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Luminescence properties of Eu^{2+} and Mn^{2+} doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors

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Abstract

Eu^{2+}, Mn^{2+} doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors were prepared by high temperature solid-state reaction method. Their luminescence properties were studied. The emission spectra of Eu^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ consist of a blue band (455 nm) and a green band (550 nm). The relative intensities of two emissions varied with Eu^{2+} concentration. Eu^{2+} and Mn^{2+} co-doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors emit three color lights and present whitish color. The blue (455 nm) and green (550 nm) emissions are attributed to the transitions of Eu^{2+}, while the red (670 nm) emission is originated from the transition of Mn^{2+} ion. The results indicate the energy transfer from Eu^{2+} to Mn^{2+}. The mechanism of the energy transfer is resonance-type energy transfer due to the spectral overlap between the emission of $Eu^{2+}$and the absorption of Mn^{2+}.

Keywords: Luminescence; Energy transfer; Phosphor

1. Introduction

With the development of LED chip, the first white light emitting diodes (W-LEDs) emerged at 1996. W-LEDs have a lot of advantages over the existing incandescent lamp and fluorescent lamp which are the fourth lighting source [1]. W-LEDs can be produced by three general methods. The first method directly mixes red, green and blue (RGB) LEDs. The second is the combination of the yellow-emitting YAG:Ce^{3+} phosphor and blue-emitting GaN chips, which is the most common and commercial ways [2–4]. But this kind of white-lighting blending method exists some problems: white emitting color changing with input power, low color rendering index because of two-color mixing, high color temperature [5–7]. The third way which can avoid these disadvantages uses an ultraviolet (UV) LED to pump a combination of red, green and blue phosphors or a single phased phosphor which emits three color lights in the blue, green and red spectral regions [1,8,9]. The research and development of full-color emitting phosphors for UV chip excitation white LED is of great significance due to their potential applications.

Silicate-based phosphors are most common employed due to their chemical stability, heat endurance, excellent crystallization properties and broad band excitation [5,10]. Eu^{2+} doped orthosilicate phosphors have been extensively used as an alternative to commercially available YAG:Ce^{3+} for color conversion in W-LEDs [11,12]. In some hosts, Mn^{2+} can give luminescence from orange to red originated from the d–d transitions of Mn^{2+} [13,14]. However, the efficiency of Mn^{2+} singly doped phosphors is not very high because the d–d transitions of Mn^{2+} are forbidden transitions. As we know, Eu^{2+} may act as an efficient sensitizer that transfers energy to Mn^{2+} in several hosts. Many efforts have been made to improve the full-color white-lighting phosphors which are based on the mechanism of energy transfer from Eu^{2+} to Mn^{2+} such as $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} [15,16], $CaAl_2Si_2O_8$:Eu^{2+}, Mn^{2+} [13] and $Sr_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} [17].

In this paper, Eu^{2+} and Mn^{2+} doped $Sr_{1.7}Mg_{0.3}SiO_4$:phosphors were prepared by high temperature solid-state reaction method. The luminescence properties and the energy transfer from Eu^{2+} to Mn^{2+} were studied. These phosphors have a broad excitation wavelength in the near UV region and can emit blue, green and red emissions simultaneously.

2. Experimental procedures

The powder samples of $Sr_{1.7}Mg_{0.3}SiO_4$:$x$$Eu^{2+}$($x = 0.005$, 0.01, 0.02, 0.04), and $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $y$$Mn^{2+}$ ($y = 0$,

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0.01, 0.02, 0.03, 0.05, 0.08, 0.1) were prepared by the conventional high temperature solid-state reaction method. Starting materials $SrCO_3$ (AR), $MgCO_3$(AR), SiO_2(AR), $MnCO_3$(AR) and Eu_2O_3 (4 N) were weighed according to the given stoichiometric amounts and mixed thoroughly by grinding in an agate mortar. Then the mixtures were fired at 1250 °C for 4 h in a reduction atmosphere (a mixture of 5% H_2 and 95% N_2).

X-ray powder diffraction (XRD) patterns of the powder samples were obtained by a BRUKER D2 PHASER diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å). The emission and excitation spectra were measured by HORIBA FL3-211-P spectrofluorometer using Xenon lamp as the light source. For lifetime measurement, the emission was analyzed with a 0.25 m Jobin–Yvon monochromator and the signal was detected by a Hammamatsu R636 photomultiplier. All the measurements were performed at room temperature.

