

# Red photoluminescent property and modification of $\text{WO}_3:\text{Eu}^{3+}$ inverse opal for blue light converted LEDs



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## ARTICLE INFO

### Article history:

Received 18 July 2017

Received in revised form

27 September 2017

Accepted 21 October 2017

### Keywords:

Inverse opal

$\text{WO}_3:\text{Eu}^{3+}$

Red luminescence

Modification

## ABSTRACT

Blue light converted light-emitting diodes is of great significance as a candidate for next generation lighting. In this work, the  $\text{WO}_3:\text{Eu}^{3+}$  inverse opal photonic crystals were prepared and their luminescence properties were studied. The results demonstrated that the main excitation peak of  $\text{WO}_3:\text{Eu}^{3+}$  inverse opals were located at 465 nm. The red luminescence peak at the 613 nm was observed in the  $\text{WO}_3:\text{Eu}^{3+}$  inverse opal upon 465 nm excitation, exhibiting better red color purity. The influence of photonic band gap on the photoluminescence of  $\text{WO}_3:\text{Eu}^{3+}$  inverse opal was obtained. When the red luminescence peak is in the regions of the photonic band gap and the edge of the band-gap, the red luminescence suppression and enhancement was observed respectively. The  $\text{WO}_3:\text{Eu}^{3+}$  inverse opals may be a promising candidate for the blue light converted LEDs.

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## 1. Introduction

Very recently, considerable research interest was focused on the white light emitting diodes (WLEDs) because of their long lifetime, environment friend, and high efficiency [1–5]. Commercially, the white light emitting diodes were prepared by combining the 465 nm blue chip with  $\text{YAG}:\text{Ce}^{3+}$  yellow phosphor. Unfortunately, the color rendering index of this WLEDs are low because of the lack of red emission of  $\text{YAG}:\text{Ce}^{3+}$  phosphor. Therefore, the preparation and development of the red phosphors excited at the 465 nm blue chip is very necessary for the improvement of the color rendering index of commercial WLEDs. At present, some phosphors with red emission such as  $(\text{Ca}, \text{Ba})_3(\text{VO}_4)_2:\text{Eu}^{3+}$  and  $\text{CaSnO}_3:\text{Eu}^{3+}$  were prepared under the excitation of 465 nm blue chip [6,7]. Generally, the  $\text{Eu}^{3+}$  ions was used as the red emission centers in the phosphors [8]. For these  $\text{Eu}^{3+}$  ions doped phosphors, the 592 nm orange red emission from the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition of  $\text{Eu}^{3+}$  and the 615 nm red emission from the transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition were extensively observed [9]. The 592 nm orange red emission is dominant when the  $\text{Eu}^{3+}$  ions were located at the inversion symmetry site of the phosphors [10]. The 615 nm red emission of  $\text{Eu}^{3+}$

is forbidden at the high symmetry site [11]. Therefore, the phosphor host properties are very important for the luminescence of  $\text{Eu}^{3+}$ , and the low symmetry doping of  $\text{Eu}^{3+}$  in the phosphor is required to obtain the pure 615 nm red emission.

The tungsten oxide ( $\text{WO}_3$ ) is an important material due to its potential applications in many fields such as gas sensors, electrochromic and photo-catalysts [12,13]. In addition, the blue and ultraviolet emission from the  $\text{WO}_3$  host was observed [14]. However, there are few investigations on the photoluminescence properties of rare earth ions doped  $\text{WO}_3$ . Photonic crystal is a kind of periodic arranged dielectric structure, exhibiting the photonic band-gap property [15]. The photoluminescence of rare earth ions in the photonic crystals could be modified by the photonic band gap effect [16], which has the potential applications in many fields such as the solar cells, high light-emitting diodes, laser and display [17,18]. In the present work, the  $\text{WO}_3:\text{Eu}^{3+}$  inverse opal photonic crystals were first prepared by sol-gel method, their luminescence property was investigated. The red photoluminescence at the 615 nm was observed in the  $\text{WO}_3:\text{Eu}^{3+}$  inverse opals upon the 465 nm excitation, exhibiting better red color purity. The influence of photonic band gap on the luminescence of  $\text{WO}_3:\text{Eu}^{3+}$  inverse opal was observed. The red luminescence suppression and enhancement was observed in the regions of the photonic band gap and the edge of band-gap, respectively.

