绿色荧光粉 Ca₃Y₂Si₃O₁₂:Tb³⁺,Ce³⁺的制备及发光特性

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摘要：采用高温固相法合成了绿色荧光粉 $Ca_3Y_2Si_3O_{12}$:Tb³⁺。XRD 检测结果显示,荧光粉主晶相为 $Ca_3Y_2Si_3O_{12}$,属单斜晶系。荧光光谱分析表明：$Ca_3Y_2Si_3O_{12}$:Tb³⁺硅酸盐荧光粉可以被 370 nm 的近紫外光激发,发射绿光,主发射峰位于 490 nm($^5D_4{\rightarrow}^7F_6$),544 nm($^5D_4{\rightarrow}^7F_5$),585 nm($^5D_4{\rightarrow}^7F_4$)和 621 nm($^5D_4{\rightarrow}^7F_3$)。用 544 nm 最强峰监测,得到主激发峰位于 370 nm 的激发光谱,此光谱覆盖了 300~450 nm 的波长范围。研究了煅烧条件、掺杂浓度及 Ce³⁺共掺杂对荧光粉发光性能的影响；在 1 400 ℃下经二次煅烧 6 h 得到的样品的发光性能最佳,Tb³⁺离子的最佳掺杂浓度为 20mol%,Ce³⁺离子共掺杂能够提高荧光粉的发光强度,其最佳掺杂量为 4mol%,说明存在 Ce³⁺→Tb³⁺的能量传递。

关键词：发光；掺杂；固相反应；绿色荧光粉

Preparation and Luminescence Properties of Green Phosphors Ca₃Y₂Si₃O₁₂:Tb³⁺, Ce³⁺

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Abstract: The green-emitting $Ca_3Y_{2-x-y}Si_3O_{12}$:xTb³⁺, yCe³⁺ silicate phosphors were synthesized by a high temperature solid-state method. The principal crystalline of the samples is $Ca_3Y_2Si_3O_{12}$, which is belonging to the monoclinic system. All the phosphors can be effectively excited in the range of 300 nm to 450 nm, and emit green light. Excited by 370 nm, the emission peaks mainly locate at 490 nm ($^5D_4{\rightarrow}^7F_6$)544 nm($^5D_4{\rightarrow}^7F_5$), 585 nm ($^5D_4{\rightarrow}^7F_4$) and 621 nm ($^5D_4{\rightarrow}^7F_3$). The effect of sintering conditions, doping concentration and Ce³⁺ co-doping was studied on the luminescence properties of the phosphors. The sample twice sintered for 6 h at 1 400 ℃ shows the best performance. The optimum doping content of Tb³⁺ is x (Tb³⁺)=20mol%. The emission intensity of the phosphors can be increased by the Ce³⁺ ion co-doping, and the test shows that the best doping amount is 4mol%. The result confirms the presence of Ce³⁺→Tb³⁺ energy transfer.

Key words: luminescence; doping; solid-state reactions; green phosphors

0　Introduction

Compared with the incandescent lamp, fluorescent lamp and high pressure discharge lamp, W-LEDs (white LEDs) are known as the fourth generation lighting source due to their small size, low power consumption, high luminous efficiency, long lifetime and environmentally friendly features, etc[1-4]. The most dominant way to create a white LED is by combing a blue InGaN chip with Y₃Al₅O₁₂:Ce³⁺ yellow phosphors. However, the device based on this phosphor exhibits a poor color-rendering index and a high correlated color

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temperature because of the lack of red light at long wavelength and limits expansion of the LED application[5]. Current lighting technology employs UV LED chips with red, green and blue phosphors to improve this problem. This approach provides white LEDs with excellent color-rendering indexes and can generate warmly white light[6]. Excited by UV or near UV light, the phosphors doped by Tb^{3+} ions can generate a strong green emission, which is considered to be a kind of important activator to synthesize green fluorescent powders[7]. Because of a broad band absorption and emission in the UV and near UV region, the Ce^{3+} ion is considered to be an efficient luminescence sensitizer, widely used in several kinds of inorganic matrix materials and sensitized the luminescence of Tb^{3+} ions[8-9].

