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Effects of Bi^{3+} Concentration on Luminescent Properties of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ Phosphor

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Abstract: Blue luminescent $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},x\text{Bi}^{3+}$ ($x=0,0.02,0.04,0.06,0.08,0.1$) powder phosphors have been successfully synthesized by sol-gel method. Their structure and luminescent properties were analyzed by XRD, DTA-TG, and PL spectra. Emission spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Bi}^{3+}$ powder phosphors with $\lambda_{\text{ex}}=286\text{ nm}$ ($^3\text{P}_1\rightarrow^1\text{S}_0$) and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},x\text{Bi}^{3+}$ ($x=0,0.02,0.04,0.06,0.08,0.1$) phosphors with $\lambda_{\text{ex}}=358\text{ nm}$ ($4f^65d^1\rightarrow4f^7$) have been analyzed. Based on the emission performance of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},x\text{Bi}^{3+}$, the optimized Bi^{3+} mole fraction is 0.04. The luminescent intensity of the phosphor increases up to 1.9 times than that of phosphors without doping Bi^{3+} , which due to the sensitization of Bi^{3+} to Eu^{2+} .

Key words: Bi^{3+} ; $\text{Sr}_2\text{MgSi}_2\text{O}_7$; sol-gel method; blue luminescence

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Bi^{3+} 掺杂对 $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ 荧光粉的结构及发光性能的影响

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摘要: 采用溶胶-凝胶法在还原气氛下制备了 $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},x\text{Bi}^{3+}$ ($x=0,0.02,0.04,0.06,0.08,0.1$) 荧光粉,并用 XRD、TG-DTA 及激发与发射谱仪对样品的结构及发光性能进行了表征。结果发现:单掺杂 Bi^{3+} 的 $\text{Sr}_2\text{MgSi}_2\text{O}_7$ 样品的发射光谱所用的材料的激发光谱为一主峰为 286 nm 的宽带谱,这是由于激发态时 Bi^{3+} 的 $^3\text{P}_1\rightarrow^1\text{S}_0$ 电子能级跃迁而造成的;单掺杂 Eu^{2+} 的 $\text{Sr}_2\text{MgSi}_2\text{O}_7$ 样品的发射光谱所用的材料的激发光谱为一主峰为 358 nm 的宽带谱,这是典型的 Eu^{2+} 的 $4f^65d^1\rightarrow4f^7$ 跃迁而引起的。当 Bi^{3+} 离子掺杂到 $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ 样品的摩尔分数为 0.04 时,样品的发射强度是未掺杂 Bi^{3+} 离子样品的 1.9 倍。

关键词: Bi^{3+} ; $\text{Sr}_2\text{MgSi}_2\text{O}_7$; 溶胶-凝胶法; 发光

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1 Introduction

In recent years, alkaline earth silicate system has attracted much attention and become an interesting topic in the field of wide excitation band of luminescent materials because of their high chemical stability, water-resistant property, low cost and easy facility. However, most of the attention has been paid to those phosphors based on after-glow property luminescent materials^[1-3]. There are few researches on Sr₂MgSi₂O₇ phosphors with doping other elements.

The spectroscopy of Bi³⁺ ion, which has the 6s² electronic configuration, has been investigated extensively in a variety of host lattice^[4-6]. It is well known that the Bi³⁺ ion is usually used not only as an activator but also a sensitizer of luminescence^[7-10]. In this paper, the phosphor Sr₂MgSi₂O₇: Eu²⁺, Bi³⁺ is synthesized by sol-gel method. The crystal structure and luminescence properties of phosphor are studied.

2 Experiments

Sr₂MgSi₂O₇: Eu²⁺, Bi³⁺ powders were prepared by the sol-gel process using SrCO₃ (A. R.), Mg(NO₃)₂ · 6H₂O (A. R.), Eu₂O₃ (99.99%), Bi₂O₃ (99.99%), nitric acid (GR), TEOS as starting materials, and alcohol was used as dispersing agent, a small amount of NaF was added into the raw materials as the flux. All starting raw materials were weighed in the proper stoichiometry. First, high-purity Eu₂O₃, Bi₂O₃ and SrCO₃ (A. R.) are dissolved in nitric acid, and then ammonia water was slowly dropped into the mixed solution until the pH value of the final solution is 1 ~ 2. Besides, the solution was heated to 35 °C and stirred constantly for 0.5 h, meanwhile adding TEOS and alcohol as dispersing agent. After stirring, the mixed solution was heated to 80 °C for 10 h in heated thermostatic water bath until it transformed into transparent sticky gel. And it was heated to 140 °C for 10 h in drying tunnel. Finally, it was put into electric furnace firing for 0.5 h at 350 °C, and the mixture was taken out and mixed with a small amount of NaF flux. The precursors were then calcined at various temperature from 700 °C to 1 000

°C for 3 h in reducing atmosphere.