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## 2. Experimental

The vertical deposition method described in our previous works were used to prepare three kinds of opal templates by using 350, 400 or 470 nm polystyrene (PS) microspheres [19–21]. A series of  $\text{WO}_3$ :  $x$  mol%  $\text{Eu}^{3+}$  ( $x = 0, 1.0, 1.5, 2.0, 2.5, 3.0$  and  $4.0$ ) inverse opals were prepared using ammonium tungstate  $((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O})$  and europium oxide ( $\text{Eu}_2\text{O}_3$ ) as raw material. Firstly, the  $\text{Eu}_2\text{O}_3$  was dissolved by the hot nitric acid to form the  $\text{Eu}(\text{NO}_3)_3$ . Stoichiometric amount of  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  and  $\text{Eu}(\text{NO}_3)_3$  were dissolved in water and alcohol, respectively. Then the above solutions were mixed together. The mixture was stirred to form a homogeneous  $\text{WO}_3$ : $\text{Eu}^{3+}$  solution. The prepared opal template was soaked in the homogeneous  $\text{WO}_3$ : $\text{Eu}^{3+}$  solution for 1 h. The pretreated opal template was removed from the  $\text{WO}_3$ : $\text{Eu}^{3+}$  solution and dried for 6 h at the room temperature. The samples were sintered at  $480^\circ\text{C}$  for 3 h, and the  $\text{WO}_3$ : $\text{Eu}^{3+}$  inverse opals were prepared.

The X-ray diffraction (XRD) data of  $\text{WO}_3$ : $\text{Eu}^{3+}$  inverse opals were obtained on Rigaku2200 diffractometer. Lifetime decay curves, photoluminescence and excitation spectra of the  $\text{WO}_3$ : $\text{Eu}^{3+}$  inverse opals were measured by Edinburgh FLS980 fluorescence spectrophotometer (UK). The absorption spectra were measured by a Hitachi U-4100 spectrophotometer. The morphology of the opal and inverse opals were observed by a field-emission scanning electron microscope (QUANTA200).

## 3. Results and discussion

### 3.1. Chemical composition and unit cell structure

Fig. 1 (a) shows the X-ray diffraction (XRD) patterns of the  $\text{WO}_3$ : $x$  mol% $\text{Eu}^{3+}$  ( $x = 0, 1.0, 1.5, 2.0, 2.5, 3.0$  and  $4.0$ ) inverse opals and the standard PDF card (NO.43–1035). It can be seen from the XRD patterns that the XRD diffraction peaks of the  $\text{WO}_3$  inverse opals with and without  $\text{Eu}^{3+}$  doping coincide well with these of the standard card, and the doping of  $\text{Eu}^{3+}$  ions does not produce additional XRD diffraction peaks in the  $\text{WO}_3$  inverse opals. The small amount of  $\text{Eu}^{3+}$  doping has no influence on the crystal structure of  $\text{WO}_3$ , and the pure monoclinic  $\text{WO}_3$  phase was obtained. The unit cell structure of  $\text{WO}_3$  was presented in Fig. 1 (b). It is clear that the  $\text{W}^{6+}$  cation sites in the  $\text{WO}_3$  host are coordinated to the six oxygen atoms. The main unit of monoclinic tungsten is the tungsten oxide octahedrons. The accumulation of  $\text{WO}_6$  octahedral units is composed of the crystal structure of the monoclinic

tungsten by sharing their vertexes [22]. The  $\text{Eu}^{3+}$  (0.95 Å) ions in  $\text{WO}_3$  host may either replace the  $\text{W}^{6+}$  (0.62 Å) ions or enter into the interstitial sites. According to previous investigation, the valence state and ionic radius between the  $\text{Eu}^{3+}$  and  $\text{W}^{6+}$  have significant difference, results in that the  $\text{Eu}^{3+}$  ions enter mainly into the interstitial sites in  $\text{WO}_3$  host [23].

