

Synthesis and photoluminescence characteristics of Eu^{3+} doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ red emitting phosphor

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Abstract. Eu^{3+} doped bismuth silicate phosphors, $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{xEu}^{3+}$ ($0.01 \leq x \leq 0.08$) were prepared via sol-gel route. XRD results show the phase of the synthesized phosphors calcinated at 650°C is isostructural with $\text{Bi}_4\text{Si}_3\text{O}_{12}$. Under the excitation of 261nm and 393nm, there are some sharp emission peaks of Eu^{3+} ions centered at 595nm, 614nm, 654nm and 706nm in the emission spectra of the Eu^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ phosphors. The strongest ones located at 595nm and 614nm are due to $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . Luminescence intensity reaches maximum value when the concentration of Eu^{3+} ions equals 7mol%. The $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ phosphors may be potentially used as red phosphors for white light-emitting diodes.

Introduction

Recently, the white light-emitting diodes (LEDs) have caused widespread concern due to the advantages of low power consumption, high efficiency, reliability, and environmental friendliness [1,2]. Conventionally, yellow $\text{Ce}^{3+}:\text{YAG}$ phosphor excited by blue LED chip is used to generate white light from LEDs [3]. However, due to lack of red light component, the color rendering index of white LEDs made by this method is low [4]. In order to solve this problem, many efforts have been done such as compensate the red light deficiency of $\text{YAG}:\text{Ce}^{3+}$ based LED with a separate red-emitting phosphor [5], doping Y_2O_3 with Eu^{3+} [6-8], which is the current red-emitting phosphor. Unfortunately, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is limited to low brightness and can not absorb efficiently in near UV region. Moreover, the lifetime of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is inadequate under near UV irradiation. The problems of red phosphors become the bottleneck of the advancement of white LEDs. Therefore, it is urgent to search for a new red phosphors with a high absorption in the near UV/blue spectral region.

The BSO crystal has many advantage such as small thermal expansion, large specific heat, high optical damage threshold, render BSO crystal the potential to function as a phosphor material for LED. [9-13]. Bismuth silicate has excellent prospects as luminescent substrate due to the advantages of special structure features and great chemical and physical stability [14, 15]. So far there are only some reports on the $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (BSO) phosphors such as $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Dy}^{3+}$ [11-13] and this kind of phosphors have yellow emission. The law of rare earth ion Eu^{3+} -doped BSO phosphor prepared via sol-gel route has not been studied. Eu^{3+} ion is widely used as an activator with reddish emission due to its $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3, 4$) transitions, which makes it as the most suitable source for synthesis of red emitting phosphors.

In this paper, a red emitting phosphor $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ was synthesized by sol-gel method. The structure and luminescent properties of as prepared samples were investigated.

Experimental

The $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ phosphors were synthesized through a sol-gel technique. The raw materials were weighted accurately according to the stoichiometric ratio $(\text{Bi}_{1-x}\text{Eu}_x)_4\text{Si}_3\text{O}_{12}$ ($x=0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08$). Then $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (A.R), Eu_2O_3 (99.99%) were added in nitric acid to dissolve. Besides, nitric acid can inhibit the hydrolysis progress and promote the reaction. The Si-solution was prepared by dissolving tetraethyl orthosilicate (TEOS) (A.R) in ethanol. The solutions were evenly mixed together and then dried at 80°C for 12h. Then the obtained precursor was loaded into the furnace, annealed at 650°C for 4h in the atmosphere.

The X-ray diffraction (XRD) pattern of the samples were characterized by X-ray power diffraction (FANGYUAN DX-2700, China) with the Ni monochromator using $\text{Cu K}\alpha$ radiation ($\lambda_k=0.154056\text{nm}$), operating at 40kV and 30mA. The XRD data was collected in the range of 10 - 80° in 2θ using a step size of 0.05° and a counting time of 0.3s per step. The surface morphology of the Sm^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ phosphor was observed by a scanning electron microscope (S-4800, Hitachi, Japan). The emission and excitation spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ were recorded on a Hitachi F-4600 spectrometer equipped with a 150W xenon lamp at a scan speed of 10nm/s and the slit width was 1nm.

