Synthesis and photoluminescence of novel red-emitting ZnWO₄: Pr³⁺, Li⁺ phosphors

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Abstract. Zn_{0.997}WO₄: Pr³⁺_{0.003} and different concentrations (0.1 mol% to 0.9 mol%) of Pr, Li co-doped ZnWO₄ red phosphors were prepared by means of solid-state reaction process. The crystalline, surface morphology and luminescent properties of Zn_{0.997}WO₄: Pr³⁺_{0.003} and Zn_{1-x-y}WO₄: xPr³⁺, yLi⁺ phosphors were investigated by the X-ray diffraction patterns (XRD), scanning electron microscope (SEM) and fluorescent measurements. From powder XRD analysis, the formation of monoclinic structure with *C*_{2h} point-group symmetry and *P*_{2/c} space group of the as-synthesized samples is confirmed. The SEM image showed that surface morphology of the phosphor power is irregular cylindricity. The luminescent spectra are dominated by the red emission peaks at 607, 621 and 643 nm, respectively, radiated from the ¹D₂→³H₄, ³P₀→³H₆ and ³P₀→³F₂ transitions of Pr³⁺ ions. The concentrations of the highest luminescent intensity is determined at 0.3mol% Pr³⁺ and 0.3mol% Li co-doped ZnWO₄ powder crystal, and the peak intensity is improved more than 3 times in comparison with that of 0.3mol% Pr³⁺ single-doped ZnWO₄. The enhanced luminescence comes from the improved crystalline and from the charge compensation of Li⁺ ions. The decay curve and CIE chromaticity coordinates of as-prepared samples are also studied in detail.

Keywords: Phosphor; photoluminescence; solid-state reaction method; charge compensation; ZnWO₄: Pr³⁺, Li⁺

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1. Introduction

Rare earth (RE) ions activated phosphors have attracted much attention of researchers due to their unique electronic, optical and chemical properties resulted from the 4f shell of the ion [1-6]. The f-f transition absorption and emission of the trivalent lanthanide ions in crystalline hosts is receiving more and more investigations because of their applications as luminescent materials emitting in the visible and near-IR regions [7-11]. Among these luminescent materials, molybdate and tungstate compounds have been extensively studied because of the superior mechanical properties, excellent chemical characteristics and thermal stabilities. Especially for zinc tungstate (ZnWO_4) crystal, there has been paid more attention due to its high conversion efficiency and high density. Single crystals of ZnWO_4 have been of considerable interest because of their potential applications for X-, γ - and particle-ray scintillation detectors [12-14] and for laser or luminescent host materials [15-17].

On one hand, among various RE ions, Pr^{3+} is a special optical activator, which provides the possibility of simultaneous blue, green and red emissions depending on the host lattice, which satisfies the complementary color relationship. On the other hand, Li^+ ions often play an important role in the enhancement of the luminescent efficiency of phosphors by modification of composition and charge compensation of phosphors [18, 19]. Herein, in this work, the variation compositions and luminescent properties of novel Pr single-doped and Pr, Li co-doped ZnWO_4 phosphors are prepared by conventional solid-state reaction method. The structure, morphology, and luminescent properties have been investigated in detail.

2. Experimental

A traditional solid-state reaction method was used to synthesize the $\text{ZnWO}_4\text{:Pr}^{3+}$ and $\text{ZnWO}_4\text{:Pr}^{3+}, \text{Li}^+$ powders by taking the stoichiometric amounts of ZnO (99.99%, Aladdin), WO_3 (99.99%, Aladdin), Pr_2O_3 (99.99%, Aladdin) and Li_2CO_3 (99.99%, Aladdin). The molar ratios of Pr^{3+} single-doped ZnWO_4 was 0.3mol% and $\text{Pr}^{3+}, \text{Li}^+$ co-doped ZnWO_4 were, respectively, 0.1 mol%, 0.3 mol%, 0.5 mol%, 0.7 mol%, and

0.9 mol%. After the full mixture of raw powder in agate mortar for 2 h, the sample was dried and then pre-calcined at 400 °C for 2 h, and calcined at 1000 °C for 3 h. The crystalline structure of the sample was analyzed by using an XRD-7000 X-ray diffraction system (Shimadzu Co., Japan) with $\text{Cu}_{K\alpha}$ radiation ($\lambda=0.154056$ nm). The surface morphologies of the phosphors were measured by a JSM-6700F scanning electronic microscope (JEOL, Japan), which was operated at 20 kV. The photoluminescence (PL) spectra were measured at room temperature by using an F-4600 fluorescence spectrophotometer (Hitachi Co. Ltd., Japan). The decay curve was detected by an FLS980 steady/lifetime fluorescence spectrometer (Edinburgh Instruments, England).

