increased with increase in Ag^+ ions concentration from 0.0 to 0.4 mol% and then decreased for 0.5 mol%. It means that the highest phosphorescent intensity was observed with 2.5 mol% of Li^+ and 0.4 mol% of Ag^+ doping, respectively. The integral intensity of the emission spectrum of SED-2.5 mol% Li and SED-0.4 mol% Ag phosphor is increased by a factor of 1.39 and 1.23 when compared to that of bare SED (without R^+) phosphor, respectively.

3.3 SEM analysis

Fig. 3 shows the typical scanning electron microscope (SEM) images of (a) SED, (b) SED-2.5 mol% Li, and (c) SED-0.4 mol% Ag phosphors. It can be seen that SED and SED-0.4 mol% Ag have similar surface morphologies. It indicates that Ag^+ co-doping does not promote the grain growth. Fig. 2(b) shows that SED-2.5 mol% Li have greater grain size and less grain boundaries. As the grain boundaries may be sources for dissipation of light generated inside the material, SED-2.5 mol% Li with enlarged grain sizes and less grain boundaries are expected to exhibit superior PL brightness [27].

3.4 Decay

Fig. 4 shows the decay curves of the long afterglow of the samples of SED, SED-2.5 mol% Li (denoted as SED-Li), and SED-0.4 mol% Ag (denoted as SED-Ag). As shown in Fig. 4, when the phosphors are doped with Li^+ or Ag^+ , the afterglow intensity is enhanced, especially Li^+ . Furthermore, the duration of the afterglow is prolonged since the intensity of both SED-2.5 mol% Li and SED-0.4 mol% Ag is stronger than that of SED all the time. To further study the afterglow curves, the fitting method is utilized for the evaluation of afterglow curves. As reported earlier, the decay process contains the rapid-decaying process and the slow-decaying process, the decay curves of the samples can be evaluated by fitting into double exponential equation which reflects the trend of the decay. The form of the equation is as follow [28,29]:

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

where, I is the phosphorescent intensity, I_1 and I_2 are the constants, t is the time, τ_1 and τ_2 are the decay constants, respectively. The fitting results of the parameters of τ_1 and τ_2 are listed in Table 1. The duration of the afterglow can be reflected by τ_2 because it associates with the slow-decaying process. Table 1 shows that the duration of both SED-2.5 mol% Li and SED-0.4 mol% Ag is much longer than SED. It indicates that the co-doping with Ag^+ and Li^+ ions can strongly enhance the afterglow duration of the SED phosphor.

3.5 Thermoluminescence (TL)

As already known, the afterglow of the phosphors is generated by the de-trapped carriers (holes and/or electrons) which recombine with the opposite carriers in the luminescent centers accompanied with the visible emission [21]. So the traps created by the lattice defects play a very important role in the generation of the afterglow. In order to study the trap states of the prepared phosphors, Fig.5 shows the thermoluminescence (TL) curves of the samples of SED, SED-2.5 mol% Li (denoted as SED-Li), and SED-0.4 mol% Ag (denoted as SED-Ag). It is important to note that the TL intensity of the $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}, \text{R}^+$ ($\text{R}^+ = \text{Li}^+, \text{Ag}^+$) phosphors are much stronger than those of bare $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ (without R^+). It indicates that the addition of R^+ could increase the number of the traps.

The TL parameters of the thermal activation energy E which are associated with the trap depth can be obtained by fitting experimental data to the general order kinetics formula. The general order kinetics formula describing the TL intensity I as a function of the temperature T can be represented by [30, 31]:

$$I(T) = sn_0 \exp\left(-\frac{E_t}{k_B T}\right) \left[\frac{(l-1)s}{\beta} \times \int_{T_0}^T \exp\left(-\frac{E_t}{k_B T'}\right) dT' + 1 \right]^{-l/(l-1)} \quad (2)$$

where n_0 is the concentration of trapped charges at $t=0$; k_B is Boltzmann's constant; and β is the heating rate. The trap depth E_t (or thermal activation energy) can be estimated by the following equation [32-34]:

