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Luminescence Properties of Eu^{2+} and Mn^{2+} Doped Sr_2MgSiO_5 Phosphors

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Abstract

Eu^{2+} ions doped Sr_2MgSiO_5 phosphors, and Eu^{2+}- Mn^{2+} ions-doped Sr_2MgSiO_5 phosphors were prepared via high-temperature solid state reaction method and sol-gel process, respectively. Luminescent mechanism and characteristics of all samples were studied. The results showed that lattice structure of Eu^{2+} ion-doped Sr_2MgSiO_5 samples was pyramidal system. The influence of flux on luminescence properties of Eu^{2+} ion-doped Sr_2MgSiO_5 phosphor was studied. The results of spectral analysis showed that flux changed the emission intensity of Sr_2MgSiO_5: Eu^{2+} samples at different wavelengths. Emission wavelength and relative intensity of the samples changed. In order to study the luminescence properties and energy transfer between Eu^{2+} and Mn^{2+}, Eu^{2+} ions and Mn^{2+} ions co-doped samples were prepared. The results showed that excitation bands of the samples ranged from 250nm to 450 nm. When excited at 365nm, the emission spectrum of the samples consisted of three bands: blue, green and red, respectively. When Eu^{2+} ions and Mn^{2+} ions co-doped, the energy of Eu^{2+} ions was transferred to Mn^{2+} ions, which made Mn^{2+} ions became luminescence center in Sr_2MgSiO_5 host.

Keywords: *Sr_2MgSiO_5 phosphor, Eu^{2+}, Mn^{2+}*

1. Introduction

Nowadays science and technology are developing faster and faster but human need better technologies. For example if people want to save energy of a building, they can find a way to control the temperature [1] or control the light system of this building [2] or they can invent a new way of lighting. Recently, white light emitting diodes (white LEDs) have received lots of attention in solid state lighting, because they have a number of advantages over the existing incandescent and halogen lamps in power efficiency, reliability, and long lifetime compared with conventional lighting techniques [3]. Thus, it seems that white LEDs show high potential for replacement of conventional lighting sources like incandescent and fluorescent lamps. At present, commercial white LEDs are realized by using two or three kinds of phosphors excited by blue or ultraviolet (UV) LED chips [4, 5]. However, white LEDs realized by the blue GaN-pumped yellow YAG: Ce^{3+} phosphor have the following problems: changing color with input power, low color rendering index (CRI) due to two color mixing, and low reproducibility due to the strong dependence of color quality on the quantity of phosphor. To solve these problems, the white LED has been fabricated by employing blue, green, and red emitting multiphase phosphors excited by a UV InGaN chip [6-9]. This type of white LED has the following advantages: high color tolerance to the UV chip's variation and excellent color rendering index due to the white color generated by phosphors.

In this paper, a kind of phosphor , Sr_2MgSiO_5:Eu^{2+}, Mn^{2+} phosphor, was synthesized by the sol-gel method and high temperature solid-state reaction method.

2. Research Method

High-temperature solid state reaction. The Sr_2MgSiO_5:Eu^{2+} , Mn^{2+} powder samples with different doping concentrations were prepared via a high-temperature solid state reaction using $SrCO_3$(4N), $MgCO_3$(AR), SiO_2(4N), Eu_2O_3(4N) and $MnCO_3$ as raw materials. The raw

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materials were mixed and then sintered at 1,350°C for 4h a reducing atmosphere (toner) in an electric furnace [10-12].The flux-doped Sr_2MgSiO_5:Eu^{2+} , Mn^{2+} phosphors were prepared. The fluxes were NH_4Cl, Na_2CO_3, H_3BO_3, NaF, BaF_2. The optimum doping concentration and optimum flux were obtained by a high temperature solid-state reaction method. The reaction equations were as follow:

$$SrCO_3 \rightarrow SrO+CO_2 \quad (1)$$

$$2SrO+MgO+2SiO_2 \rightarrow Sr_2MgSiO_5+2CO_2 \quad (2)$$

$$CO_2+C \rightarrow 2CO \quad (3)$$

$$Eu_2O_3+2\ Sr_2MgSiO_5+3CO \rightarrow 2\ Sr_2MgSiO_5{:}\ Eu^{2+}+3CO_2 \quad (4)$$