3. Results and discussion

The XRD patterns of $Sr_{1.7}Mg_{0.3}SiO_4$:0.01Eu^{2+} and $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, 0.05Mn^{2+} phosphors are shown in Fig. 1. The most host lattices match well with α'-Sr_2SiO_4 (JPCDS No. 39-1256). However, small amount of lattices are in agreement with $Sr_3MgSi_2O_8$ (JCPDS No. 10-0075). In Mn^{2+} and Eu^{2+} co-doped phosphor, the lattice structure does not change dramatically and all the peaks can also be indexed to the phases α'-Sr_2SiO_4 and $Sr_3MgSi_2O_8$, which demonstrate that introduction of Mn^{2+} ions does not lead to the appearance of new phases.

Fig. 2 shows the excitation and emission spectra of Eu^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors. For the emission spectra, the phosphors were excited by 380 nm UV light. The emission spectra consist of two emission bands centered at 455 and 550 nm which both are attributed to the 5d → 4f transition of Eu^{2+}. For the sample with low Eu^{2+} doping concentration, the intensity of 455 nm emission increases with increasing Eu^{2+} concentration until x reaches 0.02 mol, then the intensity of 455 nm emission decreases. For 550 nm emission band, the emission intensity varies slightly with increasing Eu^{2+} concentration. When Eu^{2+} concentration reaches 0.04 mol, the 550 nm emission band almost disappears. The excitation spectra monitored at 455 nm are a broad band from 300 nm to 410 nm with peak position located at 350 nm, which is ascribed to the 4f → 5d transition of Eu^{2+} ion substituted Sr^{2+}(I) site. The excitation spectra monitored at 550 nm are also a broad band from 300 nm to 500 nm with the excitation peak located at 380 nm, which is ascribed to the 4f → 5d transition of Eu^{2+} ion on Sr^{2+}(II) site [17]. However, the excitation intensity of the latter is much weaker. Under UV light excitation, Eu^{2+} doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors emit from bluish green light to nearly pure blue light with increasing Eu^{2+} doping concentration.

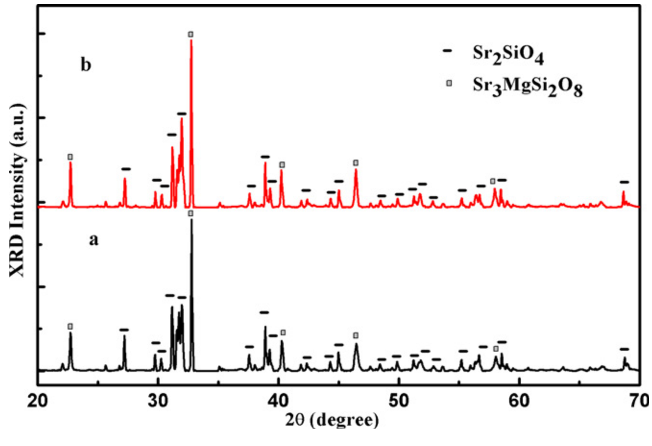

Fig. 1. X-ray diffraction patterns of Eu^{2+}, Mn^{2+} doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors (a: $Sr_{1.7}Mg_{0.3}SiO_4$:0.01Eu^{2+}; b: $Sr_{1.7}Mg_{0.4}SiO_4$:0.02Eu^{2+}, 0.05Mn^{2+}).

