Structure and Photoluminescence Properties of Sm$^{3+}$ Ion-Doped LiSrBiTeO$_6$ Phosphor

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Abstract. A series of novel Sm$^{3+}$-doped LiSrBiTeO$_6$ red-emitting phosphors were prepared by the solid-state reaction method for the first time. Its crystal structure and luminescence are investigated. The excitation spectrum indicates that the LiSrBiTeO$_6$:Sm$^{3+}$ phosphor can be excited efficiently under 405 nm irradiation, which matches well with the output wavelength of UV LED chips. The photoluminescence spectrum of LiSrBiTeO$_6$:Sm$^{3+}$ phosphor shows four peaks assigned to the $^4G_{5/2}$ to $^6H_J$ ($J = 5/2$, 7/2, 9/2, and 11/2) transitions of Sm$^{3+}$. The strong peak emits bright red luminescence at 645 nm. The luminescence intensity keeps increasing with increasing the content of Sm$^{3+}$ to 5 mol%. The critical transfer distance of Sm$^{3+}$ is calculated as 17 Å. All results indicated that LiSrBiTeO$_6$:Sm$^{3+}$ phosphors have potential application as red phosphors for near-UV chip-based white light-emitting diode and display devices.

1. Introduction

In the past decades, white light emitting diodes (w-LEDs) are undergoing rapid development and will gradually replace the conventional incandescent and fluorescent lamps which features the advantages of mercury-free operation, long lifetime, and energy-saving [1, 2]. At present, the commercial w-LED configuration is based on the combination of a InGaN blue chip and a YAG:Ce$^{3+}$ yellow phosphor. The type of W-LEDs brings out low color rendering index (CRI) and high color temperature due to the lack of red color [3-6]. Therefore, it is still necessary to develop new red-emitting phosphors with good color purity and high absorption in near UV or blue wavelength region.

Recent studies have found that the bismuthate can be an excellent host for luminescence materials due to its excellent physical, chemical and mechanical properties. Meanwhile, Bi$^{3+}$ ions are also very good sensitziers of luminescence, which can efficiently absorb the UV light and transfer the energy to the luminescence center. Many bismuthate compounds have been investigated as potential candidates for photoluminescent material, such as BiPO$_4$:Eu$^{3+}$ [7], SrBi$_2$TeO$_7$:Eu$^{3+}$ [8], Bi$_4$Si$_2$O$_9$:Eu$^{3+}$ [9], Bi$_4$Ti$_5$O$_{12}$:Er$^{3+}$ [10], Bi$_2$MoO$_6$:Sm$^{3+}$ [11], Bi$_3$TiNbO$_9$:Er$^{3+}$:Yb$^{3+}$ [12], etc.

To the best of our knowledge, no reports have been discovered on Sm$^{3+}$-doped bismuthate tellurate LiSrBiTeO$_6$ phosphors. In this context, we successfully prepared the LiSrBi$_{1-x}$Sm$_x$TeO$_6$ ($x = 0.01$–0.45) red-emitting phosphors and investigated the crystal structure, photoluminescence (PL) properties and its applications in w-LEDs.
2. Experimental Procedure

Sm$^{3+}$-activated Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$ phosphors ($x = 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, 0.40$, and $0.45$) were prepared by the conventional solid-state reaction technique. High purity raw materials are Li$_2$CO$_3$ (A.R.), SrCO$_3$ (A.R.), Bi$_2$O$_3$ (A.R.), TeO$_2$ (A.R.), and Sm$_2$O$_3$ (99.99%). Subsequently, the mixture was weighed per the following balanced equation. Samples were ground together in an agate mortar and transferred into an alumina crucible heated at 800 °C for 8 h.

X-ray powder diffraction (XRD) were done with D2 PHASER (Bruker, Germany) with Cu Kα radiation ($\lambda = 0.15405$ nm). The composition analysis has been carried out using a JEOL JSM-6490F emission scanning electron microscope (SEM). And then the photoluminescence spectra were performed with a Hitachi F-4600 fluorescence spectrophotometer with 150 W Xenon lamp used as an excitation source. The decay curves were examined on the Edinburgh FLS 980 spectrometer.

