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Effect of Tb^{3+} Doping Concentration on Luminescent Properties of $Sr_3B_2O_6$ Phosphor

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Authors' contributions

This work was carried out in collaboration between all authors. Author HVT with the help of authors NMS and VXQ designed the study, synthesized the samples, measured and analyzed the characteristic of phosphors. All authors read and approved the final manuscript.

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ABSTRACT

The $Sr_3B_2O_6:Tb^{3+}$ phosphors with different concentration of Tb^{3+} were prepared by combustion method combination with heating at high-temperature. Results of the crystalline structure measurement indicate that the $Sr_3B_2O_6:Tb^{3+}$ phosphors have a Rhomboidal single phase. The excitation spectra show that the phosphors can be excited by ultraviolet light of near 379 nm. The emission spectra under 379 nm excitation includes several narrow lines, which is $^5D_4$-^7F_i (j = 2, 3, 4, 5, 6) transitions of Tb^{3+} ion in the lattice.

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The emission intensity of Tb^{3+} in $Sr_3B_2O_6$ is influenced by the Tb^{3+} doping content and optimum concentration is 3%mol. The concentration quenching of Tb^{3+} in this phosphor occurs when Tb^{3+} concentration is over 3%mol. The concentration quenching mechanism was determined dipole-quadrupole (d-q) interaction by using Dexter's theory.

Keywords: Terbium; $Sr_3B_2O_6$; combustion method; concentration quenching.

1. INTRODUCTION

The development of luminescent materials doped with rare-earth activator is subject of extensive researches for a long time, including such applications as fluorescent lamps, light emitting diodes, field emission displays and many others. In the field of white light emitting diodes (wLED), wLED was obtained by using a blue LED chip and the yellow-emitting phosphor [1]. Besides, many efforts have been made in the search of a phosphor, which can convert ultraviolet (UV) or blue light into a combination of red-green-blue light to obtain white light emission. For this reason, it is necessary to develop green emitting phosphor in the field of optical materials. Among the green emitting phosphors, $Sr_3B_2O_6:Tb^{3+}$ has main emission wavelength at 542 nm, it have potential application for UV-convertible green phosphors in wLED.

Until now, there are not yet many reports on the spectroscopy properties of th Tb^{3+} doped $Sr_3B_2O_6$ phosphor. In recent years, the detail studies on Tb^{3+} were realized in the several materials: $K_3Gd\ (PO_4)_2:Tb^{3+}$, $Y_4Al_2O_9:Tb^{3+}$, $Ca_2BO_3Cl:Ce^{3+}$, Tb^{3+} [2-4]. On the other hand, the luminescent materials base on $Sr_3B_2O_6$ lattice have only prepared by solid-state reaction method [5,6], sol-gel method [7]. This paper presents the synthesis of the $Sr_3B_2O_6:Tb^{3+}$ phosphors by combustion method, the studies the effect of Tb^{3+} ion concentration on luminescent properties and the concentration quenching mechanism in this phosphor.

2. EXPERIMENTAL DETAILS

The $Sr_3B_2O_6$: Tb^{3+} phosphors with different concentration of Tb^{3+} were fabricated by urea - nitrate solution combustion method combination with heating at high-temperature. The raw materials include $Sr(NO_3)_2$ (Merck), H_3BO_3 (AR), Tb_4O_7 (Sigma). Terbium oxide was been nitrified to become nitrate solution of Terbium. Urea (NH_4NO_2) was used to supply fuel for combustion process.

Aqueous solution containing stoichiometric amounts of nitrate metals and urea was mixed and heated at 70ºC by magnetic stirrer in 2 hours to become a gel. Next, the gel was combusted at 590ºC in 7 minutes then it was decreased down to room temperature, the powder was obtained. The powder was heated at 900ºC in air within 1 hour, the final obtained product is white powder.

The phase structure of the products were characterized by X-ray diffraction (XRD) using a Bruker D8-Advance X-ray diffractometer. The emission and excitation spectra were recorded by a Fluorog 3-22 (Horiba Jobin-Yvon) with the 450W Xenon excited lamp at room temperature.