Results and discussion

The XRD patterns of $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{xEu}^{3+}$ phosphors with different Eu^{3+} content ($x=0.01, 0.02, 0.03, 0.04, 0.05, 0.06$) are shown in Fig.1. The diffraction peaks of all samples match well with that of standard $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (PDF#35-1007) which have orthorhombic crystal system, I-43d space group. This suggests that the doped Eu^{3+} ions well incorporated into the host lattice and did not induce significant changes of the host structure. Taking valence states and ion sizes of Bi^{3+} (0.103nm), Si^{4+} (0.026nm) and Eu^{3+} (0.0947nm) in consideration, one can suggest that Eu^{3+} ions substitute for Bi^{3+} ions easily in Eu^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ phosphors. However, when x increases to 0.06, there is a small peak of Bi_2SiO_5 due to the excess of Bi^{3+} .

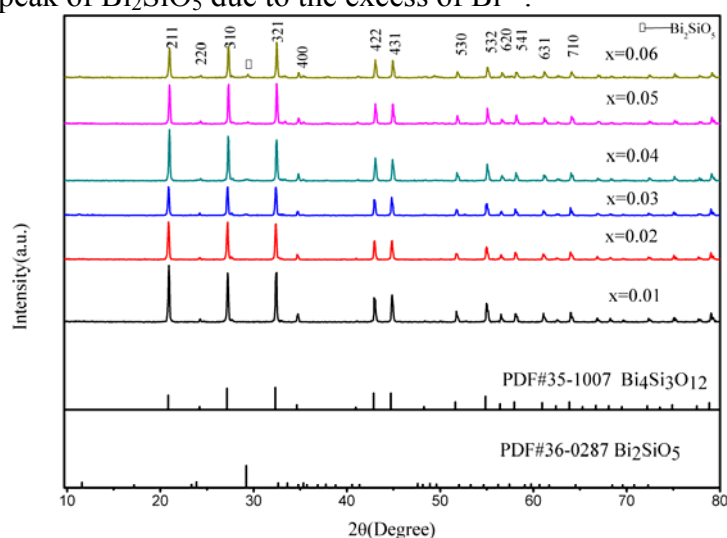


Fig.1 XRD patterns of different concentration of Eu^{3+} ions-doped BSO crystals.

Fig.2 shows the SEM image of the $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{0.07Eu}^{3+}$ composition samples. The sample particles grew to reach diameters of 1-5 μm . Besides, the $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{0.07Eu}^{3+}$ phosphor is composed of many agglomerated granules with irregular morphology and there are some small particles attached to the surface.

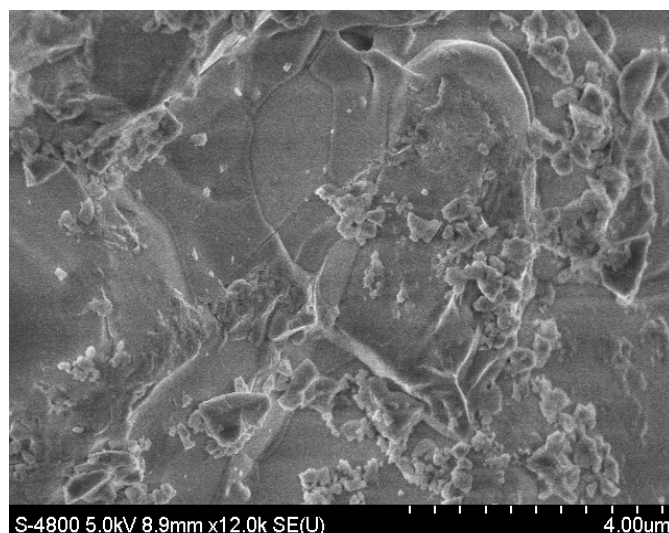


Fig.2 SEM photograph of typical $\text{Bi}_4\text{Si}_3\text{O}_{12}:0.07\text{Eu}^{3+}$ phosphor.

Fig.3 shows the excitation spectra of Eu-doped BSO crystal samples monitoring 614nm. As seen, the main peaks locate at 261nm and shoulder peaks at about 395nm and 460nm. The peaks at 261nm are ascribed to the overlap of the charge transfer state(CTS) due to an electron transfer from an oxygen ligand 2p orbital to an empty 4f orbital of europium ions($\text{Eu}^{3+}-\text{O}^{2-}$). The sharp lines in 350-500nm region belonged to the intraconfigurational 4f-4f transitions of Eu^{3+} are weaker. The excitation peaks at about 395nm and 460nm are due to the ${}^7\text{F}_0-{}^5\text{L}_6$ and ${}^7\text{F}_0-{}^5\text{D}_2$ transitions of Eu^{3+} .