3. Results and discussion

Figure 1 Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$ cell and the coordination environments therein (The red ones are oxygen atoms. Meanwhile, green balls are strontium/bismuth atoms, the gray ones are lithium atoms, and the yellow ones are tellurium atoms).

Figure 1 illustrates the crystal structure of Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$. It is a primitive cubic cell and adopts space group $Fm \overline{3} m$ [13]. As showed in Fig. 1, Bi$^{3+}$ and Sr$^{2+}$ jointly occupy the same site 8c with twelve oxygen atoms around them, forming [Bi/Sr]O$_{12}$ polyhedra. The bond lengths between the 8c site and these oxygen atoms are 2.8557 Å. In the forming of TeO$_6$ octahedron, the Te$^{6+}$ atoms occupy the octahedral 4a sites surrounded by six O atoms. The bond lengths between Te$^{6+}$ atom and six oxygen atom are 1.7366 Å.

XRD patterns of representative Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$:0.05Sm$^{3+}$ phosphors ($x = 0.01, 0.40$, and $0.45$) are presented in Fig. 2. The simulation pattern of Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$ obtained by using the reported crystallographic data [13] is taken as a standard. XRD peaks are well matched with the standard card, which indicates that the synthesized phosphors of a single phase. For the composition of Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$:0.05Sm$^{3+}$, the unit cell lattice parameters and the volume of the matrix are $a = b = c = 8.032$ Å and $V = 518.17$ Å$^3$, which are consistent with previously reported results [13]. As the ionic radii for the Bi$^{3+}$ and Sm$^{3+}$ ions were around 1.053 Å and 1.079 Å (coordination number, CN = 8) [14], the Bi$^{3+}$ ions could be easily taken place by Sm$^{3+}$ ions without inducing any distinct changes to the structure of the Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$ host lattice. The surface morphology and particle sizes of the synthesized phosphor are important for their applications in commercial WLEDs. Fig. 3 shows the SEM micrograph of a representative of Li$_{1-x}$Sr$_x$Bi$_x$TeO$_6$:0.05Sm$^{3+}$ sample. The product mainly consists of solid microcrystalline structures with some conglomeration among the crystalline grains because of the high temperature of heat treatment. Meanwhile, the particle sizes vary from a few microns to several tens of microns.
Figure 2 XRD patterns of LiSrBi(1-x)Sm_xTeO_6 phosphors (x = 0.01, 0.10, and 0.45).

Fig. 3 SEM micrograph of a representative of LiSrBiTeO_6:Sm^{3+} sample.

Figure 4 Excitation spectra of LiSrBiTeO_6:Sm^{3+} phosphor (λ_ex = 563, 598, 645 nm).

Figure 5 Emission spectra of LiSrBiTeO_6:Sm^{3+} phosphor (λ_em = 377, 405, 479 nm).

Fig.4 illustrates the representative of the excitation spectra of the LiSrBiTeO_6:Sm^{3+} phosphors under different monitoring wavelengths (λ_em = 563, 598, 645 nm). The broad excitation band (~326 nm) is ascribed to the host absorption of 1S_0→3P_1 (~300 nm) of Bi^{3+} ions and the O_2→Sm^{3+} ions charge-transfer band (CTB) [15]. A sequence of sharp excitation bands between 300 and 500 nm was attributable to the intra-configurational 4f–4f transitions of Sm^{3+} in the matrix. The sharp peaks located at 377 (^6H_5/2→^4D_1/2), 405 (^6H_5/2→^4F_7/2), and 478 (^6H_5/2→^4I_{15/2}), which are attributed to the f–f forbidden transitions of Sm^{3+}[16-18]. Obviously, the intensity of the f–f transition at 405 nm is higher than that of the other transitions. A suitable red-emitting ultraviolet light-emitting diode (UV-LED) phosphor should show an absorption of around 400 nm (LED excitation wavelength). Therefore, the LiSrBiTeO_6:Sm^{3+} phosphor has a potential value for near UV-based LEDs.

