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A novel UV pumped white-emitting phosphor La_3SbO_7:Dy^{3+} for white light-emitting diodes

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Abstract. The dysprosium activating La_3SbO_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. La_3SbO_7:Dy^{3+} phosphor with excitation at 353 nm emitted blue light (490 nm) and yellow (580 nm) which were assigned to $^4F_{9/2}$–$^6H_{J/2}$ transitions (J=15, 13), respectively. Moreover, the transition $^4F_{9/2}$–$^6H_{13/2}$ 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 La_3SbO_7:Dy^{3+} luminescent materials was realized when x= 0.15 and the concentration quenching mechanism of Dy^{3+} has also been tested. And the La_3SbO_7: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, $Y_3Al_5O_{12}$: 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, Dy^{3+} ions emit tricolor emission bands to achieve white light in a single-phase which are assigned to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ at 488 nm (blue) and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ at 580 nm (yellow), and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ 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 Dy^{3+}-doped La_3SbO_7 phosphors. From this perspective, the $La_{3-x}Dy_xSbO_7$ (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 $La_{3-x}Dy_xSbO_7$ (x = 0.02, 0.05, 0.08, 0.10, 0.15, 0.20, and 0.25) was synthesized by conventional solid stated reaction in air. The doped concentration of Dy^{3+} was altered from 2 to 25 mol%. The starting materials La_2O_3 (A.R.), Sb_2O_3 (A.R.) and Dy_2O_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:

$$Sb_2O_3+(3-x)La_2O_3+xDy_2O_3 \xrightarrow{1350℃\times 5h} 2La_{3-x}Dy_xSbO_7$$

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

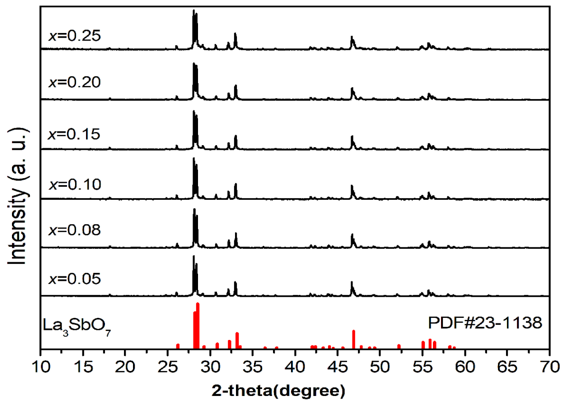

Figure 1 XRD pattern for the $La_{3-x}SbO_7$: $x Dy^{3+}$ phosphors (x= 0.05, 0.08, 0.10, 0.15, 0.20 and 0.25).

The XRD is used to describe the phase purity of the La_3SbO_7:Dy^{3+} phosphors. As is showed in the Fig. 1, the standard card (No.23-1138) is in red for the La_3SbO_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_3SbO_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.

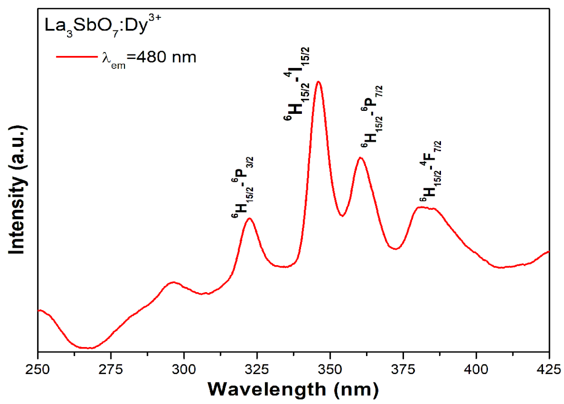

Figure 2 Excitation spectra of La_3SbO_7:0.15Dy^{3+} phosphor (λ_{em} = 480 nm).

Fig. 2 depicts the excitation spectra of La_3SbO_7:0.15Dy^{3+} 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 Dy^{3+} ions [6]. The main excitation band centered at 322, 360 and 382 nm corresponded to the $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$ and $^6H_{15/2} \rightarrow {}^4F_{7/2}$ transition, respectively [7]. The strongest peak is at 346 nm which results from $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition. Thus, the La_3SbO_7:Dy^{3+} phosphors may be suitable for w-LEDs which is built on InGaN-chip

In the Fig. 3, the emission spectra of La_3SbO_7:0.15Dy^{3+} contains two emission bands at 450-750 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{J/2}$ (J = 15, 13) transitions of Dy^{3+} respectively when is excited with 346 nm. And the two sharp lines center at 480 nm (blue), 581 nm (yellow). To our knowledge, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} attributes to hypersensitive transitions. When it is stronger than $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, Dy^{3+} 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 Dy^{3+} ions mainly occupy in high-symmetrical site.

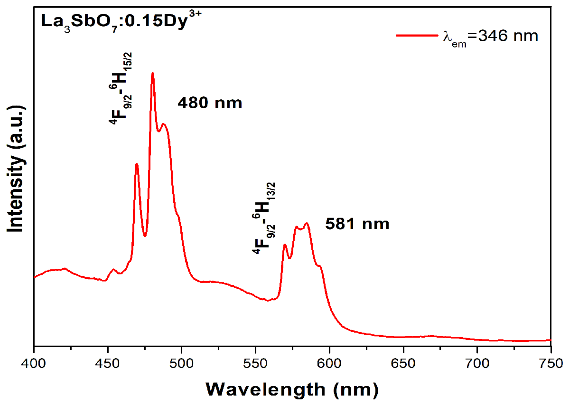

Figure 3 Emission spectra of La_3SbO_7:0.15Dy^{3+} phosphor (λ_{ex}= 346 nm).