3. RESULTS AND DISCUSSION

To demonstrate the pure phase and structure of the $Sr_3B_2O_6$: Tb^{3+} phosphors, powder X-ray diffraction (XRD) measurements of these samples were carried out and shown in the (Fig. 1). The similar diffraction patterns were observed for each sample, which indicates that doping a little Tb^{3+} content does not affect the crystalline structure of the $Sr_3B_2O_6$ lattice. (Fig. 1a and b) show the XRD pattern of $Sr_3B_2O_6$: Tb^{3+} (1%mol) and $Sr_3B_2O_6$: Tb^{3+} (3%mol), respectively. It is clearly observed that all samples have Rhombohedron single phase.

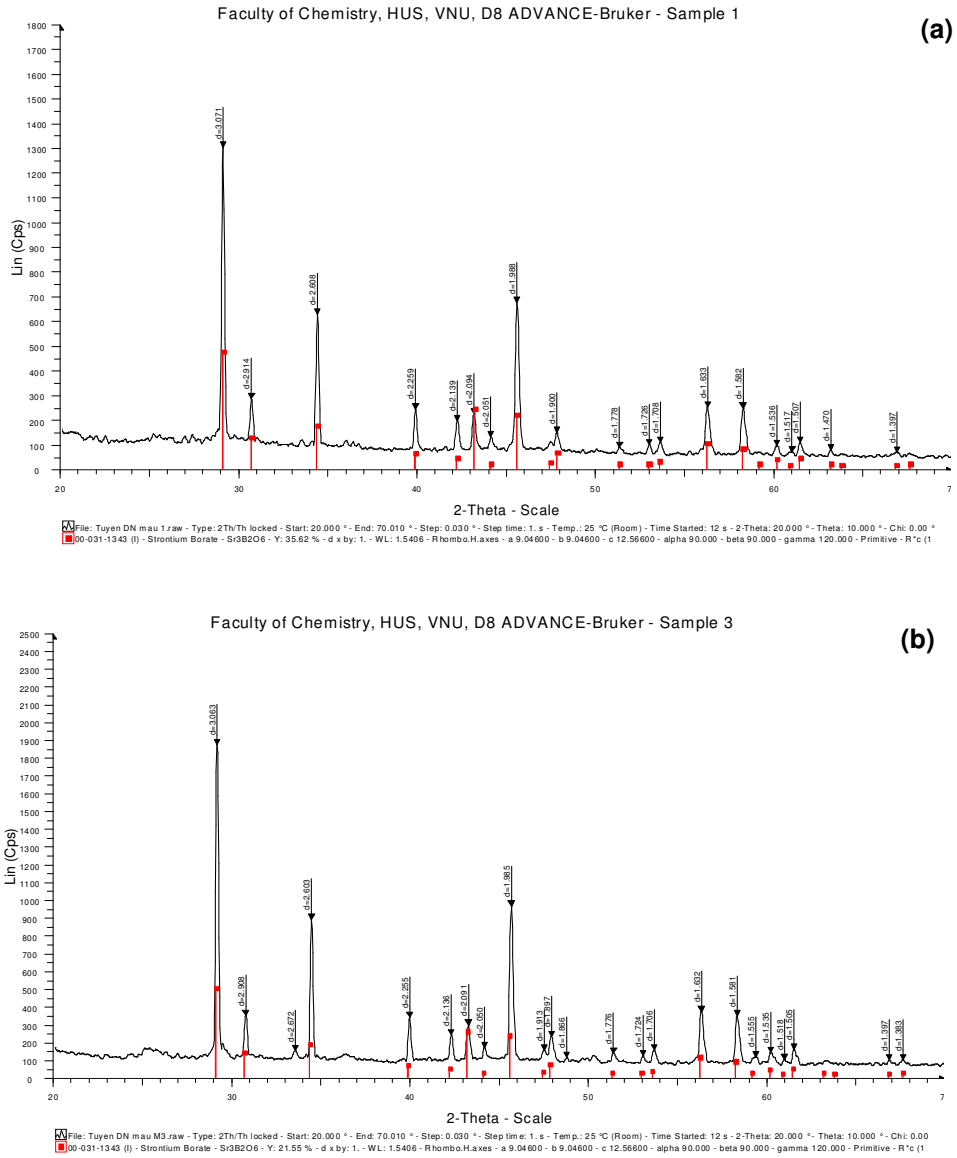

Fig. 1. XRD of Sr3B2O6: Tb3+ (1%mol) (a) and Sr3B2O6: Tb3+ (3%mol) (b)

The photoluminescence excitation (PLE) spectra monitoring at $^5D_4$-$^7F_5$ (541 nm) transition of $Sr_3B_2O_6$: Tb^{3+} (3%mol) sample is shown in (Fig. 2a). The PLE spectrum is sharp lines in the region 300-400 nm corresponding to the 4f-4f transitions in Tb^{3+} ion.

The photoluminescence emission (PL) spectra of $Sr_3B_2O_6$: Tb^{3+} (3%mol) sample under excited radiation λ_{ex} = 379 nm is shown in (Fig 2b). The emission spectra presents four narrow lines at around 486 nm, 541 nm, 592 nm and 611 nm, which originate from the transitions between the excited $^5D_4$ level and ^7F_j (j= 6, 5, 4, 3) ground levels of Tb^{3+} ion, respectively. The $Sr_3B_2O_6$: Tb^{3+} phosphor has the green light emission which due to the strong $^5D_4$-$^7F_5$ transition. The PLE spectra of all samples with different concentration of Tb^{3+} ion are shown in (Fig. 3). All spectra have the same shape and reach the maximum intensity at 3%mol.

(Fig. 4) presents PL spectra of $Sr_3B_2O_6$: Tb^{3+} with different concentration of Tb^{3+} ion. Accordingly, we can observe that the wavelength of $^5D_4$-$^7F_5$ (541 nm) transition in these samples don't change, it located at 541 nm. But emission intensity changes over Tb^{3+} concentration. The emission intensity increases with the increasing of Tb^{3+} doping content, and reaches a maximum at 3 %mol, then decreases. The result was shown in (Fig. 5). The phenomenon of decrease in emission intensity after a certain concentration is called concentration quenching and is attributed to energy migration among rare earth ions.