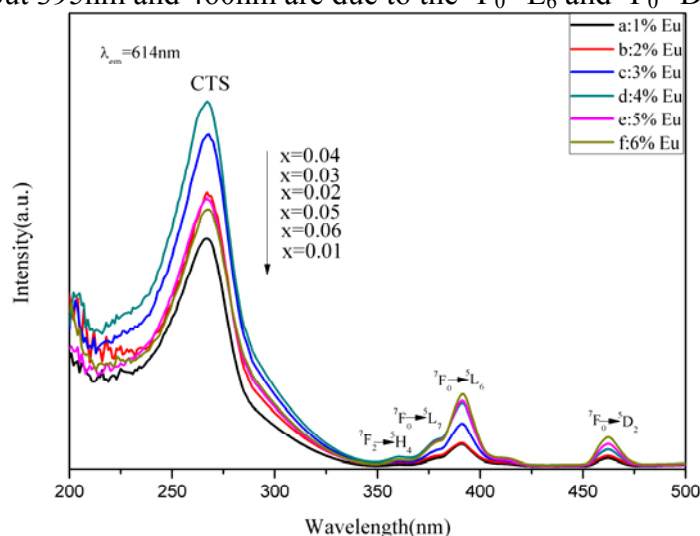


Fig.3 Excitation spectra of Eu^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ phosphors with different concentration of Eu^{3+} ions.

Fig.4 shows the emission spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ excited under 261nm at room temperature. As seen, all these samples have the same peak shape. The peaks located at 595nm, 614nm, 654nm and 706nm are ascribed to the ${}^5\text{D}_0-{}^7\text{F}_1$, ${}^5\text{D}_0-{}^7\text{F}_2$, ${}^5\text{D}_0-{}^7\text{F}_3$ and ${}^5\text{D}_0-{}^7\text{F}_4$ transitions of Eu^{3+} . The symmetry ratio, defined as the emission intensity ratio of ${}^5\text{D}_0-{}^7\text{F}_1$ relative to ${}^5\text{D}_0-{}^7\text{F}_2$ transitions, gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu^{3+} ions in the matrix. The emission line at 614nm is much stronger than that at 595nm because when the Eu^{3+} ions embedded in a site without inversion symmetry, the ${}^5\text{D}_0-{}^7\text{F}_2$ electric dipole transition is stronger than the ${}^5\text{D}_0-{}^7\text{F}_1$ magnetic dipole transition of Eu^{3+} , which suggesting a lower occupancy of Eu^{3+} ions in a crystallographic symmetric environment. The characteristic emission peaks of Eu^{3+} ions located at 595nm and 614nm are enhanced as the concentration of Eu^{3+} is increased which is strong evidence that Eu^{3+} ions mainly occupy the site in version symmetry environment of bismuth silicate lattice. When the addition of Eu^{3+} reaches more

than 4mol%, the doping concentration quenching occurs due to Eu^{3+} cross relaxation processes.

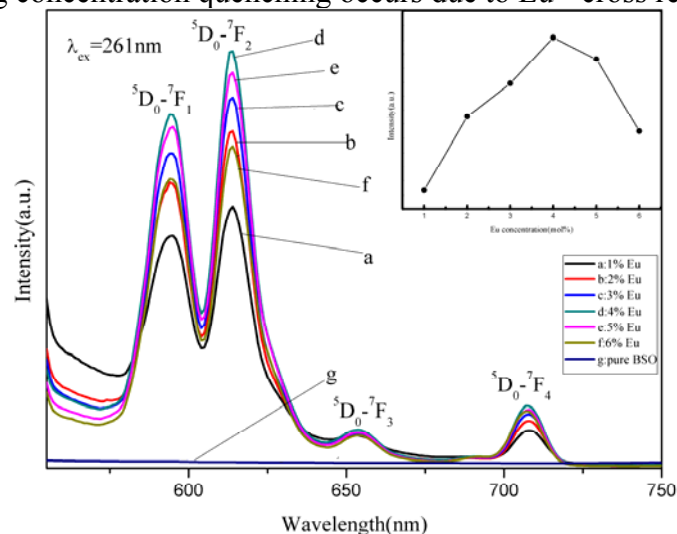


Fig.4 Emission spectra of Eu^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ phosphors with different concentration of Eu^{3+} ions($\lambda_{\text{ex}}=261\text{nm}$).

