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High thermal stability and quantum yields of green-emitting $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+} phosphor by co-doping Ce^{3+}

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Abstract: A series of Tb^{3+} mono-doped and Ce^{3+}-Tb^{3+} co-doped $Sr_3Gd_2(Si_3O_9)_2$ phosphors with high thermal stability and quantum yields were successfully prepared via the solid state reaction. The as-prepared $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+} samples showed broad excitation spectrum from 250 to 400 nm and presented characteristic emission transitions $^5D_4 \rightarrow {}^7F_J$ (J=6, 5, 4, 3) of Tb^{3+} under 313 nm excitation, which were located at about 488, 541, 584 and 620 nm. The emission intensities of Tb^{3+} rose steadily in $Sr_3Gd_2(Si_3O_9)_2$ host with the increase of Tb^{3+} concentration even though Gd^{3+} ions were completely replaced by Tb^{3+} ions. The Ce^{3+} ion as a sensitizer could efficiently improve the performance of Tb^{3+} ion. First, with Ce^{3+} co-doping, the excitation spectrum of Tb^{3+} monitored at 541 nm showed a similar band that responds to the violet emission of Ce^{3+} monitored at 416 nm. Second, the quantum yields of $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+} phosphors could be enhanced from 26.6% to 80.2% by co-doping Ce^{3+}. Finally, the co-doping of Ce^{3+} was also effective to improve the thermal stability of $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+}. As the temperature rose to 150 ºC, the emission intensity of Tb^{3+} remained at about 83.6% of that measured at room temperature, which was better than the commercial YAG:Ce phosphor in terms of their thermal quenching properties. These results indicated that the as-prepared $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+},Ce^{3+} samples could be used as green emission phosphors for possible applications in near ultraviolet based WLEDs.

Keywords: $Sr_3Gd_2(Si_3O_9)_2$; photoluminescence; quantum yields; thermal stability; luminescence; rare earths

Different from the environment around fluorescent material of traditional fluorescent lamp or CRTs, the amount of fluorescent powder encapsulated in the phosphor-converted devices is little. Importantly, the phosphors can be not only excited by high energy density, but also influenced by the heat sent out from the chip itself. Thus, the fluorescent material should promise good thermal stability at high temperatures (100–200 ºC)[1] in highly efficient phosphor-converted device, namely low heat quenching characteristics. Moreover, more and more articles have been reported and closely related with the thermal stability and quantum yields (QYs) of rare-earth (RE) activated inorganic phosphor materials recently[2]. In terms of the present study on RE-doped phosphors, the thermal stability and QYs should be paid more attention to so that they can be more suitable for application. It is well known that Tb^{3+} ion is frequently used as an activator of green emitting luminescent materials due to its predominant $^5D_4 \rightarrow {}^7F_5$ transition peaked at around 541 nm[3,4]. Moreover, the characteristic sharp emissions of Tb^{3+} originating from intra-configurational 4f→4f transitions are almost independent of the host lattice[5,6]. However, the intensities of the Tb^{3+} absorption peaks in the near ultraviolet (UV) region are very weak and their widths are very narrow due to the strictly forbidden 4f→4f transitions[7,8]. Generally, as a promising sensitizer for Tb^{3+} ions, Ce^{3+} has been widely used and expected to improve the absorption ability, thermal stability and QYs of Tb^{3+} ions because of the efficient energy transfer from Ce^{3+} to Tb^{3+} [9], such as $Ca_2Ba_3(PO_4)_3Cl$:Ce^{3+},Tb^{3+} [10], $NaBa_4(BO_3)_3$:Ce^{3+},Tb^{3+} [11], $Na_2Gd_2B_2O_7$:Ce^{3+},Tb^{3+} [12], $BaAl_{12}O_{19}$:Ce^{3+},Tb^{3+} [13], $LaPO_4$:Ce^{3+},Tb^{3+} [14], $Ca_6Ba(PO_4)_4O$:Ce^{3+},Tb^{3+} [15] and so on. Recently, RE ions activated $A_3B_2(Si_3O_9)_2$ (A and B are divalent and trivalence cations, respectively) phosphors have received much attention due to the variety and the excellent physical and chemical properties. However, there are few reports on the Tb^{3+}-Ce^{3+} co-doping, thermal stability or QYs of RE ions activated $A_3B_2(Si_3O_9)_2$.