As a representative on the (Fig. 5), concentration quenching was observed when Tb^{3+} content was over 3%mol. Non-radiative energy transfer from one Tb^{3+} to another Tb^{3+} ion may occur as a result of an exchange interaction, radiation re-absorption or multiple-multiple interaction [8]. The exchange interaction is generally responsible for the energy of forbidden transition [4,9,10]. The mechanism of radiation re-absorption comes into effect only when a broad overlap of the fluorescent spectra of the sensitizer and activator appears [8]. Due to there is not sensitizer in this phosphor, the overlap does not exist. It means that the mechanism of exchange interaction and radiation re-absorption plays no role in the energy transfer between Tb^{3+} ions in $Sr_3B_2O_6$. So the concentration quenching mechanism of Tb^{3+} must be the electric multiple-multiple interaction as suggested by Dexter.

According to Dexter's theory, if the energy transfer between the same sorts of activator, the multipolar interaction can be determined from the change of the emission intensity. The dependence of the luminescent intensity on the activator concentration can be described by the equation (1) [4,11]:

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

Where, the constant β refers to the quenching mechanism by multipolar interaction. The parameter Q is different for different types of interaction: 6, 8, 10 for dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interaction, respectively. The value Q has been determined graphically from equation (2):

$$\log\left(\frac{I}{x}\right) = c - \frac{Q}{3}\log x \quad (2)$$

Where I is the emission intensity of $Sr_3B_2O_6$: Tb^{3+} phosphor, and x is the Tb^{3+} content. (Fig. 6) presents the plot of $\log(I/x)$ as a function of $\log x$. The Q value for $^5D_4$ transitions in

this phosphor was calculated by linear slope, the slope calculated from plot is about -2.8. Therefore, the value of *Q* can be calculated to be 8.4. This result suggested that the concentration quenching mechanism in $Sr_3B_2O_6$: Tb^{3+} is the d-q interaction.

