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Synthesis and characterization of novel yellow-green emitting phosphors $SrMgSi_2O_6:Tb^{3+}$

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ABSTRACT

Yellow-green emitting phosphors $SrMgSi_2O_6:Tb^{3+}$ were synthesized by gel-combustion method in weak reductive environment. The as-synthesized phosphors were investigated by X-ray powder diffraction analysis (XRD), scanning electron microscope (SEM) and Fluorescence spectrophotometer. The results indicate that $SrMgSi_2O_6$: Tb $^{3+}$ phosphors possess the similar tetragonal crystal structure as that of $Sr_2MgSi_2O_7$. The emission spectrum is composed of a series of sharp peaks, located respectively at 473 nm, 491 nm, 547 nm, 585 nm. These emission peaks are ascribed respectively to $^5D_3\rightarrow{}^7F_3$, $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_5$ transition of Tb^{3+} ions in $SrMgSi_2O_6$ host. The emission peak at 547 nm, 491 nm and 473 nm are all strong, the samples show yellow-green emitting under UV irradiation. Moreover, it is found that the concentration of doped Tb^{3+} and reductive temperature have great significant effect on the luminescent property of the phosphors. When the concentration of Tb^{3+} is 14mol%, reductive temperature is 1000 °C, the luminescent intensity of $SrMgSi_2O_6:Tb^{3+}$ is strongest.

KEYWORDS

Phosphors;
$SrMgSi_2O_6:Tb^{3+}$;
Gel-combustion method;
Luminescence;
Excitation and emission spectrum.

INTRODUCTION

Rare earth ion Tb^{3+} can emit characteristic green fluorescence, and has high luminescent intensity and quantum efficiency, so the synthesis of Tb^{3+}-doped phosphors with different matrix has been one of the interesting research topics. Wang Ji-ye et al[1] synthesized YAG: Tb^{3+} green phosphors by combustion method; Wang Fei et al[2] prepared $Gd_2O_2S:Tb^{3+}$ green phosphors using co-precipitation method combined with high temperature post-processing; Yu Xi-bin et al[3] synthesized new green-emitting materials $SrZnO_2:Tb^{3+}$ by conventional solid- state reaction; Ren Zhou-yun et al[4] synthesized new green -emitting materials $SrAl_2B_2O_7:Tb^{3+}$ by the sol -gel method.

Silicates are good hosts with stable crystal structure, high physical and chemical stability, strong water-persistent and so on. Thereforeÿsilicate phosphors have extensive applications in many fields such as plasma display panels, (PDP), solid-state lighting, longafter glow, etc[5-6]. These silicate phosphors are usually prepared through traditional solid state reaction method[7-10]. In solid-state reactions, high reaction temperature(1200~1300°C), long heating time(several hours), and a special atmosphere(such as N_2-H_2) are required to obtain a pure phase of the multi-component particles. Therefore, producing agglomerated particles of irregular shape by solid-state reactions is unavoidable. Another disadvantage of this method is the destruction of phosphor material during grounding and milling. The destruction results in the greatly decreasing of luminescence efficiency of the phosphors.

In our present work, gel-combustion method has been developed to prepare novel yellow-green emitting silicate phosphors $SrMgSi_2O_6$:Tb^{3+}. This method has several remarkable advantages in comparison with the traditional solid state reaction method[11], all of the starting materials are mixed at the molecular or atoms level in a solution, and it is easy to control the composition. Meanwhile, a high degree of homogeneity is achievable. The combustion procedure is very facile and only takes a few minutes. This synthesis technique makes use of the heat energy liberated by the redox exothermic reaction between metal nitrates and urea or other fuels. In a word, the process is safe, instantaneous and energy saving. Moreover, the phase, micrograph, and luminescent properties of as-synthesized samples have been investigated together with the factors for luminescence properties.

EXPERIMENTAL

The phosphors $Sr_{1-x}MgSi_2O_6$:$Tb^{3+}{}_x$ were synthesized by gel-combustion method. $Sr(NO_3)_2$(A.R.), $Mg(NO_3)_2 \cdot 6H_2O$(A.R.), $Si(OC_2H_5)_4$(A.R.), anhydrous ethanol(A.R.) and Tb_4O_7(99.9%) were employed as raw materials. Small quantities of H_3BO_3 were added as flux. Urea (A.R.) was used as fuel.