Here we reported the synthesis of a novel green phosphor $Sr_3Gd_2(Si_3O_9)_2$:Tb^{3+}, which exhibited excellent photoluminescence and possessed high QYs and excellent thermal stability when co-doped with Ce^{3+}. The effect of Ce^{3+} on the absorption ability, QYs and thermal stability of Tb^{3+} was systematically investigated.

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1 Experimental

1.1 Materials and methods

The $Sr_3Gd_{2-x}(Si_3O_9)_2$:$x$$Tb^{3+}$ (x represents mol.% in this article) and $Sr_3Gd_{1.64}(Si_3O_9)_2$:$0.10Tb^{3+}$,$0.26Ce^{3+}$ (0.10 and 0.26 represents mol.% in this article) phosphors were prepared via the conventional high temperature solid state reaction. On the basis of the similar effective ionic radius and valence of the cations, we suggested that Ce^{3+} and Tb^{3+} ions preferred to occupy Gd^{3+} sites in this host. Typically, stoichiometric amounts of $SrCO_3$ (A.R.), Gd_2O_3 (A.R.), SiO_2 (A.R.), H_3BO_3 (A.R.), Tb_4O_7 (≥99.99%) and CeO_2 (≥99.99%) were thoroughly ground and mixed for 30 min. In each sample, 5 wt.% H_3BO_3 (A.R. 99.99%) was added as a flux. Then the mixtures were transferred into alumina crucibles and sintered at 1300 ºC for 4 h under a reducing atmosphere of 95% N_2 and 5% H_2.

1.2 Characterization

The phase purity of the as-prepared samples was characterized by an X-ray powder diffractometer (XRD) (Bruker D8 Focus, Bruker, Kalsruhe, Germany) with Ni-filtered Cu Kα (λ=0.1540598 nm) radiation at 40 kV tube voltage and 40 mA tube current. Excitation, emission spectra and temperature-dependent luminescence (25–200 ºC) were measured by a fluorescence spectrometer (FLUOROMAX-4) with a 150 W xenon lamp as excitation source. The QYs were measured by absolute photoluminescence quantum yield measurement system C9920-02.

2 Results and discussion

The XRD patterns of $Sr_3Gd_{2-x}(Si_3O_9)_2$:$x$$Tb^{3+}$ (x=0.40, 0.80, 1.20, 1.60, 2.00), $Sr_3Gd_2(Si_3O_9)_2$:$0.10Tb^{3+}$,$0.26Ce^{3+}$ and the $Sr_3Gd_2(Si_3O_9)_2$ phase reported by Tyutyunnik et al.[16] as a reference are shown in Fig. 1. All the diffraction peaks of the samples were well indexed to the reported $Sr_3Gd_2(Si_3O_9)_2$ phase, indicating that the obtained samples were single phase and the doped ions were completely dissolved in the $Sr_3Gd_2(Si_3O_9)_2$ host without inducing significant changes of the crystal structure. The ionic radii (nm) of Gd^{3+}, Sr^{2+}, Tb^{3+} and Ce^{3+} for the given coordination number (CN) are presented in Table 1. On the basis of ionic radius and charge balance, the Tb^{3+} and Ce^{3+} ions occupied the Gd^{3+} site. In addition, Fig. 2 depicts the partial powder XRD patterns between 28.0º and 29.6º of $Sr_3Gd_{2-x}(Si_3O_9)_2$:$x$$Tb^{3+}$ (x=0.40, 0.80, 1.20, 1.60, 2.00) samples. An obvious blue shifting of the major diffraction peaked at 2θ=28.55º could be observed with the increase of the Tb^{3+} concentration. This phenomenon was ascribed to the smaller Tb^{3+} ions substituted for the larger Gd^{3+} ions. It also verified the incorporation of Tb^{3+} into the lattice successfully and the formation of solid solutions according to the Vegard rule[17].

