

# Photoluminescent properties of Pr<sup>3+</sup> activated Y<sub>2</sub>WO<sub>6</sub> for light emitting diodes



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## ABSTRACT

A series of Pr<sup>3+</sup> activated Y<sub>2</sub>WO<sub>6</sub> phosphors are prepared by solid state reaction method. The crystalline phase and luminescent properties of samples are discussed by X-ray diffraction spectra and photoluminescence spectra, respectively. The photoluminescence excitation spectrum indicates that the sample can absorb both UV and blue light. And the samples emit a blue emission of WO<sub>6</sub><sup>6-</sup> and the characteristic red emission of Pr<sup>3+</sup>. The partial quenching of the other prominent blue luminescence from <sup>3</sup>P<sub>0</sub> state is ascribed to a radiationless relaxation pathway involving a low-lying Pr<sup>4+</sup>–W<sup>5+</sup> intervalence charge transfer (IVCT) state. Through adjusting the excitation wavelength, Y<sub>2</sub>WO<sub>6</sub>: Pr<sup>3+</sup> can not only emit warm white light with CIE coordinates of (0.33, 0.37) but also show bright red emission with CIE coordinates of (0.66, 0.33). In addition, the thermal properties of the samples are also investigated in detail. The results show that the application as a white and red component for white light emitting diodes is proposed.

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## 1. Introduction

Recently, white light-emitting diodes (w-LEDs) have attracted much attention due to their high efficiency, compactness, long operational lifetime, and resultant energy saving [1,2]. In w-LEDs, phosphors are used to down-convert the radiation of pump sources (LEDs) into emission at longer wavelength, and the choice of the phosphors controls the ultimate performance of the w-LEDs device [3,4]. The commercial w-LEDs are fabricated by the combination of a GaN-based blue chip with Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> phosphor, which exhibits poor color rendering index (CRI) and high correlated color temperature (CCT) on account of the lack of the red component [5]. The solution is to combine the near-ultraviolet (n-UV) InGaN chip with the red, green, and blue multi-phased phosphors to manufacture w-LEDs [6]. However, the poor efficiency of the red component and the reabsorption in multi-phased phosphors result in unstable white light. These disadvantages can be overcome by improving the efficiency of the red emitting phosphor or developing a single phased white light emitting phosphor. Therefore, it is necessary to develop red or single phased white light emitting phosphors.

As an important kind of Tungstate, Y<sub>2</sub>WO<sub>6</sub> has attracted great attention because of the good self-activating luminescent properties, thermal and chemical stability [7]. Meanwhile, there are three

different sites for Y<sup>3+</sup> in Y<sub>2</sub>WO<sub>6</sub>, which are suitable to be doped with rare earth ions [8]. Among various rare earth ions, Eu<sup>3+</sup>, Sm<sup>3+</sup> and Pr<sup>3+</sup> have been widely investigated as red emitting activators. Eu<sup>3+</sup> and Sm<sup>3+</sup> are used in most red phosphors because of the emission in red region, but their UV excitation efficiencies are quite low due to the partially forbidden nature of 4f intraconfiguration transitions. Among them, Pr<sup>3+</sup> has received much more attention, because it can be excited by n-UV/ blue light. Moreover, Pr<sup>3+</sup> can provide a deep-red emission attributed to the <sup>1</sup>D<sub>2</sub>–<sup>3</sup>H<sub>4</sub> transition, which suggests the total quenching of the luminescence from <sup>3</sup>P<sub>0</sub> level [9]. As previously pointed out by De Mello Donega et al. [10], the partial or total quenching of the <sup>3</sup>P<sub>0</sub> luminescence in oxide-based lattices can be realized through various non-radiative pathways between the <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> levels: multiphonon relaxation, cross-relaxation within pairs of Pr<sup>3+</sup> ions and intersystem crossing through either low lying 4f<sup>1</sup>5d<sup>1</sup> levels or through Pr<sup>3+</sup>-to-metal intervalence charge transfer (IVCT) state. As early as 1970s, Reut and Ryskin have evidenced that the formation of a metal-to-metal charge transfer state of the type Pr<sup>4+</sup>–Mo<sup>5+</sup> and Pr<sup>4+</sup>–W<sup>5+</sup> was the efficient radiationless transition to quench the emitting <sup>3</sup>P<sub>0</sub> level of Pr<sup>3+</sup> in scheelite type crystals A1MVI04 (All = Cd, Ca, Pb, Sr, Ba; MVI = Mo, W) [11]. The strong absorptions originating from IVCT state and f–f transition of Pr<sup>3+</sup> fall in the n-UV (250–370 nm) and blue (450–491 nm) spectral region, respectively, resulting in the potential application in UV- and blue-pumped w-LEDs [12].