3. Results and discussions

3.1 Crystal structure

The lattice structure of ZnWO_4 is shown in Fig. 1. It has the monoclinic structure with $P_{2/c}$ space group and $C_{2/h}$ point-group symmetry. Its lattice parameters are $a=4.72$ Å, $b=5.70$ Å, $c=4.95$ Å, and $\beta=90^\circ 05'$. In ZnWO_4 , the W and Zn ions are each surrounded by six oxygen ions, pairwise, equidistantly: the long, medium and short W-O distances are 0.2133, 0.1914 and 0.1789 nm and the Zn-O distances are 0.2227, 0.2090 and 0.2026 nm, respectively [20-22].

Fig. 2 shows the XRD patterns of the $\text{Zn}_{0.997}\text{WO}_4: \text{Pr}^{3+}_{0.003}$ and different concentrations ($x=y$: 0.1 mol%, 0.3 mol%, 0.5 mol%, 0.7 mol%, and 0.9 mol%) of Pr_xLi_y co-doped ZnWO_4 phosphors. The XRD patterns confirm that the peaks of samples are in good agreement with that of the standard card (PDF card no. 15-0774 [23, 24]) of the host. The Li contents incorporated into the ZnWO_4 lattice do not change the lattice structure and serve as a charge compensation for the better crystallization because a Pr^{3+} and a Li^+ replace two Zn^{2+} sites (i.e., $\text{Pr}^{3+} + \text{Li}^+ \rightarrow 2\text{Zn}^{2+}$) and then the charges are balance in crystal. Therefore, there are less defects of the Pr^{3+} , Li^+ co-doped ZnWO_4 than that of Pr^{3+} single-doped ZnWO_4 . The mean crystalline size can estimate by using the Scherrer equation [25, 26], $D_{hkl} = k\lambda / \beta \cos\theta$, where D is the mean crystalline size, k (0.89) is the shape factor, λ is the X-ray wavelength

(0.154056 nm), β is the full width at half maximum (FWHM) and θ is the diffraction angle of an experimental peak. The strongest three diffraction peaks are used to calculate the average crystallite size of the different concentrations of Pr single-doped or Pr, Li co-doped ZnWO₄ phosphors. The calculated average crystallite sizes of Zn_{0.997}WO₄: Pr³⁺_{0.003} and Pr_x, Li_y co-doped Zn_{1-x-y}WO₄ phosphors for the same content ($x=y$) of 0.1 mol%, 0.3 mol%, 0.5 mol%, 0.7 mol%, and 0.9 mol% are approximately 50, 46, 45, 42, 43 and 49 nm, respectively.

3.2 Surface morphology

Fig. 3 shows the typical SEM images of Zn_{0.997}WO₄: Pr³⁺_{0.003} and Zn_{0.994}WO₄: Pr³⁺_{0.003}, Li⁺_{0.003} phosphors. The morphology of the grains is irregular cylindricality. The formation reason for irregular cylindrical morphology is that the growth (or stacking) rate of the basal plane is faster than that of the side surface when the calcined temperature reaches at 1000 °C. According to the crystal-growth theory, compared with the side surface, there are more stacking faults on basal plane which lead to faster crystal growth [27]. Eventually, the analogous cylindrical powder crystals are formed.

3.3 Luminescent properties

Fig. 4 depicts the room temperature photoluminescence excitation (PLE) spectra of the Zn_{0.997}WO₄: Pr³⁺_{0.003} and different concentrations of Pr, Li co-doped ZnWO₄ phosphors at an emission wavelength 607 nm. The PLE spectra have a broad band from 200 to 240 nm which is charge transfer (CT) from metal ions (i.e., Pr³⁺, W⁶⁺, and Li⁺) to ligands O²⁻. The strong excitation peaks at 455 and 490 nm corresponding to the ³H₄→³P₂ and ³H₄→³P₀ transitions, respectively. The CT band induces very efficient radiation relaxation from ¹D₂→³H₄ and ³P₀→³H₆ and it results in the strong red emissions at 607 and 621 nm. Generally, one can choose the strongest excitation peak's value as the monitoring wavelength to collect the emission spectrum. Thus, as shown in Fig. 4, the room temperature PL spectra of Zn_{0.997}WO₄: Pr³⁺_{0.003} and different concentrations of Pr, Li co-doped ZnWO₄ phosphors by monitoring