$$MnCO_3 \rightarrow MnO+CO_2 \quad (5)$$

Sol-gel method. The powder optimum doping concentration phosphors were prepared by the sol-gel method. $Sr(NO_3)_2$(99.99%), $Mg(NO_3)_2 \cdot 6H_2O$(99.99%), $Mn(NO_3)_2 \cdot 6H_2O$(99.99%), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%), $CH_3CH_2OSi(OCH_2CH_3)_3$ (TEOS) and C_2H_5OH were employed as raw materials. The experimental procedure is as follows. TEOS, C_2H_5OH and deionized water were mixed according to the ratio of 2:2:1 under stirring at pH 2–3 and a 60ºC water bath for 15 min until we obtained SiO_2 sol. $Sr(NO_3)_2$ (99.99%), $Mg(NO_3)_2 \cdot 6H_2O$(99.99%), $Mn(NO_3)_2 \cdot 6H_2O$(99.99%), and $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%) measured by the molar ratio were introduced into deionized water under stirring. When the nitrate compounds had completely dissolved in the solution, we added it into the SiO_2 sol and kept stirring 3–5 h in the water bath until a transparent gelatin was generated. The gelatin was dried and put in the vacuum drying oven for 16 h at 80ºC, and the dried gel was obtained. The dried gel was put into the an electric furnace to sinter in the atmosphere of the carbon reduction at 1,150°C for 3h, and the sample was synthesized.

3. Results and Analysis

The final phase was checked with a conventional X-ray diffraction (XRD) technique. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature with a Hitachi F-4500 fluorescence spectrophotometer.

3.1.The XRD Analysis of Sr_2MgSiO_5: Eu^{2+} Sample

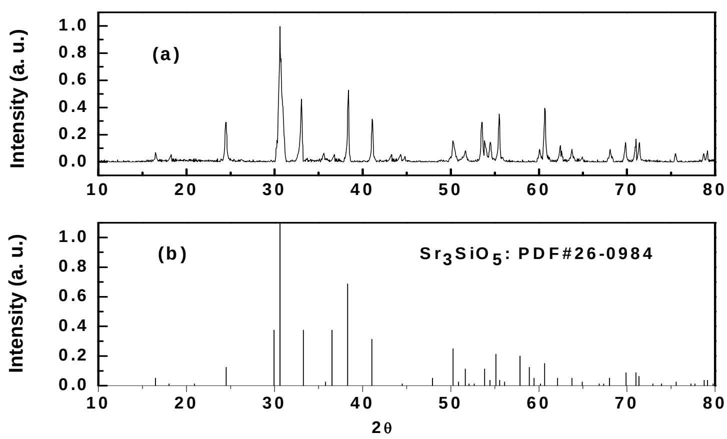


Figure 1. X-ray Diffraction (XRD) Patterns of Sr_2MgSiO_5 Samples (a) and PDF Card of Sr_3SiO_5 Samples (b)

Figure 1 shows the XRD spectra of Sr_2MgSiO_5:Eu^{2+} phosphors synthesized via high temperature solid-state reaction method. The spectra were measured in the 2θ range of 10–80° with a RigakuD/MaxIIIB using Cu K α radiation.It can be seen from Figure 1 that the peaks of Sr_2MgSiO_5:Eu^{2+} sample agreed with that of Sr_3SiO_5 (PDF No. 26-0984), which indicates that Mg^{2+} in the lattice replaced Sr^{2+} in the lattice of Sr_3SiO_5 so that form a crystal structure of Sr_2MgSiO_5. Phase analysis result showed that lattice structure of Eu^{2+} ion-doped Sr_2MgSiO_5 samples was pyramidal system, and incorporation of Eu^{2+} samples did not affect the single-phase structure.

3.2. Spectral Analysis of Sr_2MgSiO_5: Eu^{2+} Samples

Figure 2(a) shows the emission spectra of Sr_2MgSiO_5: xEu^{2+} phosphors synthesized using the high temperature solid-state reaction method. The optimum doping concentration was obtained by this method. The results show that Sr_2MgSiO_5: xEu^{2+} phosphors have blue (470nm) and green (530nm) emission bands, which is ascribed to the typical 5d-4f transitions of Eu^{2+}. The maximum luminescence intensity is obtained when the x value at 3%. Figure 2 (b) gives the excitation spectra of the sample, and the optimal excitation wavelength is 365nm.