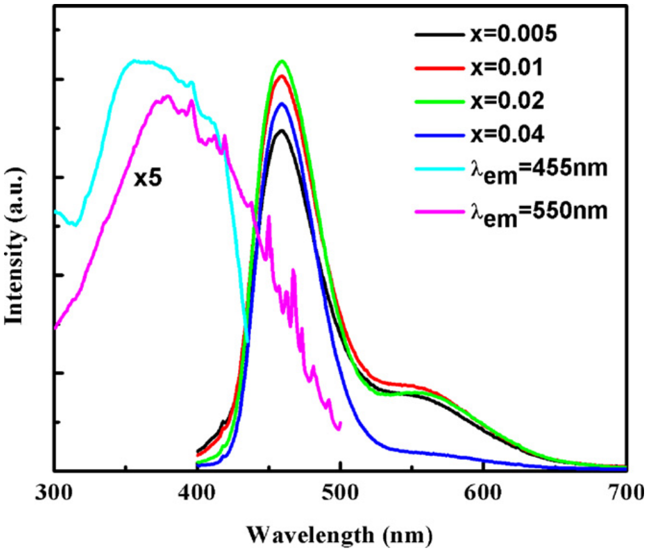

Fig. 2. Emission spectra of $Sr_{1.7}M_{0.3}SiO_4$:$x$$Eu^{2+}$ phosphors excited by 380 nm and excitation spectra of $Sr_{1.7}M_{0.3}SiO_4$:0.02Eu^{2+} phosphor monitored at 455 and 550 nm (x5).

For Mn^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ powder samples, the emission is too weak to be recorded under UV light excitation.

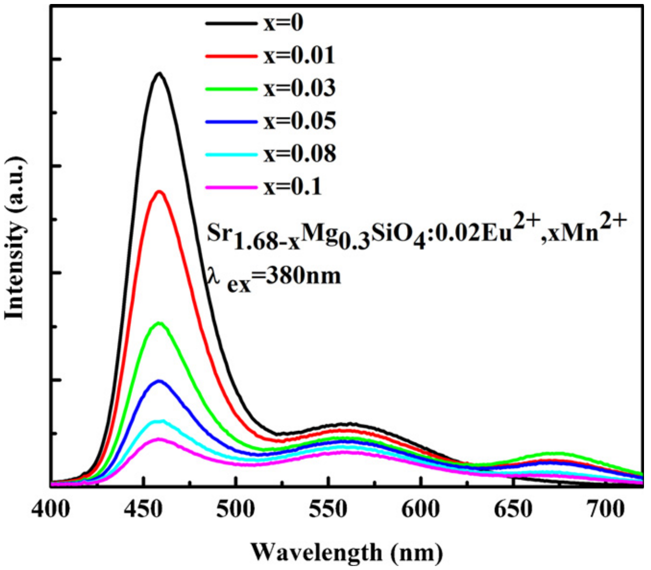

Fig. 3. Emission spectra of $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$ (x = 0.01, 0.02, 0.03, 0.05, 0.08, 0.1) phosphors excited by 380 nm light.

The reason could be attributed to the very weak absorption of Mn^{2+} in the UV region since the 3d spin forbidden transition of Mn^{2+}.

Fig. 3 shows the emission spectra for Eu^{2+} and Mn^{2+}-codoped $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $y$$Mn^{2+}$ ($y = 0.01, 0.02, 0.03, 0.05, 0.08, 0.1$) phosphors excited by 380 nm light. For comparison, the emission spectra of Eu^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphor are also shown in Fig. 3. For Eu^{2+} and Mn^{2+}-codoped phosphors, we observe three emission bands peak at 455, 550 and 670 nm. The 455 and 550 nm emission bands are attributed to 5d–4f transition of Eu^{2+} ions substituted two different Sr^{2+} sites. The 670 nm emission band originates from ^4T–^6A transition of Mn^{2+} ion on Sr^{2+} site [17]. With increasing Mn^{2+} doping concentration, 455 nm emission from Eu^{2+} decreases remarkably, while 550 nm emission of Eu^{2+} decreases slightly and 670 nm emission of Mn^{2+} increases slightly. As above mentioned, Mn^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ powder samples do not emit light under UV light excitation. Therefore, in Eu^{2+} and Mn^{2+}-codoped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors, energy transfer from Eu^{2+} to Mn^{2+} must exist. And from the emission spectra, the energy transfer is mainly from Eu^{2+} substituted Sr^{2+} to Mn^{2+}.