Because it has many excellent properties, such as physical and chemical properties of stability, resistance to ultraviolet bombardment and so on, alkaline earth silicate is considered as an effective matrix to synthesize fluorescent powders[10-11]. In this paper, a series of silicate phosphors doped by the Tb^{3+} ion are synthesized via a high temperature solid state method, and the luminescence properties are studied.

1　Experimental

1.1　Sample preparation

The $Ca_3Y_{2-x-y}Si_3O_{12}$:xTb^{3+}, yCe^{3+} phosphors were synthesized by a high temperature solid-state method. According to the stoichiometric ratio, the constituent oxides $CaCO_3$ (AR), SiO_2 (AR), Y_2O_3 (99.99%), Tb_4O_7 (99.99%) and CeO_2 (99.99%) were weighed, mixed and ground fully. Then the mixture was placed in a muffle furnace at room temperature and calcined in designated temperature to obtain the final samples.

1.2　Measurements and characterization

The structure of sintered samples was identified by powder X-ray diffraction (XRD) analysis of DX-1000 with Cu $K\alpha$ radiation (λ=0.154 18 nm) operating at 40 kV and 40 mA (scanning range of 10°~70°, 0.08° per step), made in Dandong Fangyuan Instrument Co., Ltd. The measurement of photoluminescence (PL) was performed using a Hitachi F-7000 spectrometer equipped with a 150 W xenon lamp under a working voltage of 350 V. The excitation and emission slits were both set at 10 nm. All the measurements were performed at room temperature.

2　Results and discussion

2.1　Phase analysis (XRD)

2.1.1　Effects of once sintering on phosphors at different temperatures

The XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}$:$0.2Tb^{3+}$ phosphors once sintered from 1 100 ℃ to 1 500 ℃ are shown in Fig.1. The XRD patterns of samples by once sintering for 6 h from 1 100 ℃ to 1 300 ℃ are corresponding with the PDF card No. 43-1036(Fig.1). The result shows that the main crystalline phase is Y_2O_3. However, the XRD patterns obtained at 1 400 ℃ or 1 500 ℃ are in accord with the PDF card No. 27-0093. The results prove that the main crystalline phase is $Ca_4Y_6(SiO_4)_6$, and the solid state reactions are not sufficient. Therefore, the required crystalline phase of $Ca_3Y_2Si_3O_{12}$ cannot be obtained by sintering for 6 h from 1 100 ℃ to 1 500 ℃.
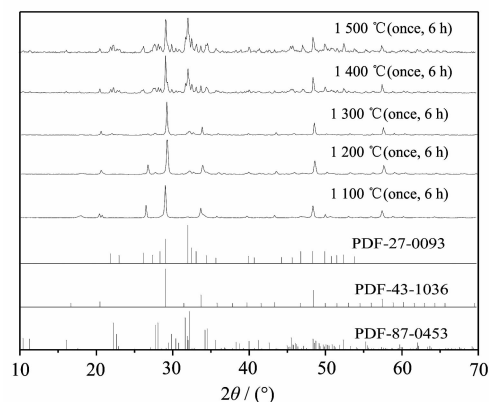

Fig.1　XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}$:$0.2Tb^{3+}$ phosphors by sintering for 6 h at different temperatures

2.1.2　Effects of twice sintering on phosphors at different temperatures

The XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}$:$0.2Tb^{3+}$ phosphors twice sintered from 1 100 ℃ to 1 500 ℃ are shown in Fig.2. The principal crystalline of the samples is Y_2O_3 by twice sintering for 6 h at 1 100 ℃ or 1 200 ℃, but it is $Ca_4Y_6(SiO_4)_6$ at 1 300 ℃ (Fig.2). However, the XRD patterns obtained at 1 400 ℃ or

The principal crystalline of the sample twice sintered for 6 h at 1 400 ℃ is $Ca_3Y_2Si_3O_{12}$, with better crystallization. Doping by a few ions has almost no effect on the crystal structure.

