Synthesis of novel Dy$^{3+}$-activated LiSrBiTeO$_6$ phosphors for white light-emitting diodes

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Abstract. Novel yellow-light-emitting LiSrBiTeO$_6$:xDy$^{3+}$ ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, \text{and} 0.40$) phosphors were synthesized. X-ray diffraction (XRD) results revealed that the prepared LiSrBiTeO$_6$:Dy$^{3+}$ phosphors are hexagonal structure. The luminescence properties showed that the phosphor can be effectively excited by UV light (388 nm) and exhibits bright emission centered at 484, 575, and 663 nm, attributed to the $^4F_{9/2}\rightarrow^6H_{15/2}$, $^4F_{9/2}\rightarrow^6H_{13/2}$, and $^4F_{9/2}\rightarrow^6H_{11/2}$ transitions of Dy$^{3+}$ ions, respectively. The optimum dopant concentration of Dy$^{3+}$ ions in LiSrBiTeO$_6$:xDy$^{3+}$ was around 10 mol% and the critical transfer distance of Dy$^{3+}$ was calculated as 14 Å. The CIE color coordinates fall into the yellow-light region. The developed phosphor has great potential as a yellow-light-emitting phosphor for UV-light-emitting diodes.

1. Introduction
Dy$^{3+}$ has attracted a lot of attention in the field of white-emitting phosphors. Because Dy$^{3+}$ with 4$f^7$ configuration has abundant f-block energy levels and strong emission in the visible range [1], Dy$^{3+}$ generally exhibits two major emissions. One is blue (488 nm) emission associating with $^4F_{9/2}\rightarrow^6H_{15/2}$ transition, the other is yellow (580 nm) associating with $^4F_{9/2}\rightarrow^6H_{13/2}$ transition ($\Delta L = 2; \Delta J = 2$), besides, we also find the feeble red emission (665 nm) due to $^4F_{9/2}\rightarrow^6H_{11/2}$ transition.

Bismuth is widely known as “green metal” due to its nontoxic and harmless properties, and it also possesses good X-ray attenuation properties [2]. Recent studies have found that the bismuthate can be an excellent host for luminescence materials due to its excellent physical, chemical and mechanical properties. LiSrBiTeO$_6$ is a primitive cubic cell and adopts space group $Fm\overline{3}m$ [3]. In the crystal structure, Bi$^{3+}$ and Sr$^{2+}$ jointly occupy the same site 8c with twelve oxygen atoms around them, forming [Bi/Sr]O$_{12}$ polyhedra. In the forming of TeO$_6$ octahedron, the Te$^{6+}$ atoms occupy the octahedral 4$a$ sites surrounded by six O atoms. 2018, LiSrBiTeO$_6$:Eu$^{3+}$ red-emitting phosphors were synthesized and can be efficiently excited by 394 nm and 465 nm light and emitted bright red luminescence at 616 nm [4]. But as we all know, Dy$^{3+}$-doped bismuthate LiSrBiTeO$_6$ are not studied in detail.

In this study, we prepared different concentrations of novel LiSrBi$_{1-x}$Dy$_{x}$TeO$_6$ ($x = 0.005-0.40$) phosphors, which can satisfy the demand of yellow-light phosphors induced by near-UV light. The phase purity, photoluminescence (PL) properties, the influence of doping concentration, and the chromaticity coordinate of the LiSrBi$_{1-x}$Dy$_{x}$TeO$_6$ phosphors were investigated.
2. Experimental

The synthesis of powder samples LiSrBi$_{1-x}$Dy$_x$TeO$_6$ ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30,$ and $0.40$) phosphors whose concentration of dysprosium was from 0.005 to 0.40 mol were prepared by the conventional solid-state reaction technique. Li$_2$CO$_3$ (99.99%), SrCO$_3$ (99%), Bi$_2$O$_3$ (99.99%), Dy$_2$O$_3$ (99.99%), and TeO$_2$ (99.9%) were as raw materials, thoroughly mixed and ground in an agate mortar. The mixture was heating at 800 °C for 8 h. Finally, switch off the muffle furnace and cool down the as-synthesized samples slowly to normal temperature and re-ground into a fine powder. The relevant reaction formulas are as shown below:

The crystalline phases of sintered samples were identified by XRD measurement with Cu Kα radiation ($\lambda = 1.5418$ nm) generated at 40 kV and Data collection was carried out in the range of $2\theta$=20°–70°. Furthermore, the luminescence properties of the synthetic phosphors were performed at room temperature using a fluorescence spectrophotometer (HITACHI, F-4600) equipped with 150 w lamp at room temperature.