Fig. 4 shows the excitation spectra monitored at 455, 550 and 670 nm and the emission spectra for Eu^{2+} and Mn^{2+} co-doped $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, 0.05Mn^{2+} phosphor excited by 380 nm light. All excitation spectra monitored at 455, 550 and 670 nm show broad bands from 340 nm to 410 nm which match well with the commercial UV LED chip. The excitation peaks center at 350, 380, and 380 nm for the spectra monitored at 455, 550 and 670 nm, respectively. The excitation intensity monitored at 455 nm is much stronger than those monitored at 550 nm (2.5 times) and 670 nm (4 times). The results are consistent with the emission spectra and indicate that the 670 nm emission of Mn^{2+} could be attributed to the energy transfer from Eu^{2+}. Fig. 4 also shows that there is a spectral overlap between the 455 nm emission of Eu^{2+} and the excitation spectra monitored at 670 nm of Mn^{2+}. The result indicates that the energy transfer is resonance-type energy transfer. According to Dexter's theory [8], the energy transfer rate is proportional to the spectral overlap between the energy donor emission and the energy acceptor absorption. Since the overlap between the emission band 455 nm of Eu^{2+} and the excitation spectra monitored at 670 nm of Mn^{2+} is small, the energy transfer rate is not large.

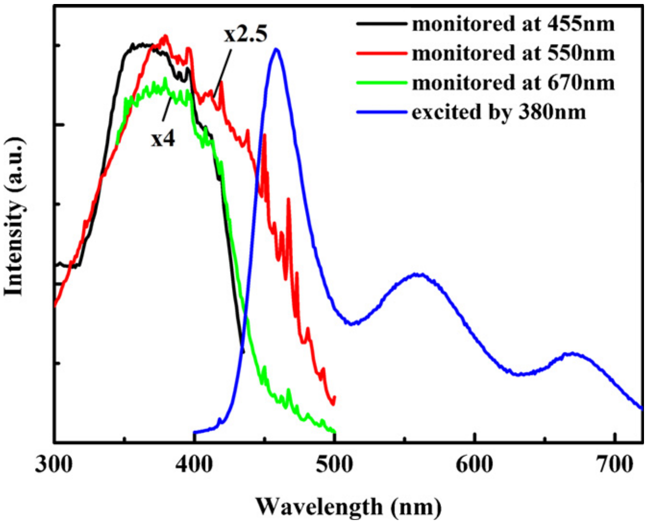

Fig. 4. Excitation spectra monitored at 455, 550 (x2.5) and 670 nm (x4) and emission spectra of $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, 0.05Mn^{2+} phosphor excited by 380 nm.

The decay curves of 455 nm emission from Eu^{2+} in $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$ ($x = 0.01$, 0.02, 0.03, 0.05, 0.08, 0.1) phosphors are shown in Fig. 5. It is found that the decay curves are mono-exponential. The lifetime of the 455 nm emission determined by the least-squares fitting of the decay curves with a mono-exponential function decreases with increasing Mn^{2+} doping concentration, which is a strong evidence for the energy transfer from Eu^{2+} to Mn^{2+}. We also investigate the energy transfer efficiency (η) of $Eu^{2+} \rightarrow Mn^{2+}$. As reported by Paulose et al. [18]. η can be expressed by

$$\eta = 1 - \frac{\tau_s}{\tau_0} \tag{1}$$

where τ_0 is the intrinsic decay time of the sensitizer (Eu^{2+}) and τ_s is the decay time of the sensitizer (Eu^{2+}) in the presence of the activator (Mn^{2+}). The energy transfer efficiencies for $Eu^{2+} \rightarrow Mn^{2+}$ in $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $y$$Mn^{2+}$ ($y = 0.01$, 0.02, 0.03, 0.05, 0.08, 0.1) are calculated and illustrated in Fig. 5(inset). With increasing Mn^{2+} concentration, the energy transfer efficiency η increases monotonically with increasing Mn^{2+} doping concentration.

Since the weak intensities of green (550 nm) and red (670 nm) emissions and the strong intensities of blue (455 nm) emission, the color rendering index (CRI) coordinates of Eu^{2+} and Mn^{2+} co-doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors are close to the white region. Fig. 6 indicates the variation of CIE chromaticity coordinates for $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$ ($x = 0$, 0.01, 0.03, 0.05, 0.08, 0.1) phosphors. With increasing Mn^{2+} concentration, the CIE chromaticity coordinates are moved to the white region. The colors of the $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+},