2.1.4　Effects of co-doped Ce^{3+} ion on phosphors

The XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}:0.2Tb^{3+}$ and $Ca_3Y_{1.76}Si_3O_{12}:0.2Tb^{3+}$, $0.04Ce^{3+}$ phosphors are shown in Fig.4. The principal crystalline of two samples is $Ca_3Y_2Si_3O_{12}$. Ce^{3+} ion co-doping has little effect on the shape and position of the peak, but does have a certain impact on the size of the peak. Again, doping by a few ions has almost no effect on the crystal structure.

Fig.2　XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}:0.2Tb^{3+}$ phosphors by twice sintering for 6 h at different temperatures

1 500 ℃ are in accord with the PDF card No.87-0453. The results show that the main crystal phase is $Ca_3Y_2Si_3O_{12}$. Under the same test condition, the diffraction peak intensity of the sample obtained at 1 400 ℃ is higher than 1 500 ℃, indicating that the crystallization of the sample at 1 400 ℃ is better.

2.1.3　Effect of sintering time on phosphors

The XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}:0.2Tb^{3+}$ phosphors twice sintered for 2 h to 10 h at 1400 ℃ are shown in Fig.3. The principal crystalline for the sample twice sintered for 2 h is $Ca_4Y_6(SiO_4)_6$, but it is $Ca_3Y_2Si_3O_{12}$ in other conditions (Fig.3). The diffraction peaks of (033) and (230) crystal plane are overlapped when calcining for 4 h, 8 h and 10 h, and under the same test condition, the diffraction peak intensity for the sample calcined for 6 h is higher than that of others, showing that the sample calcined for 6 h is better.
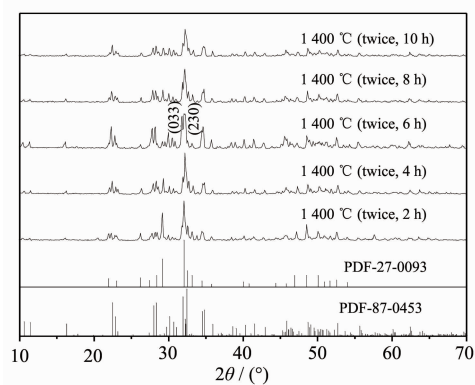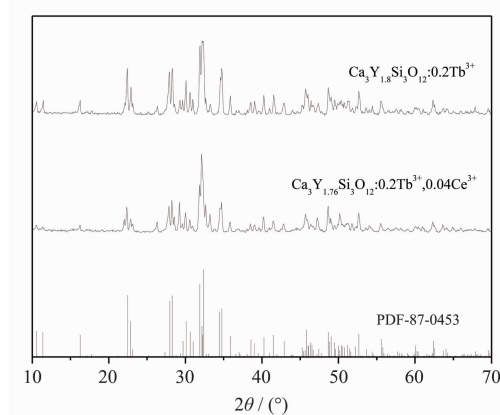

Fig.4　XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}:0.2Tb^{3+}$ and $Ca_3Y_{1.76}Si_3O_{12}:0.2Tb^{3+}$, $0.04Ce^{3+}$ phosphors

