A novel UV pumped white-emitting phosphor \(\text{La}_3\text{SbO}_7:\text{Dy}^{3+}\) for white light-emitting diodes

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Abstract. The dysprosium activating \(\text{La}_3\text{SbO}_7\) white-emitting phosphors were prepared via solid-state route at 1350°C in air atmosphere and its photoluminescence properties were examined by X-ray diffraction (XRD) and photoluminescence spectra in details. \(\text{La}_3\text{SbO}_7:\text{Dy}^{3+}\) phosphor with excitation at 353 nm emitted blue light (490 nm) and yellow (580 nm) which were assigned to \(4F_{9/2} \rightarrow 6H_{15/2}\) transitions (\(J=15, 13\)), respectively. Moreover, the transition \(4F_{9/2} \rightarrow 6H_{13/2}\) was the strongest emission intensity between two typical emission bands. The CIE of prepared phosphors entered into white region. The optimal emission intensity of the \(\text{La}_3\text{SbO}_7:\text{Dy}^{3+}\) luminescent materials was realized when \(x=0.15\) and the concentration quenching mechanism of \(\text{Dy}^{3+}\) has also been tested. And the \(\text{La}_3\text{SbO}_7:\text{Dy}^{3+}\) can be as a white-emitting phosphor applied in n-UV LEDs on results.

1. Introduction

Considerable interest was paid to develop w-LEDs arising from energy-saving, eco-friendliness and great prospect for commercial applications [1]. Nevertheless, most of them can’t gratify us owning to flat quantum efficiency and inferior thermal stability. At present, the commercial w-LEDs have been integrated with a blue InGaN LED (specific wavelength within the 450–480nm areas) with a yellow phosphor, \(\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}\) (YAG: Ce\(^{3+}\)) [2]. High color temperature and low color rendering index (CRI) have been brought out by the kind of W-LEDs because of the shortage of red color. To make use of near-UV LEDs chips coupled with multi-phosphors of red, green and blue phosphor is some other useful method [3, 4].

Being a significant activator, \(\text{Dy}^{3+}\) ions emit tricolor emission bands to achieve white light in a single-phase which are assigned to \(4F_{9/2} \rightarrow 4H_{15/2}\) at 488 nm (blue) and \(4F_{9/2} \rightarrow 4H_{13/2}\) at 580 nm (yellow), and \(4F_{9/2} \rightarrow 4H_{11/2,1}\) at 680 nm (red) [2, 5]. According to reports, the antimonate can be hosts for phosphors because of great optical properties.

As is well known for all, no report has been covered on \(\text{Dy}^{3+}\)-doped \(\text{La}_3\text{SbO}_7\) phosphors. From this perspective, the \(\text{La}_{3-x}\text{Dy}_x\text{SbO}_7\) (\(x=0.02–0.25\)) is successfully prepared and its photoluminescence (PL) characteristics as well as applications within W-LEDs are investigated comprehensively and systematically.
2. Experimental Procedure

The powder samples La$_{3-x}$Dy$_x$SbO$_7$ ($x = 0.02, 0.05, 0.08, 0.10, 0.15, 0.20$, and 0.25) was synthesized by conventional solid state reaction in air. The doped concentration of Dy$^{3+}$ was altered from 2 to 25 mol%. The starting materials La$_2$O$_3$ (A.R.), Sb$_2$O$_3$ (A.R.) and Dy$_2$O$_3$ (99.99%) were mixed and ground homogeneously. Mixtures were preheated at 600 °C in air for 3 h in an alumina crucible and then reground. After that, the final products would be obtained by keeping at 1350 °C for 5 h. As we can see, the correlated chemistry reaction is as follows:

\[
\text{Sb}_2\text{O}_3 + (3-x)\text{La}_2\text{O}_3 + x\text{Dy}_2\text{O}_3 \xrightarrow{1350°C \times 5h} 2\text{La}_{3-x}\text{Dy}_x\text{SbO}_7
\]

X-ray powder diffraction (XRD) patterns which are about samples were showed by Philips X’Pert MPD (Philips, Netherlands) with Cu Kα radiation ($λ = 1.5418$ Å). The data of structural properties were taken out in the range of 2θ = 10°−70°. And the photoluminescence properties of the synthesized phosphors were recorded at room temperature via the F-4600 spectrometer (Hitach, Japan).

3. Results and discussion

![Figure 1 XRD pattern for the La$_{3-x}$SbO$_7$: xDy$^{3+}$ phosphors (x= 0.05, 0.08, 0.10, 0.15, 0.20 and 0.25).](image)

The XRD is used to describe the phase purity of the La$_3$SbO$_7$:Dy$^{3+}$ phosphors. As is showed in the Fig. 1, the standard card (No.23-1138) is in red for the La$_3$SbO$_7$ and all the diffraction peaks of the sample were indexed to its. There are not any impurity peaks that can be observed indicating that successfully synthesized phosphors are single-phase. The comparisons indicate that the La$^{3+}$ ions were occupied perfectly by Dy$^{3+}$ ions in La$_3$SbO$_7$ are the result of the close ionic radius of Dy$^{3+}$ (0.912 Å) and La$^{3+}$ (1.16 Å) when coordination number = 6.