The emission spectra of BSO:Eu monitoring 393nm is shown in Fig.5. Compared with Fig.4, the intensity of the peak of 595nm is stronger than 614nm. This is because the Eu^{3+} ions are embedded in a site with inversion symmetry, so the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition of Eu^{3+} is stronger than the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition. When the content of Eu^{3+} reaches 7mol%, the luminescence intensity reaches maximum and then it becomes weaker even when the content of Eu^{3+} increases.

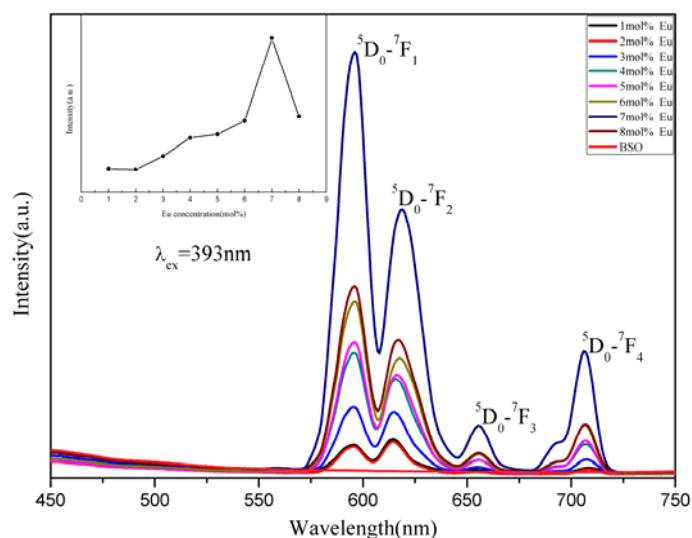


Fig.5 Emission spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ phosphors with different concentration of Eu^{3+} ions($\lambda_{\text{ex}}=393\text{nm}$).

The CIE chromaticity coordinates for the different concentration of the Eu^{3+} -doped BSO crystal under 261nm excitation were calculated in Fig.6. Upon excitation at 261nm, all the samples exhibit red light, moreover, emission color remains barely unchanged by varying the relative concentration of Eu^{3+} .

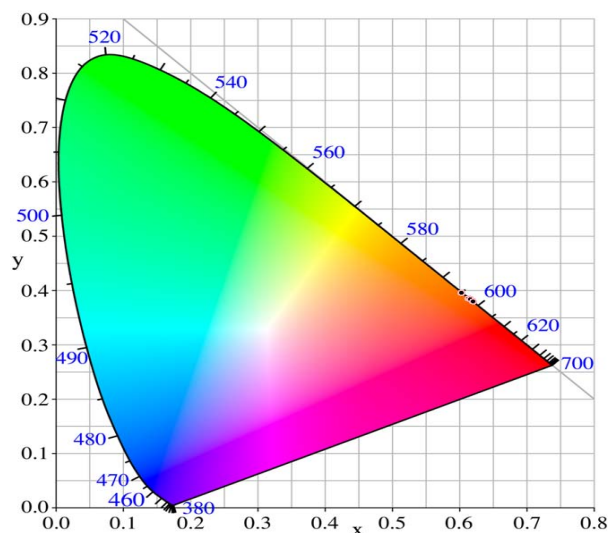


Fig.6 CIE chromatic coordinate of Eu-doped BSO crystals at 261nm excitation wavelengths

Conclusion

$(\text{Bi}_{1-x}\text{Eu}_x)_4\text{Si}_3\text{O}_{12}$ phosphors were synthesized by the sol-gel route at 650°C for 4h and its fluorescence properties were investigated. It is isostructural with $\text{Bi}_4\text{Si}_3\text{O}_{12}$ when x is not greater than 0.5 according to the XRD patterns. The broad band centered at 261nm in excitation spectrum shows strong charge transfer from oxygen ligand to europium ions and the characteristic emission peaks of Eu^{3+} ions located at 595nm and 614nm are enhanced as the concentration of Eu^{3+} is increased. The doping concentration quenching occurs when addition of Eu^{3+} reaches more than 7mol%. The Eu^{3+} -doped $\text{Bi}_4\text{Si}_3\text{O}_{12}$ crystals exhibit stable red light when the excitation wavelengths changes from 261 to 393nm. All the results indicate that $\text{Bi}_4\text{Si}_3\text{O}_{12}:\text{Eu}^{3+}$ is an excellent red emitting phosphor and can be effectively irradiated by near-UV for potential applications in white LEDs.

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