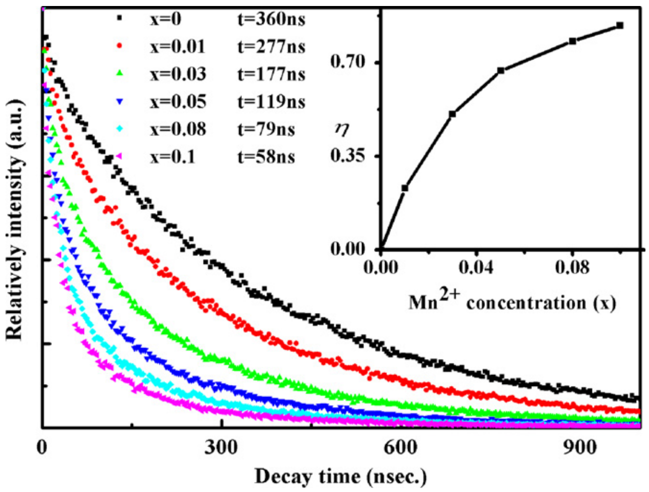

Fig. 5. Decay curves of 455 nm emission bands of $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$; Inset: dependence of the energy transfer efficiency of η in $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$ on concentration x.

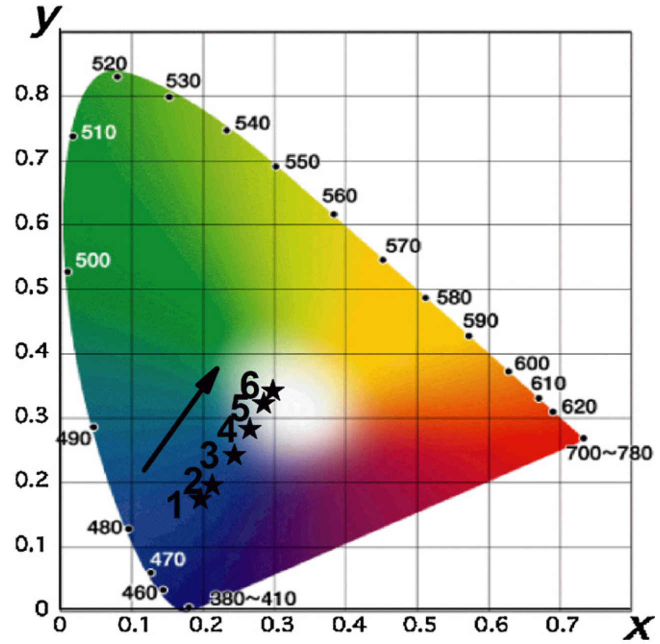

Fig. 6. CIE chromaticity diagram for $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, $x$$Mn^{2+}$ ($x = 0$, 0.01, 0.03, 0.05, 0.08, 0.1) phosphors with variation Mn^{2+} doping concentration excited by 380 nm light.

0.08Mn^{2+} and $Sr_{1.7}Mg_{0.3}SiO_4$:0.02Eu^{2+}, 0.1Mn^{2+} phosphors present whitish color. The white color of these phosphors is originated from the combination of blue, yellow and red emission bands. The results indicate that these phosphors have potential as phosphor candidates used for white LEDs pumped by UV chip.

4. Conclusions

In summary, Eu^{2+}, Mn^{2+} doped $Sr_{1.7}M_{0.3}SiO_4$ phosphors were prepared by high temperature solid-state reaction method. Their luminescence properties were studied. The emission spectra of Eu^{2+} singly doped $Sr_{1.7}Mg_{0.3}SiO_4$ consist of a blue band (455 nm) and a green band (550 nm). The relative intensities of two emissions varied with Eu^{2+} concentration. Eu^{2+} and Mn^{2+} co-doped $Sr_{1.7}Mg_{0.3}SiO_4$ phosphors emit three color lights and present whitish color. The blue (455 nm) and green (550 nm) emissions are attributed to the transitions of Eu^{2+}, while the red (670 nm) emission is originated from the transition of Mn^{2+} ion. The results indicate the energy transfer from Eu^{2+} to Mn^{2+}. The mechanism of the energy transfer is resonance-type energy transfer due to the spectra overlap between the emission of Eu^{2+} and the absorption of Mn^{2+}. The results also indicate that these phosphors have potential as phosphor candidates used for white LEDs pumped by UV chip.

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