Upon 377, 405, 479 nm excitation, the photoluminescence (PL) emission spectra of the LiSrBiTeO_6:Sm^{3+} phosphors were presented in Fig. 5. It was observed that the emission spectra did not show any other changes except for the luminescence intensity under different excitation wavelengths. Clearly, the PL emission spectrum was dominated by a strong red emission with a center of about 645 nm due to the ^4G_5/2→^4H_9/2 transition. Meanwhile, there also existed some relatively weak excitation main peaks at 562, 596, and 707 nm, which are attributed to the 4f–4f transitions of Sm^{3+} ions from the excited state of ^4G_5/2 to ^6H_{5/2}, ^6H_{7/2}, and ^6H_{11/2}, respectively. Among these transitions, the first one at 562 nm (^4G_5/2→^6H_{5/2}) is a magnetic-dipole (MD) transition, and the third at 645 nm (^4G_5/2→^4H_{9/2}) is purely electric-dipole (ED) transition sensitive to the crystal field [19, 20]. According to Judd–Ofelt
theory, the intensity ratio of $^4G_{5/2} \rightarrow ^6H_{9/2}$ to $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition is a good way to determine the symmetry of the local environment around the Sm$^{3+}$ ions [21]. The asymmetric nature is more prominent when the intensity of the ED transition is higher, and vice versa. In our work, the observed $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition (645 nm, ED) transition has much higher intensity than the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition (562 nm, MD), which specifies the asymmetry nature of the host matrix. It is consistent with the site symmetry of Bi$^{3+}$ and the above mentioned crystalline structure of LiSrBiTeO$_6$.

Figure 6 All the excitation and emission spectra of LiSrBi$_{(1-x)}$Sm$_x$TeO$_6$ ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, 0.40,$ and $0.45$) ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 645$ nm). The inset displays that the integrated excitation and emission intensity of LiSrBi$_{(1-x)}$Sm$_x$TeO$_6$ phosphors as a function of the Sm$^{3+}$ concentration.

Figure 7 The $lg(I/x)$-$lg(x)$ plot and linear fitting for LiSrBiTeO$_6$:$x$Sm$^{3+}$ phosphors.

Figure 6 displayed the composition-dependent both excitation and emission spectra of LiSrBi$_{(1-x)}$Sm$_x$TeO$_6$ ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, 0.40,$ and $0.45$) ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 645$ nm). The shapes of the excitation and emission spectra at different concentrations were very alike except for the intensities. The insets depict the concentration-dependent excitation and emission intensities of LiSrBi$_{(1-x)}$Sm$_x$TeO$_6$. The changing trend of the PL spectra is the same. When Sm$^{3+}$ doping concentration exceeds 5 mol%, the intensities of Sm$^{3+}$ excitation and emission begin to decrease, namely, concentration quenching happen.

In general, the distance between the Sm$^{3+}$ luminescent centers decreases with the increase of the doping concentration. It results in non-radiative energy transfer dominant and concentration quenching effect happens. The critical distance ($R_c$) between the activated ions in phosphors can be evaluated by the below formula given by the Equation (1) [22]:

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

Where $N$ means the formula units per unit cell, $x_c$ represents the critical concentration of Sm$^{3+}$, $V$ is the volume of the unit cell. By taking the appropriate values of $N$, $V$, and $x_c$ ($4, 518.17$ Å$^3$, and $0.05$, respectively) for LiSrBiTeO$_6$:0.05Sm$^{3+}$ phosphor, $R_c$ is estimated to be 17 Å, which was greater than 5 Å, indicating that the concentration quenching mechanism of Sm$^{3+}$ ions was mainly ascribed to the multipole-multipole interaction.