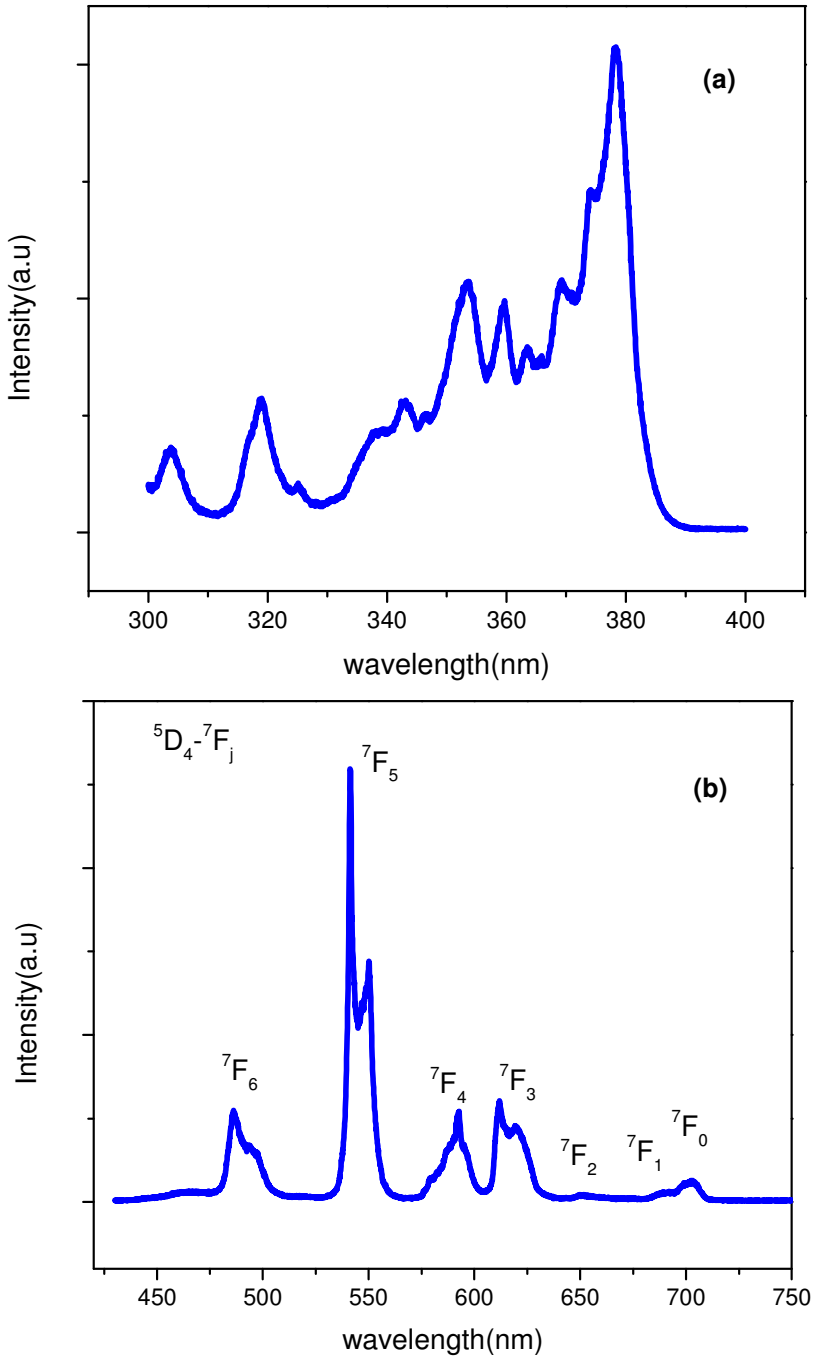

Fig. 2. PLE (a) and PL (b) spectra of $Sr_3B_2O_6$: Tb^{3+} (3%mol)

