

Luminescence properties of Tb³⁺ doped Gd₂(WO₄)₃ phosphor prepared by hydrothermal method

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Abstract. The Gd₂(WO₄)₃:Tb³⁺ phosphors have been successfully prepared using the hydrothermal method calcined at 900°C in this work. The crystal structure, PLE/PL and fluorescence decay behavior of samples were investigated in detail. Under the 270 nm excitation (4f⁸→4f⁷5d¹ transition of Tb³⁺), the (Gd_{2-x}Tb_x)(WO₄)₃ (x=0.01-0.15) phosphors emit the strong green emission at 547 nm (⁵D₄→⁷F₅ transition of Tb³⁺). The quenching concentration was found to be ~10% owing to the exchange reaction between Tb³⁺. The Tb³⁺ addition did not influence the CIE chromaticity coordinates (~0.33±0.02, ~0.60±0.02) and color temperatures (~5542 K) of the (Gd_{2-x}Tb_x)(WO₄)₃ phosphors. However, due to the energy transfer between Tb³⁺, the fluorescence lifetime for 547 nm emission decreased with the Tb³⁺ content increasing. The Gd₂(WO₄)₃:Tb³⁺ phosphors with strong green emission are expected to be widely used in white light LED and display areas.

1. Introduce

During the past decades, the rare earth (RE³⁺) doped the glass, ceramics and phosphors has been widely applied in developing the new optical devices, such as displays, biosensors, solid-state lasers and fiber amplifiers [1-3]. The characteristics of the rare earth elements 4f electron layer configuration make the corresponding compounds having various fluorescence characteristics. Due to the Tb³⁺ has 4f⁸ energy level and it is also sensitive to the surrounding environment, the samples with Tb³⁺ addition has better fluorescence excitation spectrum and emission spectrum [4]. Meanwhile, it has a long lifetime of excited state and simple mode of emission peak splitting. So it has become the focus in the green fluorescent materials research[5]. But (WO₄)₃²⁻ and Gd³⁺ can sensitization in active ion, thus streng the active ion to excited green light in Gd₂(WO₄)₃ matrix .So, the Tb³⁺ doping Gd₂(WO₄)₃ is of vital importance in the research. We have synthesized Tb³⁺ doped Gd₂(WO₄)₃ phosphor by hydrothermal method, and we studied its luminescent properties by means of XRD and PLE/PL and a series of characterization methods in detail. Besides, we studied the material synthesis, phase formation and fluorescence performance.

2. Experiment section

2.1 Materials

The original chemicals which were used in the work mainly contain the Gd₂O₃ and Tb₄O₇ (99.99%, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd., Huizhou, China), Na₂WO₄·2H₂O (99.5%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), NaOH, (96%, Sinopharm Chemical Reagent Co. Ltd.,



Shanghai, China) and HNO_3 (AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). All the chemical reagents are required without further purification.

2.2 preparation procedure

Firstly, We dissolved Gd_2O_3 and Tb_4O_7 in hot nitric acid, processing the $\text{RE}(\text{NO}_3)_3$ (RE=Gd and Tb) solutions we needed. Then, in accordance with the chemical formula of $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$, we prepared the mother salt solution with $\text{RE}(\text{NO}_3)_3$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

After the above process was completed, a certain proportion of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ white particles were dissolved in 50 ml water, then dissolve an appropriate amount of nitrate solution in 20ml of water, put in a collector type constant temperature magnetic stirrer, stirring for about 5 min; When the two kinds of raw materials are completely dissolved and stirred in deionized water, the obtained nitrate solution is uniformly dripped into the sodium tungstate solution, and the titration ends at the end of 30 min, add NaOH solution to the mixture and adjust the pH until pH=7, The resulting reaction solution is then moved to a stainless steel autoclave with a capacity of 100 ml; The reaction kettle is placed in the oven, and the oven is set at a temperature of 120°C and the reaction time is 24 h. After the reaction was completed, the reaction kettle was cooled to room temperature to remove the hydrothermal products; The obtained hydrothermal products are cleaned repeatedly through deionized water and cleaned once by anhydrous ethanol, dispersing the product into ethanol (80°C , dried 6 h) and drying the precursor after drying; Finally, the precursor was calcined in high temperature (900°C 2 h) high temperature air and the target phosphor was obtained.

