# Preparation and luminescence properties of Tm<sup>3+</sup>-doped SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> blue-emitting phosphor

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**Abstract.** Various novel SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> blue-emitting materials were achieved via solid-state synthesis. The structure and phase purity of prepared SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:*x*Tm<sup>3+</sup> (x = 0.005-0.30 mol) were examined by X-ray powder diffraction. The surface morphology of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:0.01Tm<sup>3+</sup> were studied by scanning electron microscopy. Photoluminescence properties were systematically explored under the monitoring emission ( $\lambda_{em} = 468$  nm) and excitation ( $\lambda_{ex} = 303$  nm) spectra. The optimum mole ratio of as-synthesized phosphors was 0.01 mol. The concentration quenching mechanism in the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> host was due to electric multipole interaction. Particularly, the chromaticity coordinates (0.1334, 0.0474) of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:0.01Tm<sup>3+</sup> are near to those of the commercial BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup>. These results validated the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> phosphor can be utilized good blue-emitting candidate for W-LEDs.

#### **1** Introduction

To tackle a range of energy and environmental issues, phosphor-converted white-emitting diodes (W-LED) have extensively been getting attention because of energysaving and high luminous efficiency [1-5]. Currently, W-LED are realized by combining the output from blue LED chip with yellow-emitting phosphor  $Y_3Al_5O_{12}$ :Ce<sup>3+</sup>. Unfortunately, these products lacked red composition, which lead to lower color rendering index and high correlated color temperature [6, 7]. Hence, an alternative method was proposed by combining tricolor (RGB) phosphors coated onto a near-UV (NUV) chip [8]. It is imperative to fabricate a novel blue-emitting phosphor with effective absorption in the near-UV region.

As is well-known, rare-earth ions doped tantalates have arisen extensive interest due to excellent chemical and physical stability, such as  $Ca_2YTaO_6:Dy^{3+}$ , SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Sm<sup>3+</sup>, and SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Eu<sup>3+</sup> [9-11]. Tm<sup>3+</sup> is widely used as an efficient blue light emitting center [12]. Many alternative phosphors have been reported, such as SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> blue-emitting phosphor for W-LEDs has been synthesized at 1200 °C in an ambient atmosphere by solidstate reaction. The powder XRD of the samples were taken and discussed in this paper. Meanwhile, the structural characterization, the concentration quenching, photoluminescence (PLE) properties, the emission PL spectra, and CIE coordinates were investigated in depth.

## 2 Experimental

The SrBi<sub>2(1-x)</sub>Tm<sub>2x</sub>Ta<sub>2</sub>O<sub>9</sub> powders were achieved through solid-phase synthesis method. Tm<sub>2</sub>O<sub>3</sub> (99.99%), SrCO<sub>3</sub> (analytical reagent), Bi2O3 (analytical reagent), and Ta2O5 (analytical reagent) were taken as starting materials, following proper stoichiometric ratio. First, the mixture was ground thoroughly for 15 minutes and set into proper size crucibles. Then, the mixture was calcined in air at 600°C for one hour, and further sintered at 1200 °C for 5 h. Finally, after the muffle furnace cooled down to near room temperature, the products were ground and checked for luminescence characterization. The structural properties of phosphor were measured by the X-ray diffraction (XRD) through a Bruker D2 PHASER X-ray diffractometer with Cu K $\alpha$  radiation source ( $\lambda = 0.15405$ nm) operated at 40 kV with results between the range of  $2\theta = 10^{\circ} - 70^{\circ}$ . The surface morphology was studied via a JEOL JSM-6490 emission scanning electron microscopy (SEM). The photoluminescence spectra of all the samples were characterized by FLS 980 spectrometer (Edinburgh).