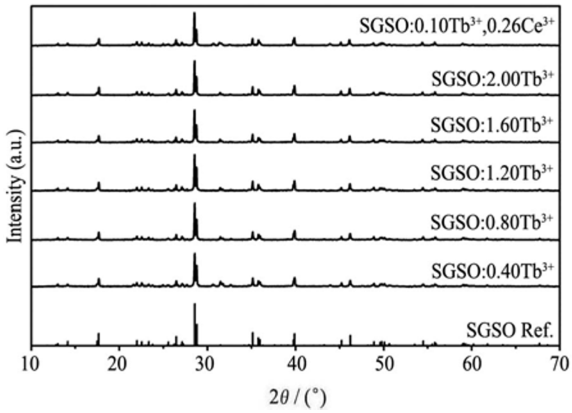

Fig. 1 XRD patterns of $Sr_3Gd_2(Si_3O_9)_2$:$x$$Tb^{3+}$ (x=0.40, 0.80, 1.20, 1.60, 2.00), $Sr_3Gd_2(Si_3O_9)_2$:$0.10Tb^{3+}$,$0.26Ce^{3+}$ (The $Sr_3Gd_2(Si_3O_9)_2$ phase reported by Tyutyunnik et al. is shown as a reference[16])

Fig. 3 presents the excitation and emission spectra of the as-obtained $Sr_3Gd_{1.90}(Si_3O_9)_2$:$0.10Tb^{3+}$ phosphor. The excitation spectrum monitored at 541 nm contained two parts: one was a broad band from 235 to 300 nm with the maximum at 279 nm corresponding to the spin-allowed $4f^8 \rightarrow 4f^7 5d$ transition of Tb^{3+} and several sharp bands between 300 and 380 nm attributed to the 4f→4f transitions of Tb^{3+} [8,18], the other was two sharp peaks around at 277 and 313 nm corresponding to the $^8S \rightarrow {}^6I$ and $^8S \rightarrow {}^6P$ transitions of Gd^{3+} ions in the host, respectively, which implied that the possibility of energy transfer from Gd^{3+} to Tb^{3+} [19–22]. The emission spectrum exhibited a series of characteristic optical transitions $^5D_4 \rightarrow {}^7F_J$ (J=6, 5, 4, 3) of Tb^{3+} under 313 nm excitation, which were located at about 488, 541, 584 and 620 nm[23]. Among

Table 1 Ionic radii (nm) of Sr^{2+}, Gd^{3+}, Ce^{3+} and Tb^{3+} for the given coordination number (CN)

Ion	Sites	Ionic radii/nm		
		CN=8	CN=7	CN=6
Sr^{2+}	8f/4e	0.126	0.121	0.118
Gd^{3+}	8f/4e	0.105	0.100	0.094
Ce^{3+}	8f/4e	0.114	0.107	0.101
Tb^{3+}	8f/4e	0.104	0.098	0.92

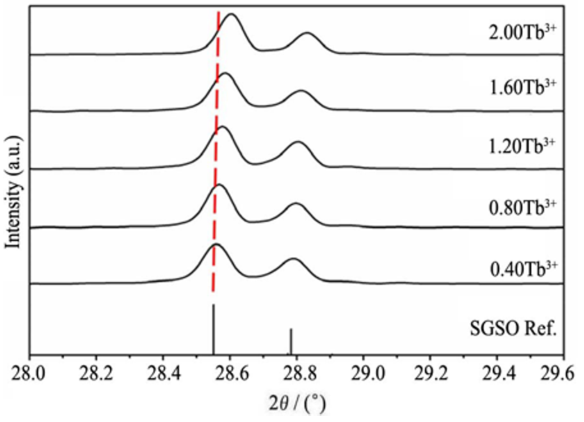

Fig. 2 Enlarged XRD patterns of $Sr_3Gd_2(Si_3O_9)_2$:$x$$Tb^{3+}$ (x=0.40, 0.80, 1.20, 1.60, 2.00) at 2θ=28.0°–29.6°