2.3 characterization

The phase purity were monitored by powder X-ray diffraction (XRD) using nickel-filtered $\text{CuK}\alpha$ radiation in the 2θ range 10 - 50° in the scanning speed of 4.0° $2\theta/\text{min}$ (Model D8 ADVANCE, BRUKER Co., Germany). In addition, the PL/PLE spectra of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors were researched by a fluorescence spectrophotometer (FP-6500, JASCO, Tokyo, Japan) which was equipped with a $\Phi 60$ -mm integrating sphere (Model ISF-513, JASCO, Tokyo, Japan) and the excitation source we used is the 150-W Xe-lamp.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ ($x=0.01$ - 0.15) phosphors composed by different Tb^{3+} contents (the x value) calcined under the condition of 900°C . It can be seen that all the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors can be well indexed to the pure bottom centered monoclinic structure of $\text{Gd}_2(\text{WO}_4)_3$ (space group: C_2/c , JCPDS: no.23-1076) [6], indicating the formation of pure phase $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$. Meanwhile, the XRD spectra has no other additional diffraction bands, which indicated that the addition of Tb^{3+} does not affect the crystal structure.

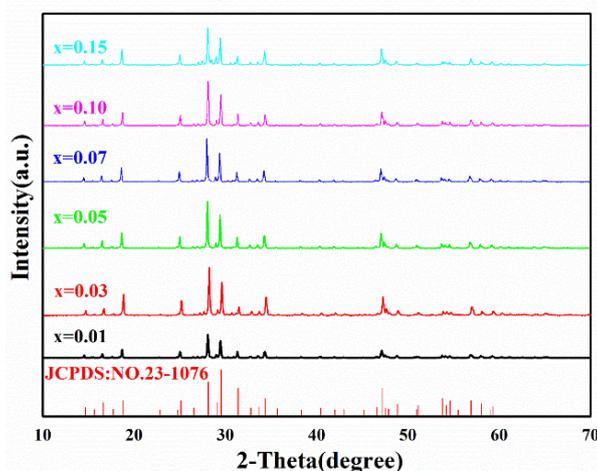


Figure 1. XRD spectra of $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ calcined 900°C at as function of Tb^{3+} content (x value)

Fig. 1 shows the XRD patterns of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ ($x=0.01-0.15$) phosphors with different Tb^{3+} contents (the x value) calcined at 900°C . It can be seen that all the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors can be well indexed to the pure bottom centered monoclinic structure of $\text{Gd}_2(\text{WO}_4)_3$ (space group: C_2/c , JCPDS: no.23-1076)^[6], indicating the formation of pure phase $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$. Meanwhile, the XRD spectra has no other additional diffraction bands, which indicated that the addition of Tb^{3+} does not affect the crystal structure.

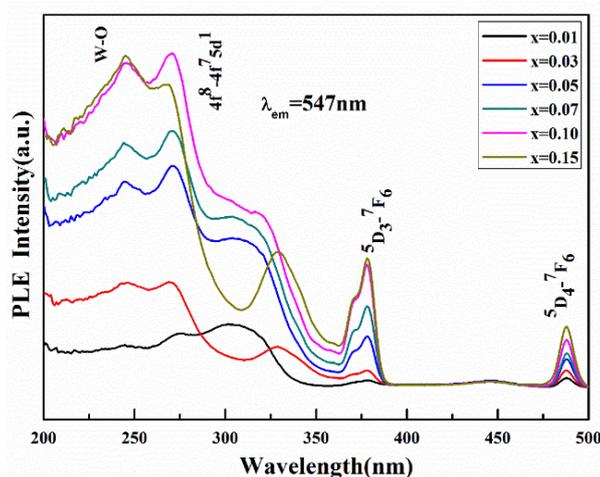


Figure 2. PLE spectra of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors calcined at the condition of 900°C . The PLE spectra were excited at 547 nm