The procedure used to prepare $Sr_{1-x}MgSi_2O_6$:$Tb^{3+}{}_x$ phosphors is as follows. Firstly, Tb_4O_7 was dissolved in appropriate nitric acid to form $Tb(NO_3)_3$ solution by dropping appropriate H_2O_2 as the reducing agent, then the accurate concentration was determined by Ethylenediaminetetraacetic acid disodium salt (EDTA) complexing titration to ensure a desired stoichiometry. According to the nominal composition of $Sr_{1-x}MgSi_2O_6$:$Tb^{3+}{}_x$, stoichiometric $Si(OC_2H_5)_4$, $Sr(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Tb(NO_3)_3$ solutions were mixed in a 100ml crucible. Appropriate anhydrous ethanol, H_3BO_3, urea and distilled water were added into it. The mixture was stirred to obtain a homogenous and transparent solution. Subsequently, a small amount of HNO_3 (2mol.L^{-1}) was added as a catalyst and pH value of the solution was adjusted to 2~3. Next, the resulting solution was heated by water bath at 70°C for 1~2 hours to evaporate superfluous water, the volume of the solution decreased and the viscosity increased continuously because of gradual polymerization. When the volume of the solution could not decrease, the solution became a transparent gel. Then the gel was put into oven and dried at 70°C for 12h. The dry gel was ignited at 800°C in muffle furnace in air atmosphere. This combustion process only required about 2min. The dry sponge sample (which was called precursor) was formed. Due to the evolved gases, the apparent volume expanded after combustion and the precursor became so loose that it could be broken into fine pieces easily. Finally, the precursor was calcined in muffle furnace under an active carbon atmosphere at temperature 900~1200°C for 75min to obtain the sample.

Phases and crystallization of the samples were identified by X-ray diffraction analysis (XRD) with a Y-2000 diffractometer using Cu-Kα radiation. The size and morphology of the samples were investigated with a KYKY-2800B scanning electron microscope (SEM). The excitation and emission spectrums of the samples were recorded on a RF-540 fluorescence spectrometer. All measurements were carried out at room temperature.

RESULTS AND DISCUSSIONS

XRD analysis

The hosts $Sr_2MgSi_2O_7$ and $SrMgSi_2O_6$ and series of samples $Sr_{1-x}MgSi_2O_6$:$Tb^{3+}{}_x$ were synthesized by gel -combustion method at 1000°C reductive temperature. Their XRD patterns are shown in Figure1. From Figure1, it can be seen that $SrMgSi_2O_6$ have the same crystal structure as $Sr_2MgSi_2O_7$, they are all tetragonal, which agrees well with the Joint Committee on Powder Diffraction Standards (JCPDS No. 75-1736). It is consistent with the research result reported by Jia Dongdong et al[12]. For the series of samples $Sr_{1-x}MgSi_2O_6$:$Tb^{3+}{}_x$, the peak intensity of host decreases with the increase of Tb^{3+} doping concentration, and the peaks of Tb compounds (Tb_2O_3, JCPDS No. 43-1032) appear and become strong gradually. This may be due to the increase of lattice distortion degree caused by the increase of Tb^{3+} doping amount.

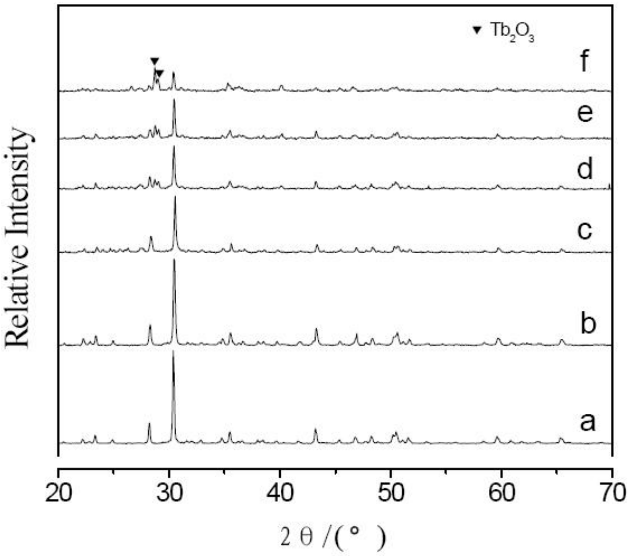

Figure 1 : XRD patterns of samples; a. $Sr_2MgSi_2O_7$; b. $SrMgSi_2O_6$; c~f: $Sr_{1-x}MgSi_2O_6$:Tb^{3+}_x (x = 0.06, 0.12, 0.14, 0.25)

SEM analysis

The morphologies of $Sr_{0.94}MgSi_2O_6$:$Tb^{3+}_{0.14}$ phosphors were observed by SEM and shown in Figure2. It can be seen that the initial particles are nearly spherical in shape, and the average diameter is about 240nm. Meanwhile, some big particles with irregular shape can be observed, which may result from large surface energy of the initial small particles during the post calcination process.