$$E_t = [2.52 + 10.2(\mu_g - 0.42)] \left(\frac{k_B T_m^2}{\omega} \right) - 2k_B T_m \quad (3)$$

where T_m is the temperature of the glow peak, T_1 and T_2 are temperature on either side of T_m corresponding to half peak intensity. τ is the half width at the low temperature side of the peak or the low temperature half width ($\tau = T_m - T_1$), δ is half width towards

the fall-off side of the glow peak or the high temperature half width ($\delta = T_2 - T_m$), $\omega = \delta + \tau$. The asymmetry parameter $\mu_g = \delta/\omega$. The parameters of TL curve and the estimating trap depths of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors are listed in Table 2.

A single glow peak of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}, \text{R}^+$ phosphors were found. It is reported that a suitable trap depth (0.65~0.75 eV) is essential for phosphors to show long persistence [1], therefore, the trap density of the both phosphors is suitable for long afterglow. What's more, the trap depth of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}, \text{Li}^+$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}, \text{Ag}^+$ is 0.72 eV and 0.71 eV respectively (shown in Table 2), both are a little deeper than that of $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ (the trap depth is 0.68 eV). As is well known, the existence of suitable charge traps in host lattice is responsible for long lasting phosphorescence. If trap is deeper, more energy is needed to release the trapped carriers. Then the duration of the afterglow will be longer since the carriers will be released slowly in the deep trap.

3.5 Discussion

Based on the above descriptions and analysis, we are trying to explain the possible mechanism of the enhanced emission by R^+ ($\text{R}^+ = \text{Li}^+, \text{Ag}^+$) doping. In general, the afterglow of the phosphors should be due to the existence of the traps which are created by the lattice defects in the host. The lattice defects in the phosphors usually are the cation vacancies, oxygen vacancies and the co-doping ions which replace the cation ions in the host. As it was reported, when Dy^{3+} ions were doped into $\text{Sr}_2\text{MgSi}_2\text{O}_7$, they would substitute the Sr^{2+} ions. To keep electroneutrality of the compound, two Dy^{3+} ions would substitute two Sr^{2+} ions and produce a $[\text{V}_{\text{Sr}}'']$. The process can be expressed as $2\text{Dy}^{3+} + 3\text{Sr}^{2+} \rightarrow 2\text{Dy}_{\text{Sr}}^{\bullet} + \text{V}_{\text{Sr}}''$. Each substitution of two Dy^{3+} ions would create two positive defects of $[\text{Dy}_{\text{Sr}}^{\bullet}]$ and one negative vacancy of $[\text{V}_{\text{Sr}}'']$. The oxygen vacancies are created probably during the synthesis process with the reducing atmosphere. As the oxygen vacancy $[\text{V}_{\text{O}}^{\bullet \bullet}]$ is positively charged, some vacancies of Sr^{2+} $[\text{V}_{\text{Sr}}'']$ would also be created during the synthesis process to compensate the difference of the charges.

When R^+ ions are incorporated in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$, the R^+ ions can occupy Sr^{2+} sites and produce R_{Sr}' , the exceed charge -1 can be compensated by one oxygen vacancy on two R^+ impurity ions for charge neutrality. From Fig. 5, we can see that the TL intensity of the $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}, \text{R}^+$ ($\text{R}^+ = \text{Li}^+, \text{Ag}^+$) phosphors are

much stronger than those of bare $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} (without R^+), and the trap depth of former are deeper. The reason is that the addition of Li^+ or Ag^+ increase the number of oxygen vacancies, which might act as a sensitizer for the energy transfer to rare-earth ions due to the strong mixing of charge transfer states. Since Li^+ has smaller radius as compared to Ag^+ , it can be doped more easily and produce more oxygen vacancies [35]. Besides of the above function, Li^+ ion can also serve as flux, the enhancement of luminescence performance with Li-doping may be attributed to the improved crystallinity and the enlarged grain sizes, therefore the effect of doped with Li^+ is better than that of doped with Ag^+ . However, the phosphorescence quenching also occurs at higher doping content of R^+ due to the excess oxygen vacancies at the host, which destroy the crystallinity of the host material [18,24].