Fig. 2 shows the PLE spectra of $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors with the different Tb^{3+} content monitoring the 547 nm emission ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+}). From which it can be seen that the PLE spectra mainly contain main four excitation peaks and the strongest excitation bands is located at ~ 270 nm ($4f^8-4f^75d^1$ transition of Tb^{3+}). The appearance of the W-O charge transfer band transition at ~ 245 nm wavelength indicates the energy transfer of $\text{WO}_4^{2-} \rightarrow \text{Dy}^{3+}$. Meanwhile, the excitation band at ~ 245 nm which was attributed to the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_1$ transition of Gd^{3+} give an evidence that the $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer. The other two bands at ~ 378 nm and ~ 488 nm are corresponded to the $^5\text{D}_3 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_6$, transitions of Tb^{3+} , respectively^[7,8].

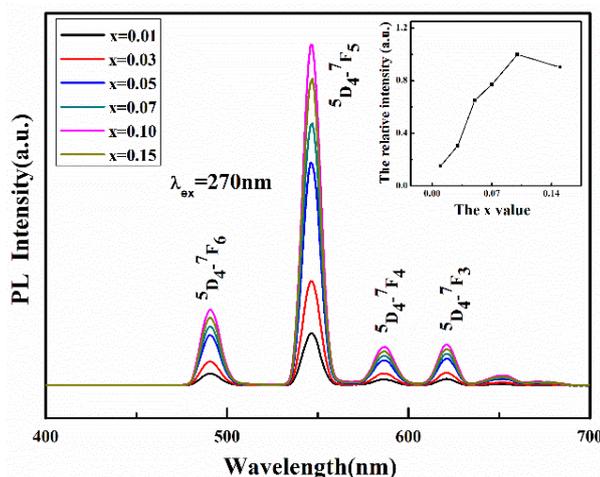


Figure 3. PL spectra of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors calcined at the condition of 900°C . The PL spectra were measured under $\lambda_{\text{ex}}=270$ nm. As a function of the Tb^{3+} content, the inset, normalized to that of the $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ phosphors, is the relative intensity of the 547 nm emission.

Fig. 3 shows the PL spectra of the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors calcined at 900°C under 270 nm wavelength excitation. The $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors mainly contain four groups of typical Tb^{3+} emission peaks at ~ 490 nm (blue), ~ 547 nm (green, the strongest), ~ 588 nm (orange-red) and ~ 621 nm (red), which were correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions of Tb^{3+} marked in the Fig. 3, respectively^[9]. Further observation is that the Tb^{3+} addition does not influence the position and the shape of emission bands, but the intensity varied^[11]. The relative intensity of 547 nm emission was shown in Fig. 3 inset. From which it can be seen that the intensity steadily increased with the Tb content increasing up to the 10.0 at%, and then rapidly decreased owing to concentration quenching. Thus, the optimal Tb^{3+} content is found to be 10.0 at% ($x=0.10$).