Excitation and emission spectra of $SrMgSi_2O_6$:Tb^{3+}

The as-synthesized $SrMgSi_2O_6$:Tb^{3+} phosphors emit strong yellow-green fluorescence by excitation through the ultraviolet ray. Figure 3 shows that the excitation spectrum (monitored by 547 nm) and emission spectrum (excited by 249 nm) of $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$ phosphors. It can be seen that the excitation spectrum of $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$ consists of three excitation peaks, located at 249 nm (belonging to $4f^8 \rightarrow 4f^7 5d$ transition of Tb^{3+}), 324 nm and 380 nm ($f \rightarrow f$ forbidden transition of Tb^{3+}), respectively[13]. Among these peaks, the strongest one is at 249 nm, the second one is at 380 nm, the weakest is at 324 nm. The emission spectrum of $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$ is composed of four emission peaks, located at 473 nm, 491 nm, 547 nm and 585nm, belonging to $^5D_3 \rightarrow {}^7F_3$, $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$ transition of Tb^{3+}, respectively. Usually, for the doped-Tb^{3+} phosphors[14-15], only the peak at about 547 nm is strong. But, for as-synthesized $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$, not only the emission peak at 547 nm is very strong, but also the peaks at 473 nm and 491 nm are also very strong. So, the samples show yellow-green emitting.

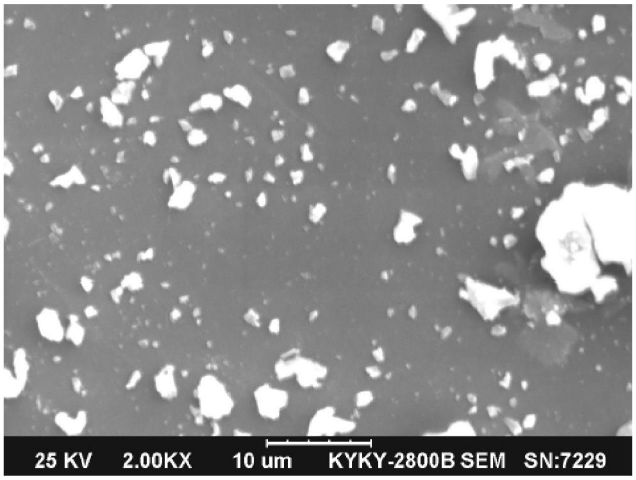

Figure 2 : SEM photographs of $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$

Effect of Tb^{3+} concentration on luminescence intensity of $SrMgSi_2O_6$:Tb^{3+}

The luminous intensity of phosphors depends on luminescence center, so the concentration of Tb^{3+} has the great effect on emission intensity of $SrMgSi_2O_6$:Tb^{3+}.

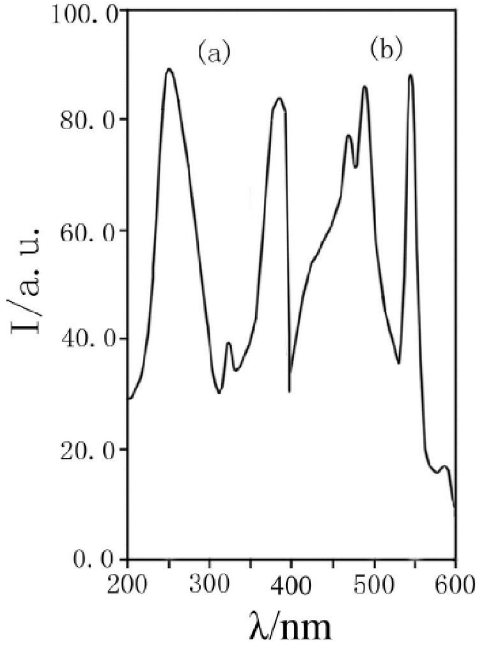

Figure 3 : Excitation spectrum(a) and emission spectrum (b) of $Sr_{0.86}MgSi_2O_6$:$Tb^{3+}_{0.14}$

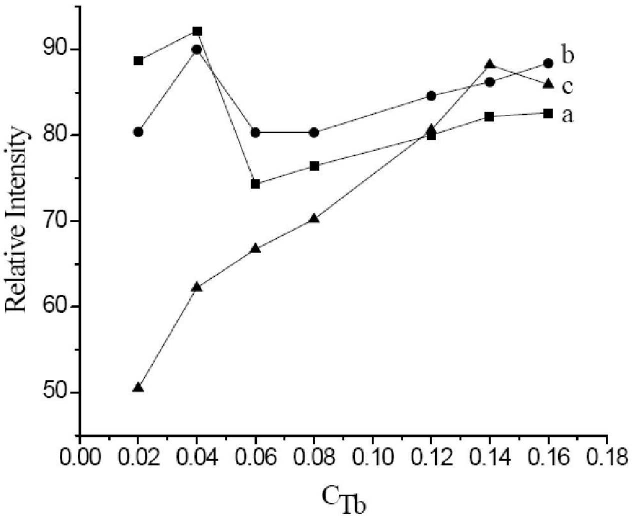

Figure 4 : The plots of luminescent intensity of $Sr_{1-x}MgSi_2O_6:Tb^{3+}_x$ at different wavelength vs the concentration(x) of doped Tb^{3+}(λex=249nm); a. 473nm, b. 491nm, c. 547nm