Previous studies and the above results lead to a possible mechanism of long afterglow of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ ($\text{R}^+ = \text{Li}^+$, Ag^+) phosphors and it illustrated in Fig. 6 [36-39]. In $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host, the defects with positive charge such as $[\text{V}_\text{O}^\bullet \bullet]$ and $\text{Dy}_{\text{Sr}}^\bullet$ can act as electron trapping centers, while those with negative charge such as $[\text{V}_{\text{Sr}}'']$ can $[\text{R}'_{\text{Sr}}]$ act as hole trapping centers. Under UV excitation, the ground-state electrons of Eu^{2+} ions are promoted to the excited state, a large number of free holes and electrons formed (progress 1). The free holes and free electrons transferred via the lattice directly to luminescence centers Eu^{2+} , followed by the $\text{Eu}^{2+} 4\text{f}^6 5\text{d}^1 \rightarrow 4\text{f}^7$ emission as luminescence (progress 2). Some of the **excitons** trapped by oxygen vacancies instead of returning to the ground state, and some of the holes were released into the valance band and captured by the hole trap (progress 3). The captured electrons near the host conduction band were released to the conduction band with thermal energy and the captured holes were also release (progress 4). The released holes and electrons recombined, and the luminescence (long afterglow) was regenerated (progress 5).

4. Conclusions

The phosphors $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ ($\text{R}^+ = \text{Li}^+$, Ag^+ , respectively) have been prepared via the high-temperature solid state reaction in this work. The co-dopants have no influence on the position of the emission peak which is determined by the $4\text{f}^7 \rightarrow 4\text{f}^6 5\text{d}^1$ Eu^{2+} ions. However, the intensity of the emission and the afterglow are changed with different co-dopants. The optimum doping content of

Li^+ is 2.5 mol%, and the optimum doping content of Ag^+ is 0.4 mol%. The samples have stronger afterglow and TL intensity and therefore a longer duration of the afterglow with the Li^+ or Ag^+ co-doping. The reason is that the addition of Li^+ or Ag^+ increases the number of oxygen vacancies, which might act as a sensitizer for the energy transfer to rare-earth ions due to the strong mixing of charge transfer states. Since Li^+ has smaller radius than Ag^+ , it can be doped more easily and produce more oxygen vacancies. What's more, Li^+ ion can serve as flux, therefore the effect of doped with Li^+ is better than that of doped with Ag^+ .

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Figures

Fig. 1 XRD patterns of SED, SED-x Li and SED-y Ag phosphors

Fig. 2 The emission and excitation spectrum of SED, SED-x Li and SED-y Ag phosphors

Fig. 3 SEM of (a) SED, (b) SED-2.5 mol% Li, and (c) SED-0.4 mol% Ag phosphors.

Fig. 4 The afterglow decay curves of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Fig. 5 The TL glow curves of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Fig. 6 The schematic diagram of luminescent mechanism of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , R^+ phosphors.

Tables

Table 1 The fitting results of τ_1 and τ_2 of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Table 2 The estimating trap depths of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Table 1 The fitting result of τ_1 and τ_2 of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Samples	τ_1 (s)	τ_2 (s)
SED	18.8	92.2
SED-2.5 mol% Li	30.5	145.6
SED-0.4 mol% Ag	25.4	120.9

Table 2 The estimating trap depths of SED, SED-2.5 mol% Li and SED-0.4 mol% Ag phosphors

Samples	$T_1(K)$	$T_m(K)$	$T_2(K)$	ω	δ	μ_g	E(eV)
SED	341	367	393	52	26	0.50	0.68
SED-2.5 mol% Li	336	359	379	43	20	0.47	0.72
SED-0.4 mol% Ag	338	363	389	51	26	0.51	0.71