According to Dexter’s theory, if the energy transfer occurs between the same sorts of activators, the multipolar interaction can be determined from the change of the emission intensity from the emitting level which has a multipolar interaction. The emission intensity ($I$) per activator ion is given by the formula [23]:

$$
I = I_0 \left( 1 - \frac{C_1}{x_c} \right)^{1/3}
$$

where $I_0$ is the emission intensity at zero concentration, $C_1$ is the multipole-multipole interaction coefficient.
\[
\frac{I}{x} = K \left[ 1 + \beta (x)^{Q/3} \right]^{-1}
\]  
(2)

where \(\chi\) is the activator concentration; \(Q\) is a constant of multipolar interaction and equals 3, 6, 8, or 10 corresponding to the nearest-neighbor ions, dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interaction, respectively; \(K\) and \(\beta\) are constants for the given host at the same excitation condition [23, 24]. Then we use this equation to fit the experimental results of the relationship between integrated emission intensity and \(\text{Sm}^{3+}\) concentration. The content dependence curve of \(\log I / x\) vs. \(\log x\) in \(\text{LiSrBiTeO}_6: \text{Sm}^{3+}\) phosphor based on Fig. 6 is shown in Fig. 7. The figure clearly shows that the relation between \(\log I / x\) and \(\log x\) is approximately linear and the slope is about -1.98. The \(Q\) value calculated based on the linear fitting using Eq. (2) is 6.0. This finding indicates that the concentration quenching for \(\text{Sm}^{3+}\) luminescence centers should be derived from dipole–dipole interaction in the \(\text{LiSrBiTeO}_6: \text{Sm}^{3+}\) phosphor.

Figure 8 Decay curve of \(\text{LiSrBiTeO}_6: x\text{Sm}^{3+}\) (\(x = 0.01, 0.10, 0.30, \text{and} 0.45\)) at room temperature when \(\lambda_{\text{ex}} = 405\) nm and \(\lambda_{\text{em}} = 645\) nm.

The fluorescence decay time of \(\text{Sm}^{3+}\) in the phosphor \(\text{LiSrBiTeO}_6: x\text{Sm}^{3+}\) sample (\(\lambda_{\text{ex}} = 405\) nm, \(\lambda_{\text{em}} = 645\) nm) was measured at room temperature and shown in Fig. 8. The average decay can be acquired by the equation as follows:

\[
\tau_m = \frac{\int_0^\infty t \times I(t) dt}{\int_0^\infty I(t) dt}
\]  
(3)

where \(I(t)\) is the luminescence intensity at a time \(t\) of the sample. The average lifetime \(\tau_m\) of \(\text{Sm}^{3+}\) is calculated to be 0.608, 0.552, 0.448, and 0.379 ms for \(\text{LiSrBiTeO}_6: x\text{Sm}^{3+}\) (\(x = 0.01, 0.10, 0.30, \text{and} 0.45\)), respectively. The decay time of these transitions is in the millisecond range. And we can see the decay time significantly shorten with increased \(\text{Sm}^{3+}\) concentration arising from the increasing of non-radiative transition [25].

4. Conclusion

We successfully synthesized red-emitting phosphors \(\text{LiSrBiTeO}_6: \text{Sm}^{3+}\) via the solid-state reaction. The main emission peak of the samples was at 645 nm and \(\text{Sm}^{3+}\) occupied the lattice site of noncentrosymmetric environment. The optimal doping content of \(\text{Sm}^{3+}\) was 0.05 mol and the critical transfer distance of \(\text{Sm}^{3+}\) is calculated as 17 Å. The mechanism of concentration quenching of the \(\text{Sm}^{3+}\) emission in the \(\text{LiSrBiTeO}_6\) phosphors is ascribed to the energy transfer among the electric dipole-dipole interaction. The fluorescence lifetime of the \(\text{LiSrBiTeO}_6:0.10\text{Sm}^{3+}\) phosphor was measured to be 0.552 ms. The results suggest that the phosphors have potential applications in displays and lighting.
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