2.2　Luminescence properties

2.2.1　Effect of Tb^{3+} doping concentration on luminescence properties of $Ca_3Y_{2-x}Si_3O_{12}:xTb^{3+}$ phosphors

The excitation and emission spectra of $Ca_3Y_{2-x}Si_3O_{12}:xTb^{3+}$ phosphors doped with different concentrations of Tb^{3+} ion are shown in Fig.5. The excitation spectrum is a broadband peak, covering the wavelength region of 300 nm to 450 nm (monitored at 544 nm), which shows that $Ca_3Y_{2-x}Si_3O_{12}:xTb^{3+}$ phosphors can be effectively excited by near ultraviolet LED (350~420 nm) (Fig.4). The excitation spectrum contains three components, having peaks at 316 nm, 350 nm and 370 nm, corresponding to the characteristic transitions of the Tb^{3+} ion from $^7F_6$ to $^5D_0$, $^5L_9$ and $^5G_5$, respectively. The main peak is located at 370 nm. Excited by 370 nm, the emission spectrum contains four main emission
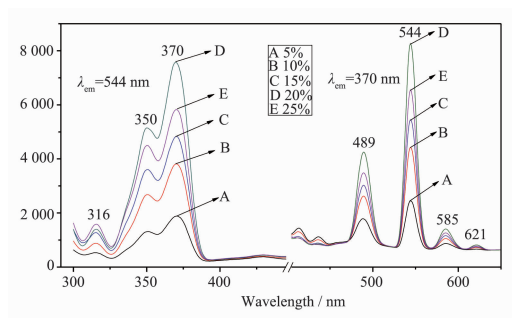

Fig.3　XRD patterns of $Ca_3Y_{1.8}Si_3O_{12}:0.2Tb^{3+}$ phosphors twice sintered for 2 h to 10 h at 1 400 ℃

Fig.5　Excitation and emission spectra of $Ca_3Y_{2-x}Si_3O_{12}$:
xTb^{3+} phosphors

peaks, 489 nm ($^5D_4\rightarrow{}^7F_6$), 544 nm ($^5D_4\rightarrow{}^7F_5$), 585 nm ($^5D_4\rightarrow{}^7F_4$) and 621 nm ($^5D_4\rightarrow{}^7F_3$), respectively, where the peak of 544 nm is the maximum. The shape and position of the excitation and emission peaks have little change with the changing of the doping concentration, but have a great influence on the peak value. When the concentration of Tb^{3+} ion is lower, the luminous intensity is weak because fewer luminescent center ions are in the matrix. With the increasing of the doping concentration, the luminescence center number increases, so the emission intensity increases gradually, the maximum value is reached when $x =$ 20mol% . The luminous intensity of the fluorescent powders begins to decrease when further increasing the concentration of Tb^{3+} ion, showing the concentration quenching.

　　The mechanism of the concentration quenching may be interactions between ions. When the concentration of Tb^{3+} ion is increased to a certain value, the mutual distance between the ions is shorter, and the interaction occurs at the same time. The concentration quenching occurs when the energy migration among Tb^{3+} ions goes to the concentration quenching centers. The cross relaxation of the $^5D_4$ level is impossible to emerge because there is no energy cross relaxation pathways[12].

2.2.2　Effect of sintering time on luminescence properties of $Ca_3Y_{2-x}Si_3O_{12}$:xTb^{3+} phosphors

　　The emission spectra of $Ca_3Y_{1.8}Si_3O_{12}$:0.2Tb^{3+} phosphors twice sintered for 2 h to 10 h at 1 400 ℃ are shown in Fig.6. With the sintering time changing, the shape and position of the emission spectra have little change, but have a great influence on the peak

intensity　(Fig.6). The peak intensity of the emission spectra is very low when the sintering time is 2 h. With the increasing of the sintering time, the intensity of the peaks increases, reaching the maximum when the sintering time is 6 h. The emission peak intensity decreases with further increase in the sintering time. The results show that the samples twice sintered for 6 h at 1 400 ℃ are better, which is consistent with the result of XRD analysis. This also shows that the pure crystalline phase of $Ca_3Y_2Si_3O_{12}$ is better to luminescence, while Y_2O_3 or $Ca_4Y_6 (SiO_4)_6$ is not conducive to luminescence. Thus the luminous intensity of phosphors can be increased by improving the crystallization effect.
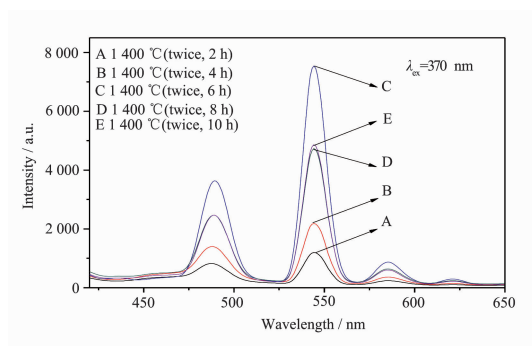