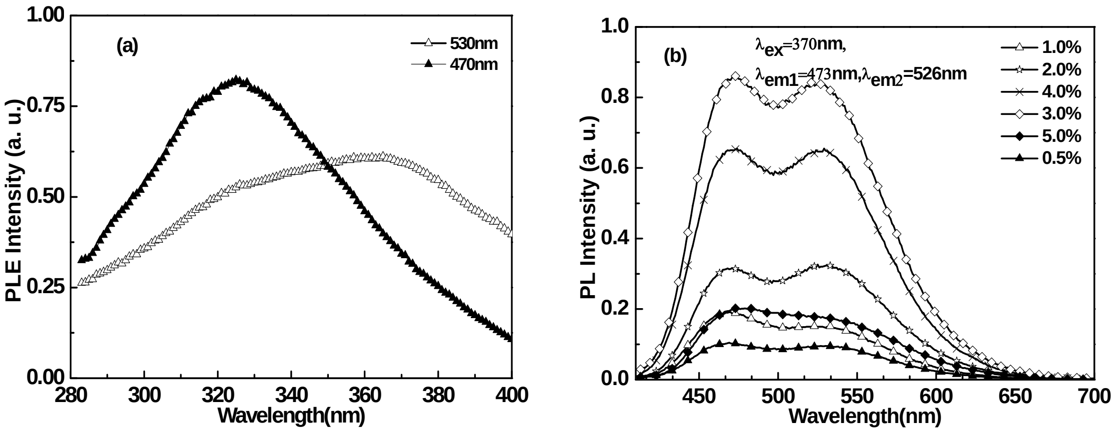


Figure 2. Excitation Spectra (a) and Emission Spectra with Different Eu^{2+} Concentration (b) of Sr_2MgSiO_5: Eu^{2+} Sample

3.3. The Influence of Flux on Luminescence Properties of Sr_2MgSiO_5: Eu^{2+} Sample

Figure 3 shows the effects of light flux on Sr_2MgSiO_5: Eu^{2+} samples. It can be seen: Na_2CO_3, H_3BO_3 and NaF to promote the emission of blue light, while suppressing a yellow and green emission while NH_4Cl and BaF_2 enhanced the emission of yellow and green light.

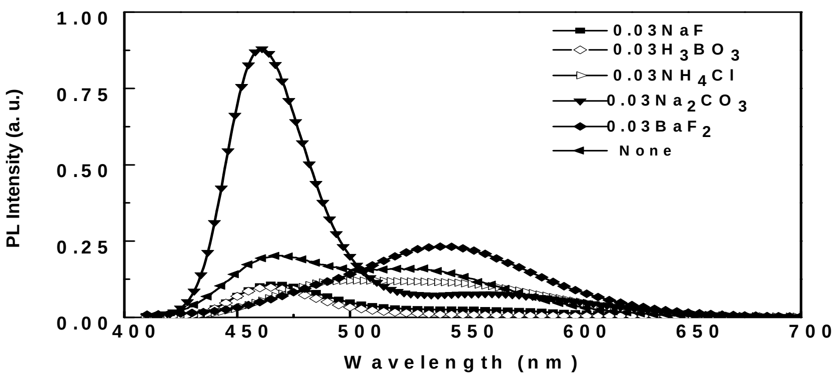


Figure 3. Emission Spectra of Sr_2MgSiO_5: Eu^{2+} Samples with Different Fluxes

3.4. The XRD Analysis of Sr_2MgSiO_5: Eu^{2+}, Mn^{2+}

Figure 4 is the XRD patterns of Sr_2MgSiO_5: Eu^{2+}, Mn^{2+}. The XRD patterns of samples included in the main diffraction peaks of Sr_3SiO_5 which indicates that Mg^{2+} in the lattice replaced Sr^{2+} in the lattice of Sr_3SiO_5, so that form a crystal structure of Sr_2MgSiO_5. In addition, the diffraction peaks of Sr_2SiO_4 were found in the XRD patterns (PDF No. 39-1256).