3. Results and discussion

![Fig. 1 XRD patterns of LiSrBi$_{1-x}$Dy$_x$TeO$_6$ samples ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30,$ and $0.40$)].

The as-prepared LiSrBi$_{1-x}$Dy$_x$TeO$_6$ ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30,$ and $0.40$) samples were characterized by X-ray diffraction(XRD) patterns to verify the phase purity. As indicated in Fig. 1, all the peaks could be referred according to the patterns generated by the structural parameters given by Azimov et al. for LiSrBiTeO$_6$ [5,6]. The sample crystallized in the hexagonal crystal structure with space group P6$_3$/m. It indicated that a pure phase of Dy$^{3+}$ ions doped LiSrBiTeO$_6$ was successfully crystallized according to simulated XRD pattern of LiSrBiTeO$_6$. Due to the close radius and the same valence [7], Bi$^{3+}$ ions could be readily substituted by Dy$^{3+}$ ions, meanwhile, no significant changes in the main lattice structure of LiSrBiTeO$_6$ were induced.
Fig. 2 Excitation spectra of typical LiSrBiTeO$_6$:0.10Dy$^{3+}$ phosphor at room temperature ($\lambda_{em} = 484$, 575, 663, and 764 nm).

Fig. 2 shows the excitation spectrum of LiSrBiTeO$_6$:0.10Dy$^{3+}$ phosphor. There’s no difference between the excitation bands under different monitoring wavelengths ($\lambda_{em} = 484$, 575, 663, and 764 nm), except the excitation intensity. There was an obvious charge-transfer absorption of Dy$^{3+}$–O$^{2-}$ interaction band around 325 nm that could be detected in the UV excitation spectrum. The peak at 388 nm is the most intense, which is ascribed to $^6H_{15/2}$–$^4F_{7/2}$ transition. A series of sharp peaks are located at 340-480 nm corresponding to the intraconfigurational f–f transitions of Dy$^{3+}$ ions [8]. The excitation spectra of these phosphors show the strongest absorption at about 350-410 nm which matches well with the commercially available n-UV LED chips [9, 10].

Fig. 3 Emission spectrum of typical LiSrBiTeO$_6$:0.10Dy$^{3+}$ phosphor at room temperature ($\lambda_{ex} = 328$, 353, 366, 388, 454 nm).

Fig. 3 depicts the emission spectrum of LiSrBiTeO$_6$:0.10Dy$^{3+}$ phosphors upon excitation at different wavelengths ($\lambda_{ex} = 328$, 353, 366, 388, 454 nm). Four emission bands centered associate with 484 nm (blue), 575 nm (yellow), 663 nm (red), and 764 nm(red), which originate from transitions of $^4F_{9/2}$→$^6H_{15/2}$, $^4F_{9/2}$→$^6H_{13/2}$, $^4F_{9/2}$→$^6H_{11/2}$, and $^4F_{9/2}$→$^6H_{9/2}$ transitions of Dy$^{3+}$ respectively. The 484 nm peak results from magnetic dipole (MD) transition and is usually not sensitive to the local site symmetry, however, the 575 nm peak is a hypersensitive electric dipole (ED) transition ($\Delta L = \Delta J = 2$) and is strongly influenced by the environment/crystal field around the Dy$^{3+}$ ion [8, 11]. The fact that the 484 nm peak (MD) is weaker than the 575 nm peak (ED) indicates that the Dy$^{3+}$ ion is located at a site with low symmetry without any centre of inversion. It is consistent with the site symmetry of
Bi$^{3+}$ and the above mentioned crystalline structure of LiSrBiTeO$_6$. The Sr$^{2+}$/Bi$^{3+}$ are randomly distributed in the [Bi/Sr]O$_{12}$ polyhedra in the LiSrBiTeO$_6$ unit cell. Therefore, when Dy$^{3+}$ gets into the crystal lattice and occupies the Sr$^{2+}$/Bi$^{3+}$ site, it will experience a non-centrosymmetric local symmetry group and strongly influence its luminescence properties.