Fig.6　Emission spectra of $Ca_3Y_{1.8}Si_3O_{12}$:0.2Tb^{3+} phosphors twice sintered for 2 h to 10 h at 1 400 ℃

2.2.3　Effect of Ce^{3+} co-doping on luminescence properties of $Ca_3Y_{2-x}Si_3O_{12}$:xTb^{3+} phosphors

　　The emission spectra of $Ca_3Y_{1.8}Si_3O_{12}$:0.2Tb^{3+} phosphors doped by the Ce^{3+} ion are shown in Fig.7. When only changing the Ce^{3+} concentration while keeping the Tb^{3+} doping amount at 20mol% , the shape and position of the emission spectra peaks has little change as seen from the Fig.7 (a). The range of 300 nm to 450 nm can be ascribed to the broadband emission of the Ce^{3+} ion, and the 450 nm to 650 nm is due to the characteristics emission of the Tb^{3+} ion. Also from the Fig.7(b), with the increasing in Ce^{3+} ion concentration, the peak intensity of the emission spectra gradually increases, reaching the maximum when the doping amount is to 4mol% . When the doping concentration is further increased, the emission peak intensity decreases, showing the concentration quenching, however, the intensity is still greater
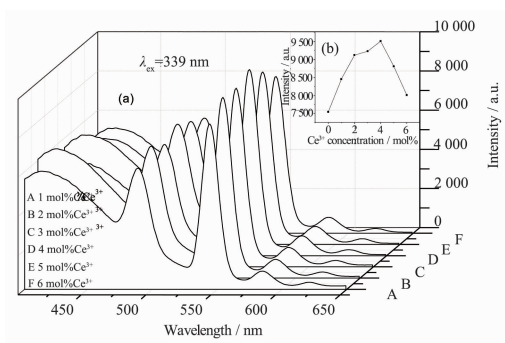
Fig.7   Emission spectra of $Ca_3Y_{1.8-x}Si_3O_{12}$:$0.2Tb^{3+}$, xCe^{3+} phosphors

than that of $Ca_3Y_{1.8}Si_3O_{12}$:$0.2Tb^{3+}$ phosphors. This demonstrates the existence of energy transfer from Ce^{3+} to Tb^{3+} in $Ca_3Y_{1.8-x}Si_3O_{12}$:$0.2Tb^{3+}$, xCe^{3+} phosphors.

The transfer process of $Ce^{3+} \rightarrow Tb^{3+}$ in $Ca_3Y_{1.8-x}Si_3O_{12}$: $0.2Tb^{3+}$, xCe^{3+} phosphors is shown in Fig.8. Ce^{3+} can be excited from the ground state ^2F_J to the high energy level of $5d$ band, then to the low state of $5d$ band by the non-radioactive relaxation. At this time, a part of the excitation energy is used for transition to the ground state ^2F_J, presenting a broadband emission. At the same time, another part of the energy is transmitted to $^5D_3$ or $^5D_4$ levels of Tb^{3+} by non-radioactive relaxation. However, the $^5D_3$ level of the Tb^{3+} ion has two kinds of transitions. One is direct transition to the ground state from the $^5D_3$ level, but the other is firstly transferred to the $^5D_4$ level, and then to the ^7F_J levels, producing the characteristics emission of the Tb^{3+} ion, and emitting the green light[13]. Therefore, the emission intensity of the Tb^{3+} ion will be significantly enhanced by the Ce^{3+} ion co-doping.
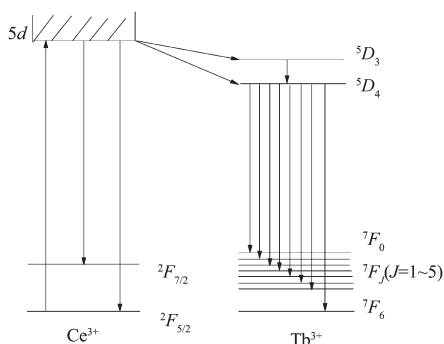