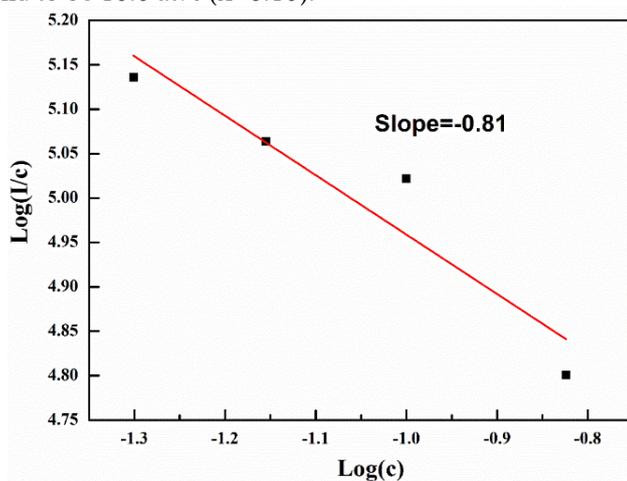


Figure 4. $\log(I/c)$ versus $\log(c)$ for the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ samples calcined at the condition of 900°C

The interaction type of luminescence quenching in phosphors can be obtained via calculating the constant s through the following given formula^[12, 13]:

$$\log(I/c) = (-s/d)\log c + \log f \quad (1)$$

where the c is the activator concentration, I is the emission intensity, f is a constant, s is the index of electric multipole, and d is the sample dimension ($d=3$ for regular sample). The s values of 6, 8, and 10 in consist with the dipole-quadrupole, dipole-dipole, and quadrupole-quadrupole electric interactions, respectively. Besides, $s=3$ corresponds to exchange interaction. The relative relationship between $\log(I/c)$ and $\log(c)$ at the emission of 547 nm is shown in Fig. 4. The slope ($-s/3$) was calculated to be -0.81 , thus, the s value of the $\text{Gd}_2(\text{WO}_4)_3:\text{Tb}^{3+}$ samples is determined to be ~ 2.43 indicating that the concentration quenching is mainly caused by the energy transfer between $\text{Tb}^{3+}-\text{Tb}^{3+}$ [^{14, 15}].

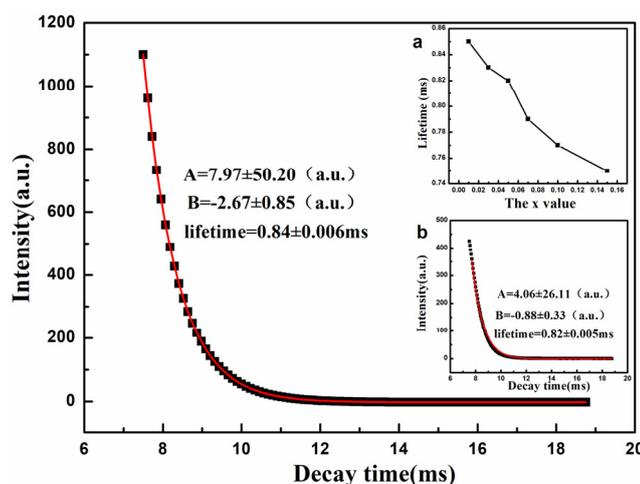


Figure 5. Fluorescence decay curve of $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ phosphors calcined at 900°C for 2 h in the emission of 547 nm. The inset (a) is the lifetime values as function of Tb^{3+} content, (b) is the fluorescence decay curve of $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ in the emission of 547 nm at 423 K

Fig. 5 shows the luminescence decay curves of the $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ samples in the emission of 547 nm. The decay curves can be calculated with the following equation:

$$I = A\exp(-t/\tau_R) + B \quad (2)$$

where t is the decay time, I is the relative fluorescence intensity, τ_R is the fluorescence lifetime. A and B are constants [16-18]. The fitting results are $A=7.97\pm 50.20$, $B=-2.67\pm 0.85$, $\tau_R=0.84\pm 0.006$ ms. The fluorescence lifetime of the phosphors which are a function of Tb^{3+} content was shown in Fig. 5 inset (a). With the Tb^{3+} content increasing from $x=0.01$ to $x=0.15$, the values of fluorescence lifetime decreased from 0.85 ms to 0.75 ms. The reason for this phenomenon is that the distance between Tb^{3+} is relatively long when the content of Tb^{3+} is low, thus, the interaction between luminescent centers can be neglected. However, resonant energy transfer networks can form when the content of Tb^{3+} is higher, and it can be used as the non-radiative centers of the additional channels to reach the surface. Therefore, the fluorescence lifetime will be shortened. The lifetime of the $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ sample at the used temperature of 423 K was shown in Fig. 5 inset (b). It can be seen that the fitting results are $A=4.06\pm 26.11$, $B=-0.88\pm 0.33$, $\tau_R=0.82\pm 0.005$ ms, and the lifetime is almost the same as at room temperature. It can be concluded that the fluorescence lifetime is not affected by the used temperature, and the lifetime in the temperature range 298-573 K was similar to be $\sim 0.80\pm 0.05$ ms.