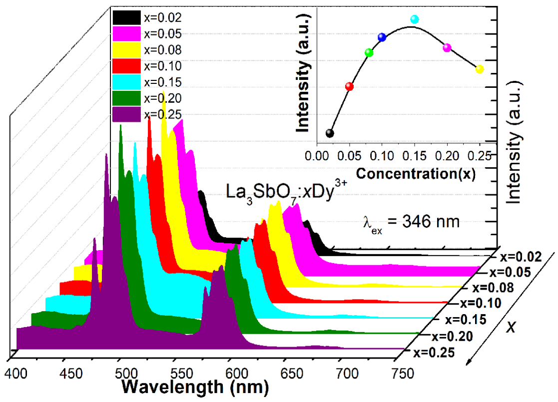

Figure 4 Luminescence spectra of $La_{3-x}Dy_xSbO_7$ phosphor (x = 0.02, 0.05, 0.08, 0.10, 0.15, 0.20, and 0.25) at different doped concentrations.

The La_3SbO_7:$x$$Dy^{3+}$ phosphors are synthesized with different doping concentrations of Dy^{3+} (ranging from 0.02 to 0.25) and the PL intensities are exhibited in Figure 4. It obviously presents that the emission intensity keeps increasing when Dy^{3+} concentration ranges from 2 mol% to 25 mol%, and after that it decreases. Therefore, the optimal doping Dy^{3+} ion content for La_3SbO_7:$x$$Dy^{3+}$ phosphor is about 15 mol%.

According to Blasse, the critical energy transfer distance (R_c) between Dy^{3+} ions in $La_{3-x}Dy_xSbO_7$ phosphors can be calculated as follows [10]:

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

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 $La_3SbO_7:Dy^{3+}$ phosphors V, N, 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.

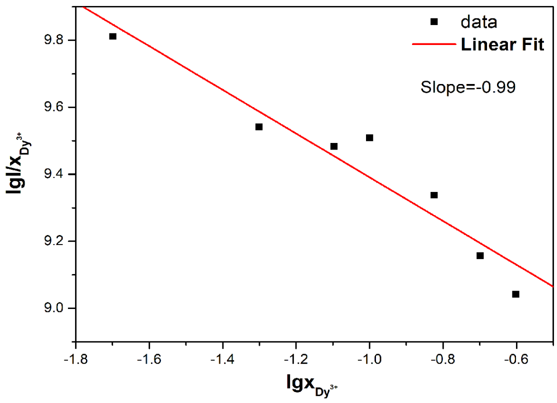

Figure 5 Curve of lgI /x vs. lgx in La_3SbO_7: xDy^{3+} phosphor (λ_{ex} = 346 nm).

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]:

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

where χ represents the activator doping concentration, K and β are constants for the same excitation for each interaction, θ equals 3, 6, 8, or 10, meaning nearest-neighbor ions, dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interaction, respectively [12,13]. The relation between lgI/x and lg$x$ is shown in Fig. 5, which is nearly linear. And the curves clearly shows that the slope is -0.99, whose linear fitting is -θ/3. Therefore, θ = 3, demonstrating that the energy transfer is dominated to result in concentration quenching in the $La_{3-x}Dy_xSbO_7$ phosphor.

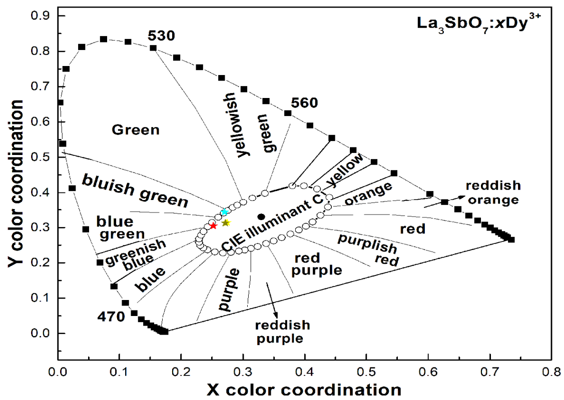

Figure 6 CIE chromaticity coordinates for the La_3SbO_7:xDy^{3+} sample.

The CIE chromaticity diagram of Dy^{3+}-doped La_3SbO_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 La_3SbO_7:$x$$Dy^{3+}$ locate at the white light region. Hence, La_3SbO_7:Dy^{3+} phosphor may possess a potential application for WLEDs exciting at 346 nm.

4. Conclusion

In short, a series of antimonate white-emitting La_3SbO_7: Dy^{3+} phosphors have been successfully synthesized via solid-state-reaction method. As is presented in the XRD patterns, the space group $P2_1/c$ where all the samples crystallize in it. In the PL spectrum of phosphor for La3SbO7: Dy^{3+}, a strong blue-emitting emission is showed as well as the yellow-emitting emission exciting at 346 nm, which originate from Dy^{3+} 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 Dy^{3+}-activating La_3SbO_7 phosphors possess potential value for the application of white light-emitting diode.

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