Fig.8   Energy level structures and the transfer process of Tb^{3+} and Ce^{3+}

2.3   Chromatographic analysis

The CIE diagram for different doping concentra-

tions of the Ce^{3+} ion is shown in Fig.9. The color coordinate of the $Ca_3Y_{1.8}Si_3O_{12}$: $0.2Tb^{3+}$ phosphor is (0.26, 0.52), in the range of the green color coordinate. With certain amount of Ce^{3+} ions doping, the color coordinate begins to shift towards the short wavelength, and the blue component is increased, although it is still in the green range. The range of color coordinate can be changed by changing the doping concentration of Ce^{3+} ions. This indicates that $Ca_3Y_2Si_3O_{12}$:Tb^{3+} silicate phosphors are a kind of fluorescent powders suitable for near ultraviolet LED.

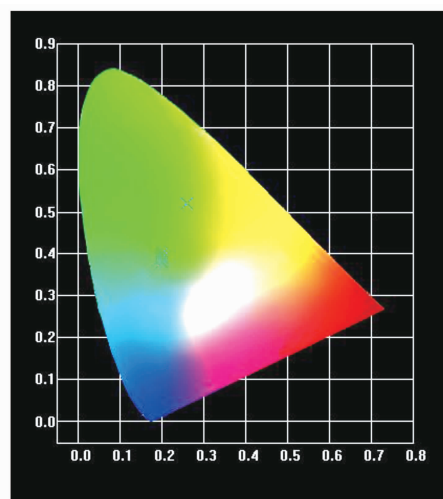Fig.9   CIE diagram of $Ca_3Y_{1.8-x}Si_3O_{12}$:$0.2Tb^{3+}$, xCe^{3+} phosphors

3   Conclusions

In summary, a series of green-emitting $Ca_3Y_{2-x-y}Si_3O_{12}$: xTb^{3+}, Ce^{3+} phosphors have been prepared by a high temperature solid-state method. The principal crystalline of the samples twice sintered for 6 h is $Ca_3Y_2Si_3O_{12}$. Excited by 370 nm, the emission peaks mainly locate at 490 nm, 544 nm (the strongest), 585 nm and 621 nm, corresponding to the characteristic transitions of the Tb^{3+} ion from $^5D_4$ to $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ respectively. Monitored by 544 nm, the excitation spectrum is broadband (300 ~450 nm). With the changing of the Tb^{3+} ion concentration, the emission intensity of the phosphors firstly increases and then decreases. The optimum doping amount is 20mol%, and the mechanism of the concentration quenching is the cross relaxation between $^5D_3 \rightarrow ^5D_4$ and $^7F_6 \rightarrow ^7F_0$. The sintered conditions on the luminescence proper-

ties are studied. The sample twice sintered for 6 h at 1 400 ℃ shows the best performance. The luminous intensity of phosphors can be increased by the Ce^{3+} ion co-doping, and the optimum is 4mol%, which shows that there exists the transfer process of $Ce^{3+}\rightarrow$ Tb^{3+} in $Ca_3Y_{1.8-x}Si_3O_{12}$:$0.2Tb^{3+}$, $x$$Ce^{3+}$phosphors. The results prove that $Ca_3Y_2Si_3O_{12}$:Tb^{3+}, Ce^{3+} silicate phosphors are a kind of fluorescent powders, suitable for near ultraviolet LED.

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