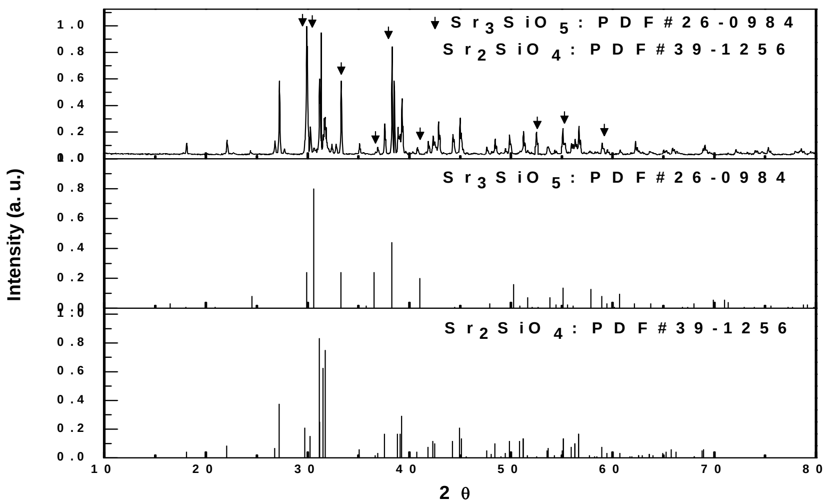
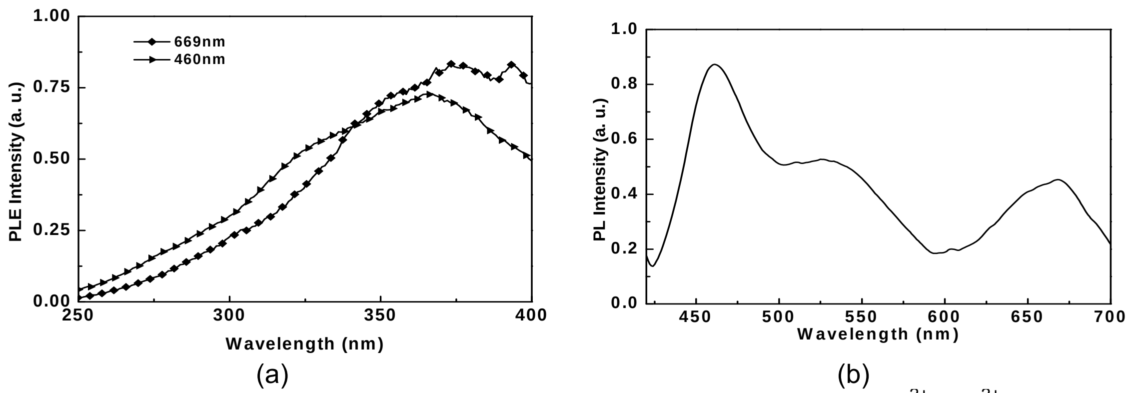


Figure 4. XRD Patterns of Sr_2MgSiO_5 Samples

3.5. Spectral Analysis of Sr_2MgSiO_5: Eu^{2+}, Mn^{2+} Samples

Figure 5 shows the excitation spectra (a) and emission spectra (b) of Sr_2MgSiO_5: Eu^{2+}, Mn^{2+} sample synthesized by sol-gel method. The emission spectra of the sol-gel method-synthesized Sr_2MgSiO_5: Eu^{2+}, Mn^{2+} phosphors has blue (460nm), green (533nm), and red (669nm) emission bands. The red emission band is attributed to the energy transfer from Eu^{2+} to Mn^{2+}. White light could be obtained by mixing the three emission color.

When Eu^{2+} ions and Mn^{2+} ions co-doped Sr_2MgSiO_5 phosphors were excited by the 365nm UV irradiation, the emission spectra samples contained the characteristic emission of Mn^{2+} ions, which is due to energy transfer between Eu^{2+} and Mn^{2+} in Sr_2MgSiO_5 host. In the near-UV irradiation, the electrons in the ground level of Eu^{2+} ions, that was $4f^7$, were excited to $4f^65d^1$ energy level then the electrons soon relax to the lowest energy level of 5d configuration in the way of idler transition. $4f^65d^1 \rightarrow 4f^7$ emission wavelength of Eu^{2+} ions closed to the absorption wavelengths of Mn^{2+} ions, these wavelengths were overlapped, which easily caused the cross-relaxation phenomenon between Eu^{2+} ions and Mn^{2+} ions and then energy transfer generated tow ions.



(a) (b)

Figure 5. Excitation Spectra (a) and Emission Spectra (b) of Sr_2MgSiO_5: Eu^{2+}, Mn^{2+} Sample

4. Conclusion

The Sr_2MgSiO_5: xEu^{2+} phosphors prepared via high-temperature solid state reaction method have blue (470nm) and green (530nm) emission bands. Fluxes (Na_2CO_3, H_3BO_3, NaF, NH_4Cl and BaF_2) changed the emission intensity of Sr_2MgSiO_5: Eu^{2+} samples at different wavelengths. Emission wavelength and relative intensity of the samples changed. Na_2CO_3 and BaF_2 caused the greatest change. The Sr_2MgSiO_5: Eu^{2+}, Mn^{2+} phosphors synthesized by the sol-gel method have three emission bands: the blue (460nm), the green (533nm), and the red (669nm) when excited at 365nm. When Eu^{2+} ions and Mn^{2+} ions co-doped, the energy of Eu^{2+} ions was transferred to Mn^{2+} ions, which made Mn^{2+} ions became luminescence center in Sr_2MgSiO_5 host.

Acknowledgements

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