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To our knowledge, there is no report about the photoluminescent (PL) performance of  $\text{Pr}^{3+}$  doped  $\text{Y}_2\text{WO}_6$ . Based on the basic research, the crystalline phase of the products, PL and photoluminescence excitation (PLE) spectra were studied at room temperature in this work. The thermal stability of  $\text{Y}_2\text{WO}_6$ :  $\text{Pr}^{3+}$  was also carefully investigated.

## 2. Experimental

The composition of  $\text{Y}_{2(1-x)}\text{WO}_6$ :  $x\text{Pr}^{3+}$  ( $0.005 \leq x \leq 0.03$ ) were prepared by the conventional solid state reaction method in air. According to the stoichiometric ratio, the starting materials of  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{WO}_3$  (99%) and  $\text{Pr}_6\text{O}_{11}$  (99.99%) were thoroughly mixed on an agate mortar by using ethanol. The mixture was then put into the alundum crucible and sintered at 1100 °C for 6 h. The desired phosphors were obtained after the samples were cooled down to room temperature.

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-2400 powder X-ray diffractometer (XRD) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) operating at 40 kV and 60 mA. The  $2\theta$  ranges from  $10^\circ$  to  $80^\circ$  with the step size of  $0.02^\circ$ . The powder morphology was investigated by using a scanning electron microscope (SEM; S-3400, Hitachi, Japan). Diffuse reflection spectra (DRS) was obtained by an ultraviolet–visible (UV–Vis) spectrophotometer (PE lambda950) using  $\text{BaSO}_4$  as a reference. The PL, PLE spectra and the decay curves of the samples were measured by using a FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. Thermal quenching was tested by a heating apparatus (TAP-02) in combination with the PL equipment.

## 3. Results and discussion

Successful synthesis of  $\text{Pr}^{3+}$  doped  $\text{Y}_2\text{WO}_6$  phosphors were verified by XRD patterns and plotted in Fig. 1.  $\text{Y}_2\text{WO}_6$  has a crystalline monoclinic structure with space group of  $P2/c$  (13) and lattice constants of  $a = 7.5879 \text{ \AA}$ ,  $b = 5.3362 \text{ \AA}$ ,  $c = 11.3717 \text{ \AA}$  and  $\beta = 104.3728^\circ$  [8]. It is observed that all the peaks are in fundamental agreement with the standard data of  $\text{Y}_2\text{WO}_6$  (PDF#73-0118), indicating all the samples are of single phase. The strong diffraction peaks reveal the high crystallinity of the as-prepared products, which is very beneficial for luminescent properties.

The morphology of  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$  sample is measured by SEM and shown in Fig. 2. The grains of  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$  with good dispersibility exhibit irregular shape with particle size ranging

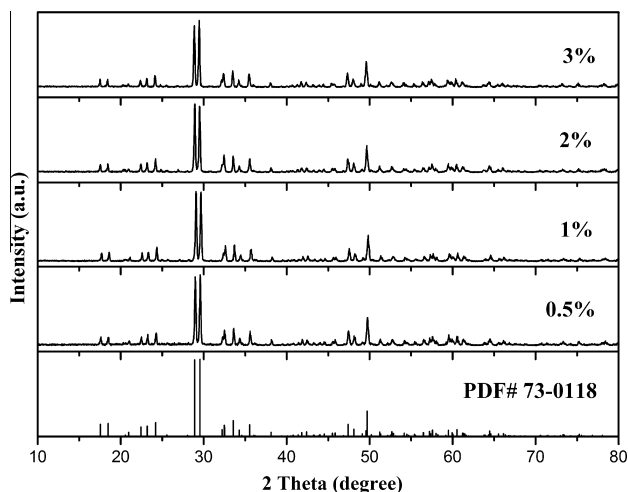


Fig. 1. Powder XRD patterns of  $\text{Y}_2\text{WO}_6$ :  $x\text{Pr}^{3+}$  with different  $\text{Pr}^{3+}$  content.