![Photoluminescence emission spectra of LiSrBiTeO$_6$:xDy$^{3+}$ phosphors at doping concentrations from 0.5 mol% to 40 mol%. Under the excitation of 388 nm, the emission intensity first increased with an increase in concentration up to 10.0 mol%, which was the optimum concentration. At higher concentrations, the non-radiative energy transfer process occurs between adjacent Dy$^{3+}$–Dy$^{3+}$ ions cause the concentration quenching. There is no difference in the emission spectra when the concentration of Dy$^{3+}$ ions is varying. The inset depicts the concentration-dependent emission intensity of LiSrBiTeO$_6$:xDy$^{3+}$.](image)

The critical distance ($R_c$) between the activated ions in phosphors can be evaluated by the Equation (1):

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

Where N refers to the number of Dy$^{3+}$ ions in the unit cell, $x_c$ represents the critical concentration of Dy$^{3+}$, V is the volume of the unit cell. By taking the experimental and analytic values of N, V, and $x_c$ (517.39 Å$^3$, 4, and 0.10, respectively), for phosphor, $R_c$ is estimated to about 14 Å, which was far greater than 5 Å, which points out that the quenching mechanism of Dy$^{3+}$ ions concentration was mainly attributed to the multipole-multipole interaction.
As an alternative, the electric multipolar interaction should be the main mechanism. According to the Dexter theory, when the doping amount of the activator ions is large enough, the luminescence intensity $I$ and the activator ions' mole fraction $x$ are as follows (2):

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

Where $\chi$ is the dopant concentration; In given host, $K$ and $\beta$ are constants for each interaction at the same excitation condition; $Q$ is an index of an electric multipole, including 6, 8, 10 for energy transfer among nearest-neighbor ions, d-d, d-q, q-q interaction, respectively. Then the experimental results of the relationship between the integrated emission intensity and the Dy$^{3+}$ concentration are obtained by using this equation. Fig.5 shows the fitting line of $\log(I/x)$ vs. $\log(x)$ in LiSrBiTeO$_6$:Dy$^{3+}$ phosphor which is on the basis of Fig.5. Obviously, the dependence of $\log(I/x)$ on $\log(x)$ is linear and the slope is about -2.10. Thus, the value of $Q$ is 6, which indicates that d-d interaction is the concentration quenching mechanism of Dy$^{3+}$ in LiSrBiTeO$_6$ phosphor.

Fig. 5 Curve of $\log(I/x)$ vs. $\log(x)$ in LiSrBiTeO$_6$:Dy$^{3+}$ phosphor ($\lambda_{ex} = 388$ nm).

![Fig.5 Curve of $\log(I/x)$ vs. $\log(x)$ in LiSrBiTeO$_6$:Dy$^{3+}$ phosphor ($\lambda_{ex} = 388$ nm).](image)

Fig. 6 shows the chromaticity color coordination values for LiSrBiTeO$_6$:Dy$^{3+}$ phosphors by 388 nm light excitation. The CIE chromaticity coordinates for LiSrBiTeO$_6$:Dy$^{3+}$ are located in $(0.429, 0.466)$, $(0.441, 0.476)$, $(0.441, 0.474)$, $(0.442, 0.473)$, $(0.439, 0.471)$, $(0.437, 0.471)$, $(0.440, 0.473)$, and $(0.457, 0.477)$ corresponding to the LiSrBiTeO$_6$:Dy$^{3+}$ phosphors ($x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, 0.40$), respectively. It is observed from Fig. 6, the chromaticity coordinates of the

![Fig. 6 CIE chromaticity coordinates of LiSrBiTeO$_6$:Dy$^{3+}$ (x = 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.30, and 0.40) phosphors.](image)
phosphors all fall into the yellow light region. The as-prepared phosphors might be applicable for the generation of yellow light emission excitable under UV light excitation.

4. Conclusions
We successfully synthesized yellow-light-emitting LiSrBiTeO$_6$:Dy$^{3+}$ phosphors via the solid-state reaction. Upon 388 nm excitation, these phosphors exhibit three emission bands centered at 484, 575, and 663 nm, which ascribes to $^4$F$_{9/2}$$\rightarrow^4$H$_{15/2}$, $^4$F$_{9/2}$$\rightarrow^4$H$_{13/2}$, and $^4$F$_{9/2}$$\rightarrow^4$H$_{11/2}$ transitions of Dy$^{3+}$, respectively. The luminescence intensities are influenced by the concentration of Dy$^{3+}$. When the concentration is about 10 mol%, we can get the maximum luminous intensity and the critical transfer distance of Dy$^{3+}$ is calculated as 14 Å. The results indicate the LiSrBiTeO$_6$:Dy$^{3+}$ has potential applications in displays and lighting.

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