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#### 3 Results and discussion



Figure 1 presents the representative XRD patterns of  $SrBi_2Ta_2O_9:xTm^{3+}$  (x = 0.005, 0.01, 0.05, 0.15, and 0.30) phosphors. Obviously, with the increase of Tm<sup>3+</sup> dopant concentration, all the diffraction peaks were in accordance with the standard SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> referenced card (JCPDS no. #49-0609). It indicated the small amount of  $Tm^{3+}$  ions does not evidently influence the crystal structure of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. the unit cell lattice parameters, for the composition of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:0.01Tm<sup>3+</sup>, are a = 25.016 Å, b = 5.509 Å, c = 5.509 Å, V=755.87 Å<sup>3</sup>, respectively, which are indexed to the reported parameters [18]. Hence, the ionic radii of the Bi3+ and Tm3+ ions are approximate corresponding to 1.310 Å and 1.052 Å (coordination number, CN = 8), respectively [19]. Apparently, a small amount of Bi<sup>3+</sup> ions can be readily replaced by Tm<sup>3+</sup> ions in the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> host lattice



Generally, the mean size of commercial phosphor particles was in the range of  $5-10 \mu m$ . Figure 2 presents the SEM micrograph of a representative of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:0.01Tm<sup>3+</sup> sample. The particle sizes were distributed in the range of a few microns to a few hundred microns. The particles shape was irregular and nonuniform because of the annealing process under high temperature. In order to break up the agglomerations and improve the quality of the powders, a further long ballmilling step is necessary in real application.

The excitation spectrum of representative sample  $SrBi_2Ta_2O_9:0.01Tm^{3+}$  is monitored at 468 nm and shown in Figure 3 curve (1). A broad band in the range of 200-250 nm related to  $O^2 \rightarrow Bi^{3+}$  charge transfer band [10]. Another peak in the excitation spectrum at 303 nm is assigned to the typical 4f-4f transition of  ${}^{3}H_{6} \rightarrow {}^{1}I_{6}$  of  $Tm^{3+}$ . Figure 3 curve (2) displays the emission spectrum of  $SrBi_2Ta_2O_9:0.01Tm^{3+}$  at near-UV light  $\lambda_{ex} = 303$  nm. The main emission band at 468 nm due to the electronic dipole transition of  ${}^{1}G_4 \rightarrow {}^{3}H_6$  of  $Tm^{3+}$  [20]. Importantly, the emission peaks situated in the blue region suggested  $SrBi_2Ta_2O_9:Tm^{3+}$  can be a promising blue emitting



phosphors. The typical transitions of excitation and emission are shown in the energy level diagram of  $\text{Tm}^{3+}$  ion Fig. 3(b). When the higher energy level  ${}^{1}\text{D}_{2}$  was excited by a 303 nm photon, it gives rise to the transition of  ${}^{1}\text{G}_{4} \rightarrow {}^{3}\text{H}_{6}$  to emit the sharp blue light.



Figure 4. The PL spectra ( $\lambda_{ex} = 303$  nm) of SrB<sub>12(1-</sub> x)Tm<sub>2x</sub>Ta<sub>2</sub>O<sub>9</sub> (x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.15, 0.20, and 0.30 mol) phosphors. The upper inset showed the influence of Tm<sup>3+</sup> icon with different concentrations.

The PL spectra of SrBi<sub>2(1-x)</sub>Tm<sub>2x</sub>Ta<sub>2</sub>O<sub>9</sub> (x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.15, 0.20, and 0.30) as with different Tm<sup>3+</sup> ions content are presented in Figure 4. It is obvious that all the emission spectra have similar shape profiles with the increasing concentration. When the doping Tm<sup>3+</sup> concentration in SrBi<sub>2(1-x)</sub>Tm<sub>2x</sub>Ta<sub>2</sub>O<sub>9</sub> was x = 0.01 mol, the emission intensity of sample reached the most intense. Subsequently, exceeding 0.01 mol, the emission intensities of Tm<sup>3+</sup> began to decrease gradually owing to concentration quenching phenomena which is induced through the resonant energy transfer.