Figure 4 shows the emission intensity of the samples at different concentration of Tb^{3+}. From Figure 4, it can be seen that the emission intensity at 473nm and 491nm increases with the increase of Tb^{3+} concentration, then decrease when the Tb^{3+} concentration x>0.04, which maybe due to the concentration quenching. It is interesting that the emission intensity at 473nm and 491nm increases again but slowly with the increase of Tb^{3+} concentration when the Tb^{3+} concentration x>0.06. The possible reason is the appearance of Tb_2O_3. The emission intensity at 547nm increases with the increase of Tb^{3+} concentration, then decreases when Tb^{3+} concentration x>0.14, i.e., concentration quenching occurs when x is beyond 0.14. The reason for the concentration quenching is that if the concentration of Tb^{3+} is excessive, the probability of energy transfer is beyond that of emission, since the excitation energy was consumed by crystal lattice transfer, leading to the decrease of emission intensity. So, the optimum concentration of Tb^{3+} x=0.14.

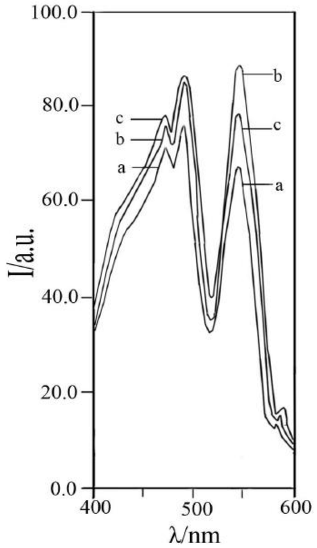

Figure 5 : Emission spectrums of $Sr_{0.86}MgSi_2O_6:Tb^{3+}_{0.14}$ obtained at different reductive temperature(λex=249nm)

Effect of reductive temperature on luminescence intensity of $SrMgSi_2O_6:Tb^{3+}$

Taking into account too low reductive temperature is not conducive to form single phase, the crystallization of material may not be complete; overhigh temperature can lead to hard aggregate or vitrification, which makes the material difficult to be ground,0even causes the destruction of the material during grounding and milling and results in the greatly decreasing of luminescence intensity of the phosphors. So, the effect of reductive temperature on luminescence intensity of $SrMgSi_2O_6:Tb^{3+}$ in the range of 900°C and 1200°C was investigated. It is found that the sample obtained under 1200°C was vitrified. Figure 5 shows that the emission spectra of the samples obtained at different reductive temperature 900°C, 1000°C and 1100°C (while other conditions are fixed). It can be seen that the shape and location of emission peaks are nearly not changed, but reductive temperature has great effect on the intensity of emission peaks. The intensity of emission peak at 547nm firstly increases with the temperature increasing, and then decreases. When reductive temperature is 1000°C, the peak at 547nm is the strongest. The intensity of emission peaks at 473nm and 491nm increases with the reductive temperature gradually, but compared with the sample obtained at 1000 °C the improvement of emission-peak intensity at 473nm and 491nm is not obvious for the sample obtained at 1100 °C Therefore, under UV light, it can be observed that the sample obtained at 1000 °C shows the strongest luminescent intensity. So, the appropriate reductive temperature is 1000 °C.

CONCLUSION

Novel yellow-green emitting phosphors $SrMgSi_2O_6:Tb^{3+}$ were prepared by gel-combustion method for the first time in this work. Gel-combustion method has many advantages of uniformity of product ingredients, low calcination temperature, short calcination time, easy operation, energy saving, and so on. $SrMgSi_2O_6:Tb^{3+}$ phosphors have tetragonal crystal structure. The excitation spectrum of $SrMgSi_2O_6:Tb^{3+}$ consists of two strong peaks at 249 and 380 nm and one weak peak at 324nm. The emission spectrum is composed by four emission peaks at 473nm, 491nm, 547nm and 585nm, which can be ascribed to $^5D_4$–^7F_J (J=6,5,4,3) electronic transition of Tb^{3+}, respectively. The three emission peaks at 473nm, 491nm and 547nm are all strong, which results in a yellow-green emitting. The appropriate process conditions were confirmed as follows: the reductive temperature is 1000°C, and the doping concentration of Tb^{3+} is 14mol%.

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