![Figure 2 Excitation spectra of La$_3$SbO$_7$:0.15Dy$^{3+}$ phosphor (λ$_{em} =$ 480 nm).](image)
Fig. 2 depicts the excitation spectra of La3SbO7:0.15Dy3+ phosphor monitored at 480 nm. Other sharp PLE peaks were observed in the range from 250 to 425 nm are attributed to f–f transition of Dy3+ ions [6]. The main excitation band centered at 322, 360 and 382 nm corresponded to the 6H15/2 → 4P3/2, 6H15/2 → 4P7/2 and 6H15/2 → 4F7/2 transition, respectively [7]. The strongest peak is at 346 nm which results from 6H15/2 → 4I15/2 transition. Thus, the La3SbO7:Dy3+ phosphors may be suitable for w-LEDs which is built on InGaN-chip.

In the Fig. 3, the emission spectra of La3SbO7:0.15Dy3+ contains two emission bands at 450-750 nm corresponding to the 4F9/2 → 6HJ/2 (J = 15, 13) transitions of Dy3+ respectively when is excited with 346 nm. And the two sharp lines center at 480 nm (blue), 581 nm (yellow). To our knowledge, 4F9/2 → 6H13/2 transition of Dy3+ attributes to hypersensitive transitions. When it is stronger than 4F9/2 → 6H15/2 transition, Dy3+ is at a low-symmetry local site. And then the yellow emission performs a leading role in emission spectra. Otherwise the result is inverse [8, 9]. In our experiment, it displays that the blue emission is a leading role. So it is clear to know that Dy3+ ions mainly occupy in high-symmetrical site.

The La3SbO7:xDy3+ phosphors are synthesized with different doping concentrations of Dy3+ (ranging from 0.02 to 0.25) and the PL intensities are exhibited in Figure 4. It obviously presents that the emission intensity keeps increasing when Dy3+ concentration ranges from 2 mol% to 25 mol%, and after that it decreases. Therefore, the optimal doping Dy3+ ion content for La3SbO7:xDy3+ phosphor is about 15 mol%.

According to Blasse, the critical energy transfer distance (Rc) between Dy3+ ions in La3-xDy3SbO7 phosphors can be calculated as follows [10]:

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

(1)

where \( V \) means the unit cell volume, \( x_c \) is the critical concentration of Dy\(^{3+} \) and \( N \) represents the number of cations in the unit cell. In the \( \text{La}_3\text{SbO}_7: \text{Dy}^{3+} \) phosphors \( V, N, \text{and} \ x_c \), 640.48 Å\(^3\), 4, and 0.15, the \( R_c \) can be worked out to be about 29 Å. The calculated \( R_c \) is larger than 5 Å, therefore, the multipole–multipole interaction mainly could be the concentration quenching mechanism of Dy\(^{3+} \) ions.

Non-radiative energy transition results from three reasons: radiation reabsorption, an exchange interaction or multipole–multipole interaction. The emission intensity (\( I \)) per dopant concentration follows the equation [11]:

\[ \frac{I}{x} = K [1 + \beta(x)^{\theta/3}]^{1/\theta} \]  

(2)

where \( \chi \) represents the activator doping concentration, \( K \) and \( \beta \) are constants for the same excitation for each interaction, \( \theta \) equals 3, 6, 8, or 10, meaning nearest-neighbor ions, dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interaction, respectively [12,13]. The relation between \( \log I/x \) and \( \log x \) is shown in Fig. 5, which is nearly linear. And the curves clearly shows that the slope is -0.99, whose linear fitting is \(-\theta/3\). Therefore, \( \theta = 3 \), demonstrating that the energy transfer is dominated to result in concentration quenching in the \( \text{La}_3\text{SbO}_7: \text{Dy}^{3+} \) phosphor.

The CIE chromaticity diagram of Dy\(^{3+}\)-doped \( \text{La}_3\text{SbO}_7 \) were measured under 346 nm excitation in the light of the PL spectra. As is presented in Fig. 6, all the CIE chromaticity coordinates denoted as stars...
of La₃SbO₇:xDy³⁺ locate at the white light region. Hence, La₃SbO₇:Dy³⁺ phosphor may possess a potential application for WLEDs exciting at 346 nm.

4. Conclusion

In short, a series of antimonate white-emitting La₃SbO₇: Dy³⁺ phosphors have been successfully synthesized via solid-state-reaction method. As is presented in the XRD patterns, the space group P2₁/c where all the samples crystallize in it. In the PL spectrum of phosphor for La₃SbO₇: Dy³⁺, a strong blue-emitting emission is showed as well as the yellow-emitting emission exciting at 346 nm, which originate from Dy³⁺ ions. The phosphor appeared concentration quenching phenomenon when the doping concentration was studied at 15 mol%. The CIE chromaticity coordinates suggested the phosphor can emit white light. All above properties indicated the Dy³⁺-activating La₃SbO₇ phosphors possess potential value for the application of white light-emitting diode.

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