The critical transfer distance ( $R_c$ ) was proposed by Blasse for analyzing the energy transfer mechanism, and the value can be estimated by this equation (1) [2, 21]:

$$R_c \approx 2 \left( \frac{3V}{4\pi \ x_c N} \right)^{1/3}$$

where  $x_c$  points to the critical concentration of Sm<sup>3+</sup> ions ( $x_c = 0.01$  mol), V means the volume of the host (V = 755.87 Å<sup>3</sup>), and N reveals the number of substitutable sites in a unit cell (N = 4).  $R_c$  is calculated to be 33 Å, which greatly exceeds 5 Å. That is, concentration quenching is dominantly caused by electric multipole interaction.

Furthermore, the following equation was used to evaluate specific type of interaction mechanism in the energy transfer process of  $Tm^{3+}$  ions according to the theory of Dexter [22, 23]:

$$\frac{I}{x} = K \left[ 1 + \beta \left( x \right)^{Q/3} \right]^{-1}$$
(2)



Here, Q is constant at 3, 6, 8, and 10. They represent different energy transfer interaction, such as the nearestneighbor ions (Q=3), electric dipole-dipole (Q=6), dipolequadrupole (Q=8), or quadrupole-quadrupole (Q=10) interactions, respectively. x stood for the activator concentration, K and  $\beta$  were constants at the same excitation condition. Figure 5 illustrates the linear plot. The slope parameter of the line was found to be -1.04. The Q value was fitted to 3.12, which approaches 3, indicating that the nearest neighbor ions interaction was the major for the concentration quenching reason of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> phosphors.



samples ( $\lambda_{ex} = 303 \text{ nm}$ ,  $\lambda_{em} = 468 \text{ nm}$ ).

Fig. 6 exhibits the decay curve and luminescence time of  $SrBi_2Ta_2O_9:0.01Tm^{3+}$  samples ( $\lambda_{ex} = 303 \text{ nm}$ ,  $\lambda_{em} = 468 \text{ nm}$ ). The average lifetime ( $\tau_m$ ) is calculated by the following equation [24-26]:

$$\tau_m = \frac{\int_0^\infty t \times I_{(t)} dt}{\int_0^\infty I_{(t)} dt}$$
(3)

in which I(t) denotes the PL intensity at time t. As shown, the average lifetimes of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> sample was 1.670 ms.

The CIE chromaticity coordinate is a vital parameter to evaluate the performance of the synthesized phosphor in W-LED. The CIE chromaticity diagram of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:xTm<sup>3+</sup> (x = 0.005-0.30 mol) under 303 nm

(1)

excitation were displayed in Figure 7 with the red stars (x = 0.1334, y = 0.0474). The color purity of the obtained phosphors can be calculated via Eq.(4)[27]:

$$Color \ purity = \sqrt{\frac{(x-x_i)^2 + (y-y_i)^2}{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100$$
(4)

where  $(x_d, y_d)$  is the chromaticity coordinates of dominant wavelength point, the  $(x_i, y_i)$  is the illuminant point, (x, y)is the calculated CIE coordinates [23]. The calculated color purity of the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:0.01Tm<sup>3+</sup> were about 96.8%, which was superior to KBaBP<sub>2</sub>O<sub>8</sub>:Tm<sup>3+</sup> (93.3%). Meanwhile, it can be found that they were very approximate to standard blue position of the BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup>, indicating that SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> possessed a high color purity and emitted blue light excited by UV light effectively.



## 4 Conclusions

Solid-state reaction method was successfully used to prepare the  $SrBi_2Ta_2O_9:Tm^{3+}$  phosphors with different concentration. When excited at 303 nm, the  $SrBi_2Ta_2O_9:Tm^{3+}$  phosphors presented main emission peaks at 468 nm. The highest relative intensity was at 0.01 mol doping level, after that, concentration quenching occurred due to the interaction of the nearest-neighbor ion. The critical distance related to concentration quenching to be 33 Å. The CIE color coordinate were close to the standard blue position. These indicated that the phosphor can emit blue light with high purity. In conclusion, the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>:Tm<sup>3+</sup> phosphor is a promising blue-emitting candidate for W-LEDs.

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