Three kinds of opal templates were prepared by the 350, 400 and 470 nm PS microspheres, respectively. The  $\text{WO}_3$ :1.0 mol % $\text{Eu}^{3+}$  inverse opals were prepared by the 350, 400 and 470 nm opal templates. Fig. 2 (a)–(c) showed the SEM images of opal prepared by the 350, 400 or 470 nm PS microspheres, respectively, exhibiting a long-range ordered hexagonal arrangement of PS microspheres. It can be seen that PS microspheres form a highly ordered face-centered cubic structure, whose (111) plane is parallel to the surface of the substrate. The  $\text{WO}_3$ : 1.0 mol%  $\text{Eu}^{3+}$  inverse opals were obtained when the opals filled with  $\text{WO}_3$ :1.0 mol % $\text{Eu}^{3+}$  solution were sintered at the  $480^\circ\text{C}$ , as shown in Fig. 2 (d)–(f). The  $\text{WO}_3$ :1.0 mol % $\text{Eu}^{3+}$  inverse opals prepared by the 350, 400 and 470 nm opal templates were denoted as the IPC-I, IPC-II and IPC-III, respectively. Based on the SEM images shown in Fig. 2, the average center-to-center distance between the air spheres of inverse opals was calculated. The average center-to-center distance between the air spheres for the IPC-I, IPC-II and IPC-III was about 290, 352 and 400 nm, respectively, which is about 15% smaller than the original size of the PS template due to the shrinkage of the samples during calcination.

### 3.2. Optical properties and mechanism

The excitation spectrum by monitoring the 615 nm emission of  $\text{WO}_3$ :1.0mol% $\text{Eu}^{3+}$  inverse opal is shown in Fig. 3. (a). The broad excitation band in the wavelength range of 230–300 nm can be attributed to the charge transfer from  $\text{O}^{2-}$  to  $\text{Eu}^{3+}$ . In addition, the 380, 393 and 465 sharp excitation peaks were observed in the excitation spectrum of  $\text{WO}_3$ : $\text{Eu}^{3+}$  inverse opals, which correspond to the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$  (380 nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  (393 nm) and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  (465 nm) transitions of  $\text{Eu}^{3+}$ , respectively. The preparation and development of the phosphors excited at the 465 nm is very necessary because the blue chip was extensively applied in the commercial WLEDs. It is noted that the 465 nm excitation peak is most intensive in the excitation spectrum of  $\text{WO}_3$ :  $\text{Eu}^{3+}$  inverse opals, which suggested that the  $\text{WO}_3$ : $\text{Eu}^{3+}$  inverse opals may be a promising candidate for the blue light converted LEDs. The photoluminescence spectra of  $\text{WO}_3$ : $x$  mol% $\text{Eu}^{3+}$  inverse opals with a series of  $\text{Eu}^{3+}$  concentration gradients are measured under the

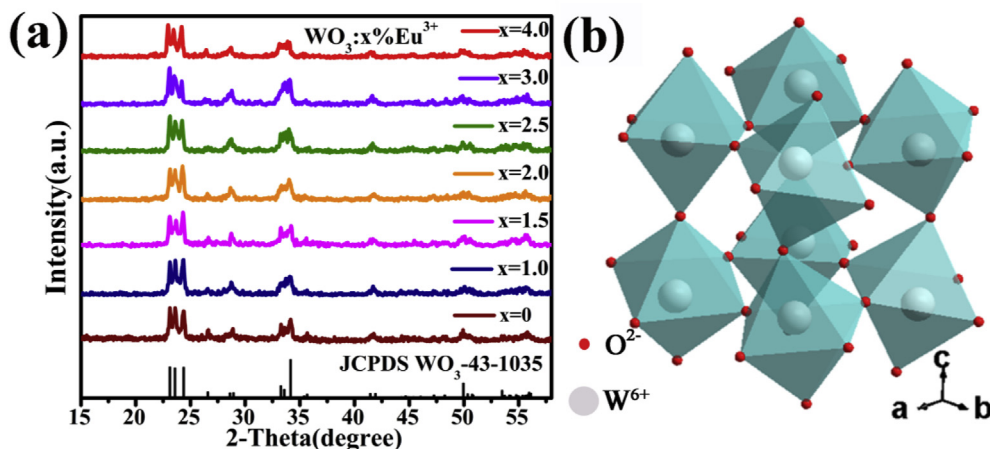


Fig. 1. (a) The XRD patterns for the  $\text{WO}_3$ : $x$  mol% $\text{Eu}^{3+}$  ( $x = 0, 1.0, 1.5, 2.0, 2.5, 3.0$  and  $4.0$ ) inverse opals; (b) the unit cell structure of  $\text{WO}_3$ .

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