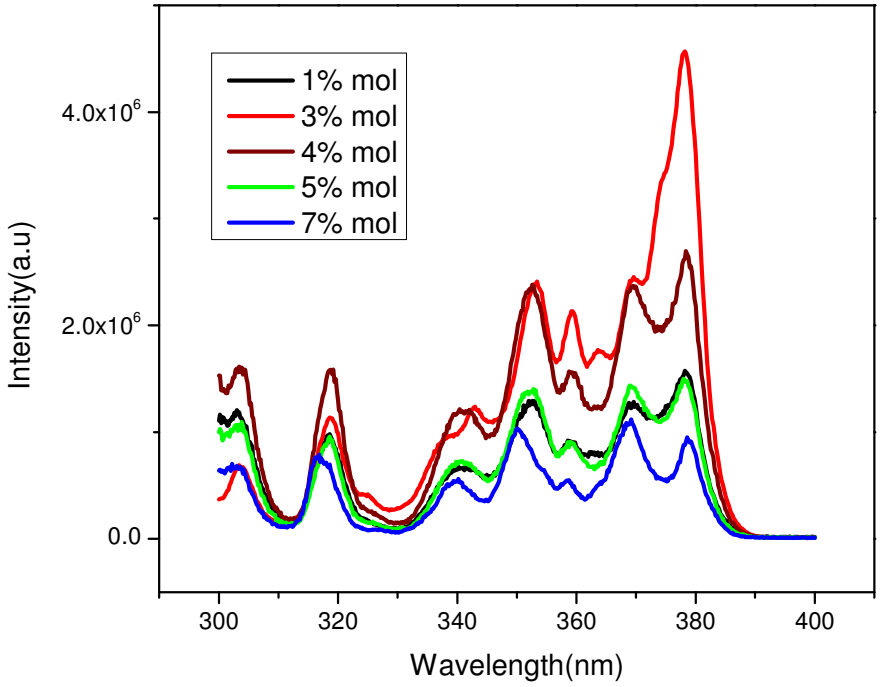

Fig. 3. PLE spectra of $Sr_3B_2O_6$: Tb^{3+} phosphors with various Tb^{3+} concentration

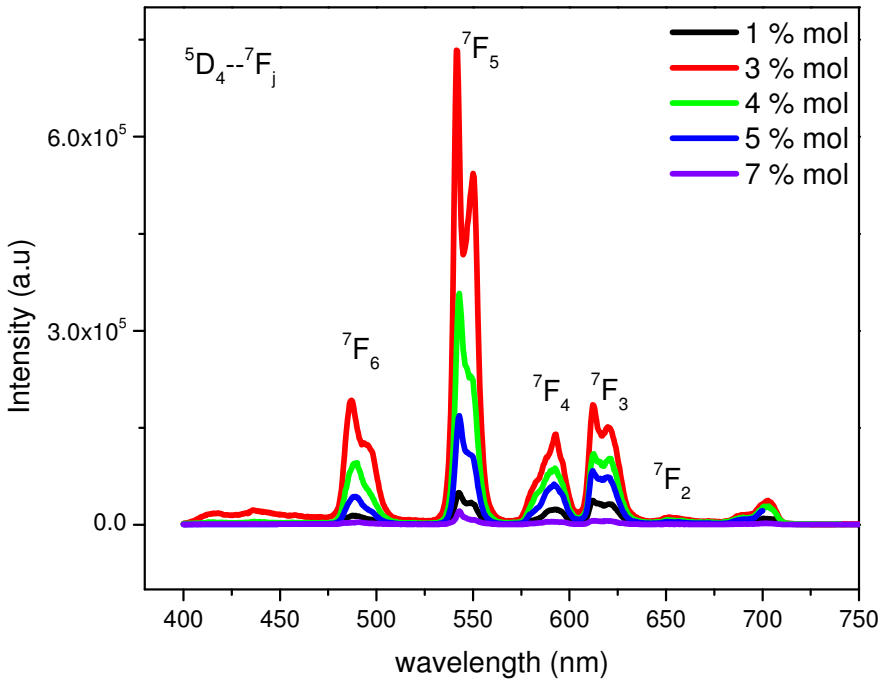

Fig. 4. PL spectra of $Sr_3B_2O_6$:Tb^{3+} phosphors with different concentration of Tb^{3+} ion