Thermo gravimetric analysis (TG) coupled with differential thermal analysis (DTA) were conducted (PerkinElmer), using a sample weight of about 10 mg and a heating rate of 20 °C/min in air atmosphere. The X-ray diffraction patterns of the samples were recorded using Bruker D-8 mode XRD DI System (Cu Kα radiation, 40 kV, 30 mA, λ = 0.154 178 nm). Photoluminescence excitation and emission spectra of all the phosphors were measured by using Hitachi F-4500 fluorescence spectrophotometer with a 400 V photomultiplier tube and a 150 W xenon lamp. All the measurements were carried out at room temperature.

3 Results and Analysis

3.1 TG-DTA Analysis

To understand its pyrolysis behavior and crystallization process, the TG-DTA curves of the Sr₂MgSi₂O₇: Eu²⁺, Bi³⁺ complex precursor are studied, as shown in Fig. 1. As it can be seen, the weight loss of the precursor occurs with the increase of temperature from room temperature to 650 °C. This decomposable process can be separated into two parts: the first weight loss section occur under 200 °C, which is ascribed to the removed of the surface incidental water, deionized water molecule and alcohol molecule. There is a very strong absorption peak at around 150 °C from DTA curve corresponding to the first section. The second weight loss section mainly occurs from 200 °C to 650 °C, and there are several absorption peaks in DTA curve corresponding to the second section, which is ascribed to the removal of crystal water, expelling from ammoniac, resolution of excessive nitric acid and nitrate. With rising temperature, no absorption peak occurs on the TG curve, which indicates that the crystalline phase of the sample had already been formed basically after 650 °C. Further comparing curve 1 with curve 2 of TG in Fig. 1, it can be seen that the lost weight of precursor with doping Bi³⁺ is less than that of without doping Bi³⁺. From corresponding DTA curve, we can see that the absorption peaks in precursor doping with Bi³⁺ are smaller than those of no doping

Bi^{3+} before 600 °C. Moreover, the precursor doping with Bi^{3+} has two different absorption peaks while the precursor without doping Bi^{3+} has one absorption peak after 600 °C, mainly due to the resolution of nitrate of bismuth.

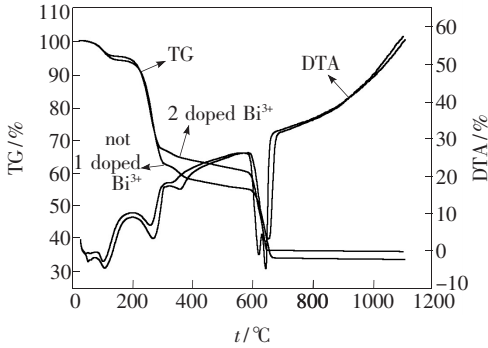


Fig. 1 Combined TG-DTA curves of the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, Bi^{3+} precursors in following air.

3.2 XRD Analysis

In order to further analyze the crystalline phase of sample, Fig. 2 shows the X-ray diffraction (XRD) patterns of the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, Bi^{3+} phosphor obtained by calcining the precursor for 3 h at different temperature. At 700 °C, the characteristic peaks of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phases were rather weak, in which some new peaks which don't correspond to $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phases. At 800 °C, the characteristic peaks of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phases grow, while the new peaks reduce, which indicates that $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phases mostly form at this temperature. At 900 ~ 1 000 °C, the characteristic peaks of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ phases increase and the new phases continue to reduce which was in accordance with a tetragonal crystal structure in JCPDS card (no. 75-1736) with $P-421m$ (113) space group and lattice parameters of the matrix at $a = 0.7996 \text{ nm}$, $b = 0.7996 \text{ nm}$, $c = 0.5152 \text{ nm}$.

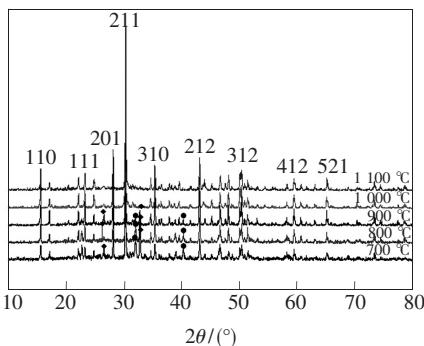


Fig. 2 XRD patterns of precursor and powders calcined at various temperatures

It indicates that crystalline structure of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ grows with the increase of calcining temperature. When the Eu^{2+} and Bi^{3+} ions are doped in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host, no difference is observed between $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Bi}^{3+}$, which indicates that Eu^{2+} , Bi^{3+} ions replace Sr^{2+} ion in crystalline of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ sample.