The CIE chromaticity coordinates of $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ sample for the 574 emission under 270 nm excitation was shown in Fig. 6. The $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ sample is calculated to have the color coordinate (x, y) of $(\sim 0.33, \sim 0.60)$, corresponding to the green colors. The corresponding color temperature can be calculated via the given formulas [19]:

$$T = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (3)$$

and

$$n = (x - 0.332)/(y - 0.1858) \quad (4)$$

The color temperature of $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ sample for $(\sim 0.33, \sim 0.60)$ was calculated to be ~ 5542 K. Meanwhile, all the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors has been investigated in present work to have the similar CIE chromaticity coordinate and color temperature of $(0.33\pm 0.02, 0.60\pm 0.02)$, and ~ 5542 K, respectively.

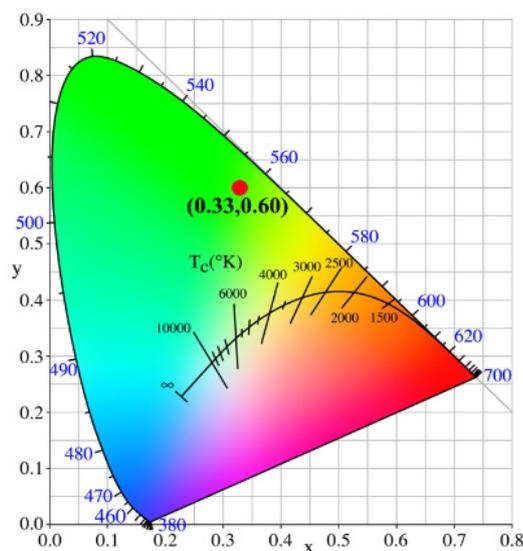


Figure 6. CIE chromaticity diagram for the $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ system under 270 nm excitation

4. Conclusion

The $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ ($x=0.01-0.15$) phosphors has been successfully obtained via the hydrothermal method calcined at 900°C in this work. The phase-pure $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ with needle-like shape and good dispersion can form at 900°C . Under 270 nm UV excitation ($4f^8 \rightarrow 4f^7 5d^1$ transition of Tb^{3+}), the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ phosphors emit the strong green emission at 547 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+}). The appearances of the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ transition of Gd^{3+} at 270 nm and the W-O charge transfer band transition at ~ 245 nm wavelength indicate the energy transfer of $\text{WO}_4^{2-} \rightarrow \text{Dy}^{3+}$ and $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$, respectively. The quenching concentration of $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ samples was found to be $\sim 10\%$ owing to the exchange reaction between Tb^{3+} . All the $(\text{Gd}_{2-x}\text{Tb}_x)(\text{WO}_4)_3$ samples have the similar CIE chromaticity coordinates and color temperatures of $(\sim 0.3 \pm 0.02, \sim 0.60 \pm 0.02)$, ~ 5542 K. The fluorescence lifetime of best $(\text{Gd}_{1.90}\text{Tb}_{0.10})(\text{WO}_4)_3$ sample was calculated to be 0.84 ± 0.006 ms through investigating the fluorescence decay curves, and the lifetime decreased with the Tb^{3+} content increasing, but hardly changes with the increase of used temperature.

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