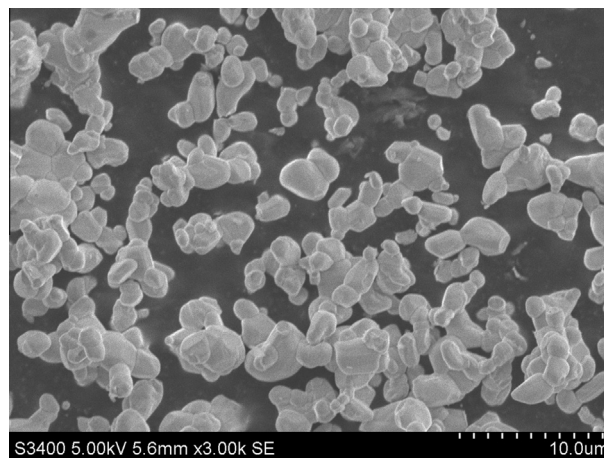


Fig. 2. SEM image of  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$  sample.

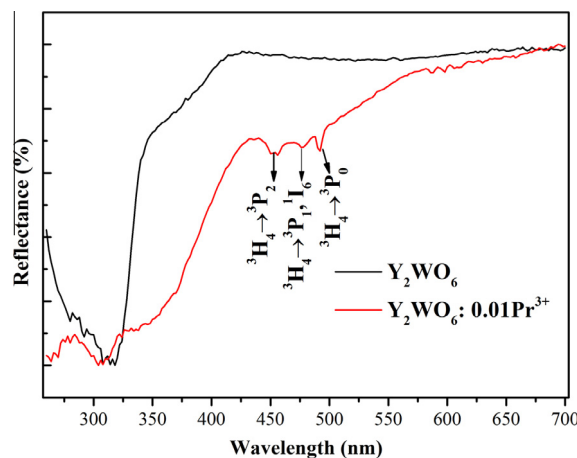


Fig. 3. DRS of  $\text{Y}_2\text{WO}_6$  and  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$ .

from 1 to 5  $\mu\text{m}$ . The grains show smooth surfaces, which could be helpful for luminescent properties [13].

The DRS of  $\text{Y}_2\text{WO}_6$  and  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$  are shown in Fig. 3. The spectrum of  $\text{Y}_2\text{WO}_6$  exhibits the fundamental absorption edge at about 330 nm, which should be ascribed to the host absorption. While doping 1%  $\text{Pr}^{3+}$ , a very broad absorption band between 250 and 420 nm is observed attributing to host absorption and the IVCT state, which was discussed in detail seeing below. Compared with the DRS of  $\text{Y}_2\text{WO}_6$ , the absorption ranged from 320 to 420 nm is increased. Moreover, there are also several weak diffuse reflection peaks locating at 450, 476 and 491 nm in the  $\text{Y}_2\text{WO}_6$ :  $0.01\text{Pr}^{3+}$  sample, which can be ascribed to the characteristic transition of  $\text{Pr}^{3+}$ . The DRS are approximately consistent with the PLE spectra in Fig. 4(a). These results indicate  $\text{Y}_2\text{WO}_6$ :  $\text{Pr}^{3+}$  can be excited by UV- and blue-LEDs. However, the difference between the DRS and PLE spectra is a broad absorption band covering the range of 400–570 nm in the DRS of  $\text{Y}_2\text{WO}_6$ :  $\text{Pr}^{3+}$ , which is ascribed to the lattice defect introduced by the  $\text{Pr}^{3+}$ .

PLE and PL spectra of un-doped and  $\text{Pr}^{3+}$  doped  $\text{Y}_2\text{WO}_6$  are displayed in Fig. 4(a). The excitation spectrum of  $\text{Y}_2\text{WO}_6$ :  $0.005\text{Pr}^{3+}$  (solid line) monitored at 611 nm shows an asymmetric broad band peaking at 337 nm and relatively sharper lines locating at 450, 476 and 491 nm ascribed to  ${}^3\text{H}_4$ – ${}^3\text{P}_2$ ,  ${}^3\text{H}_4$ – ${}^3\text{P}_1$ ,  ${}^3\text{I}_6$  and  ${}^3\text{H}_4$ – ${}^3\text{P}_0$  transitions within the  $4f^2$  configuration of  $\text{Pr}^{3+}$ , respectively. The peak position of the excitation spectrum of  $\text{Y}_2\text{WO}_6$ :  $0.005\text{Pr}^{3+}$  shifts from

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