3.3 Effects of Bi^{3+} Doping in $\text{Sr}_2\text{MgSi}_2\text{O}_7:0.05\text{Eu}^{2+}$

Fig. 3 shows the excitation spectra and emission spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:0.05\text{Eu}^{2+}$ sample in different Bi^{3+} doping concentration. As can be seen, there is no excitation and emission peak of Bi^{3+} in $\text{Sr}_2\text{MgSi}_2\text{O}_7:0.05\text{Eu}^{2+}, x\text{Bi}^{3+}$ ($x = 0.02, 0.04, 0.06, 0.08, 0.1$) sample. However, the luminescent intensities of the samples change with Bi^{3+} concentration. It indicates that the increasing luminescent intensity of sample is due to the energy transfer from Bi^{3+} to Eu^{2+} . When $x = 0.04$, the luminescent intensity of phosphor increases up to 1.9 times than that of phosphor without doping Bi^{3+} . But exceeding this concentration level, the luminescent intensity gradually decreases with the Bi^{3+} concentration, which is accordance with the principle of concentration quenching. Because the increase of Bi^{3+} concentration will enhance the interaction of $\text{Eu}^{2+}-\text{Eu}^{2+}$ as activator and lead to the increase in radiationless transition, thus the luminous efficiency declines.

In order to analyze the sensitization effect of Eu^{2+} to Bi^{3+} , Fig. 4 shows the excitation spectrum

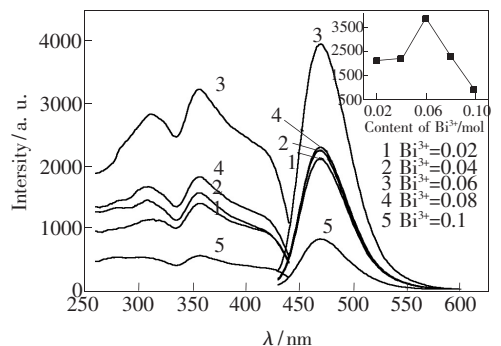


Fig. 3 Excitation spectra(left) and emission spectra(right) corresponding to different Bi^{3+} concentrations ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$), keeping Eu^{2+} concentration unchanged ($x(\text{Eu}^{2+}) = 0.05$). The inset shows the dependence of luminescent intensity of Bi^{3+} on its doping concentration.

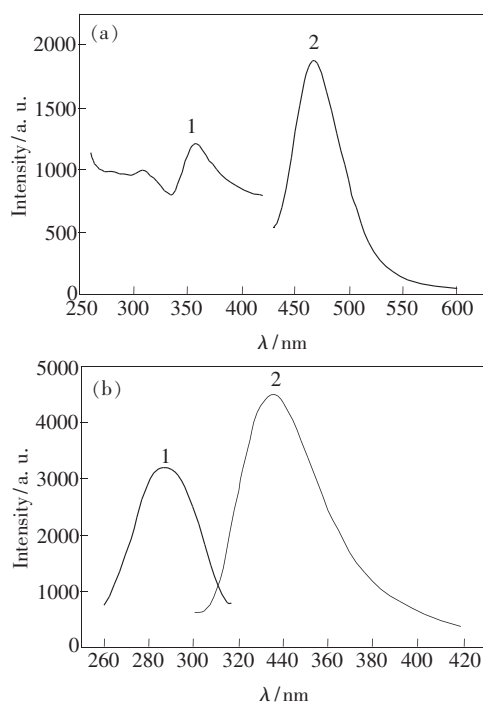


Fig. 4 The excitation spectrum (1) and emission spectrum (2) of Sr₂MgSi₂O₇ samples with only doping of Eu²⁺ (a) and Bi³⁺ (b)

and emission spectrum of Sr₂MgSi₂O₇ samples with only doping of Eu²⁺ (a) and Bi³⁺ (b), respectively. From Fig. 4, it can be seen that the excitation spectrum of Sr₂MgSi₂O₇: Bi³⁺ sample exhibits a wide

band centered at 286 nm, and the excitation spectrum for 286 nm emission has a wide band from 300 nm to 420 nm which peaking at 335 nm. This can be ascribed to the transition from ground state ³P₁ to excited state ¹S₀ of Bi³⁺. The wide band of emission spectrum overlaps excitation peak centered of 358 nm (4f⁶5d¹→4f⁷) of Sr₂MgSi₂O₇: Eu²⁺ sample.

4 Conclusions

In summary, a series of Sr₂MgSi₂O₇: 0.05Eu²⁺, xBi³⁺ (x = 0, 0.02, 0.04, 0.06, 0.08, 0.1) blue phosphors were synthesized using sol-gel method. The luminescence properties of Bi³⁺ and Eu²⁺, and the energy transfer from Bi³⁺ to Eu²⁺ were investigated through the measurement of XRD, DTA-TG, and PL spectra. Bi³⁺ in Sr₂MgSi₂O₇ emits one broad band peaking at 335 nm, which is attributed to the transition from excited state ³P₁ to ground state ¹S₀. Eu²⁺ in Sr₂MgSi₂O₇ emits one broad band peaking at 470 nm, which is attributed to the transition from excited state 4f⁶5d¹ to ground state 4f⁷. The co-doping Bi³⁺ into Eu²⁺ doped Sr₂MgSi₂O₇ increases the luminescent intensity of Eu²⁺ by 1.9 times due to the sensitizing of Bi³⁺ to Eu²⁺.

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