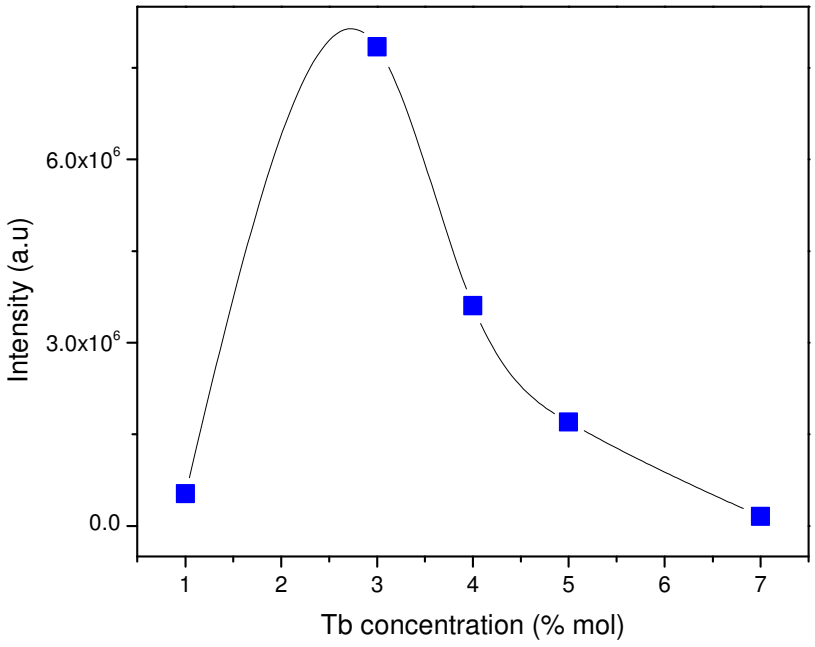

Fig. 5. The plot of intensity ($^5D_4$-$^7F_5$) versus Tb^{3+} ion concentration

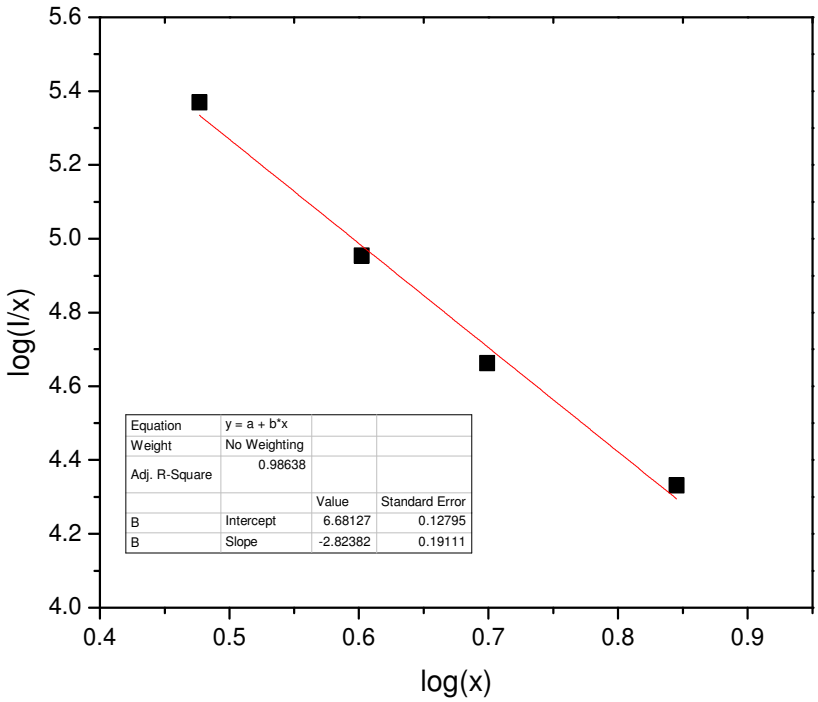

Fig. 6. Plot of log(I/x) versus logx in $Sr_3B_2O_6$:Tb^{3+} phosphors

Fig. 7 shows the CIE chromaticity coordinates of $Sr_3B_2O_6:Tb^{3+}$ (3%mol) under 379 nm excitation. The CIE coordinates are x = 0.38, y = 0.52, z = 1.10, it can found in the yellowish-green region. It shows that $Sr_3B_2O_6:Tb^{3+}$ phosphors have potential application for UV-convertible green phosphors in wLED.

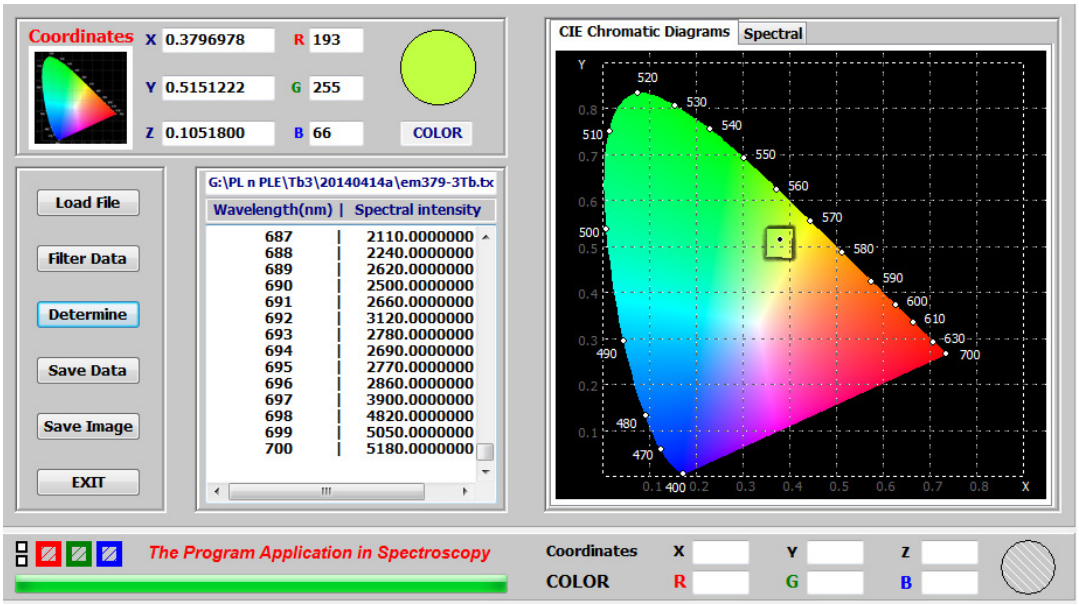

Fig. 7. CIE chromaticity diagram for $Sr_3B_2O_6:Tb^{3+}$ (3% mol) phosphor

4. CONCLUSION

In summary, $Sr_3B_2O_6$: Tb^{3+} green emitting phosphors were prepared by urea-nitrate solution combustion method, after combustion process samples were annealed at 900ºC in air within one hour. These phosphors have rhomboidal single phase structure. The results of PL and PLE spectra indicate that the emission intensity changes over concentration of Tb^{3+} ion. The emission intensity increases with the increasing of Tb^{3+} doping content, and reaches a maximum at 3%mol. The concentration quenching was observed when Tb^{3+} content over 3%mol and the concentration quenching mechanism in the phosphors was determined dipole-quadrupole (d-q) interaction by using Dexter's theory.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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