wavelength at 490 nm. The characteristic red emission peaks of Pr^{3+} are observed at 607 nm ($^1\text{D}_2 \rightarrow ^3\text{H}_4$), 621 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_6$), 643 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_2$) and 740 nm ($^1\text{D}_2 \rightarrow ^3\text{H}_5$) for both $\text{Zn}_{0.997}\text{WO}_4: \text{Pr}^{3+}_{0.003}$ and Pr, Li co-doped ZnWO_4 phosphors. As shown in Fig. 4, the PL brightness of Pr, Li co-doped ZnWO_4 is enhanced more than 3 times compared with that of $\text{Zn}_{0.997}\text{WO}_4: \text{Pr}^{3+}_{0.003}$, as Pr^{3+} and Li^+ ions contents increase from 0.1 mol% to 0.3 mol%. However, as Pr^{3+} and Li^+ content increases to 0.9 mol%, the PL brightness of the sample is decreased but higher than that of single-doped case, therefore the higher doping concentration of Pr^{3+} and Li^+ ions will lead to quench the luminescence. The enhanced PL performance for the Li-doped phosphors comes from the improved crystalline due to the charge balance [28, 29]. However, with the dopant contents further increase, because the radii are different between replaced host ions Zn and dopants Li and Pr, more and more defects (such as oxygen vacancies) will produce and result in the luminescent decrease or quenching.

3.4 Decay curve

Fig. 5 shows the typical fluorescence decay pattern in $\text{Zn}_{0.994}\text{WO}_4: \text{Pr}^{3+}_{0.003}, \text{Li}^{+}_{0.003}$. Considering the complexity of the real system, the fluorescence decay is often described by the multi-exponential or non-exponential decay equation. In the present work, the decay curve is nonexponential and well fitted into a two-exponential function [30]

$$I = A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} \quad (1)$$

in which τ_1 and τ_2 are time constants and A_1 and A_2 are coefficients. The average lifetime can be calculated by using the formula

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

As can be seen, the average lifetime in $\text{Zn}_{0.994}\text{WO}_4: \text{Pr}^{3+}_{0.003}, \text{Li}^{+}_{0.003}$ is 5.4 μs which is caused by the radiation relaxation channels and reduction of the $^1\text{D}_2$ lifetime in the $\text{Zn}_{0.994}\text{WO}_4: \text{Pr}^{3+}_{0.003}, \text{Li}^{+}_{0.003}$ phosphor.

3.5 The CIE chromaticity coordinates

The Commission Internationale d'Eclairage (CIE) system of colorimetry is a method of describing colors that has been widely used in the field of luminescent materials for lighting and displays. As shown in Fig. 6, the CIE average chromaticity coordinates (0.44, 0.30) of the $\text{Zn}_{0.997}\text{WO}_4:\text{Pr}^{3+}_{0.003}$ and different concentrations ($x=y$: 0.1 mol%, 0.3 mol%, 0.5 mol%, 0.7 mol%, and 0.9 mol%) of Pr_x, Li_y co-doped ZnWO_4 phosphors are obtained from the calculations of optical spectra and intensity data. It is clearly observed that the color of the as-prepared samples is in the red region.

4. Conclusions

In summary, $\text{Zn}_{0.997}\text{WO}_4:\text{Pr}^{3+}_{0.003}$ and $\text{Zn}_{1-x-y}\text{WO}_4:\text{Pr}^{3+}_x, \text{Li}^+_y$ (x, y : 0.1 mol%, 0.3 mol%, 0.5 mol%, 0.7 mol%, and 0.9 mol%) phosphors were synthesized by using solid-state reaction method. From the powder X-ray diffraction studies, the phosphor samples are indexed to monoclinic structure. The average crystallite size for Pr^{3+} ($x=0.3\text{mol}\%$) single-doped and $\text{Pr}^{3+}, \text{Li}^+$ ($x, y=0.1\text{mol}\%, 0.3\text{mol}\%, 0.5\text{mol}\%, 0.7\text{mol}\%$ and $0.9\text{mol}\%$) co-doped ZnWO_4 phosphors are calculated as 50, 46, 45, 42, 43 and 49 nm, respectively. The SEM image shows irregular cylindrical-type morphology. The optimized PL intensity of $\text{Zn}_{1-x-y}\text{WO}_4:\text{Pr}^{3+}_x, \text{Li}^+_y$ is determined at x and $y=0.3\text{ mol}\%$, respectively, and which intensity is increased by more than 3 times in comparison with that of $\text{Zn}_{0.997}\text{WO}_4:\text{Pr}^{3+}_{0.003}$ phosphor. The improvement in PL performance with the Li-doping results from improved crystalline due to charge balance and less defect centers in the samples. The fluorescence decay time (5.4 μs) in $\text{Zn}_{0.994}\text{WO}_4:\text{Pr}^{3+}_{0.003}, \text{Li}^+_{0.003}$ is obtained. The CIE average chromaticity coordinates of the as-prepared phosphors are in the red color area.

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Figures and Captions:

Fig. 1. The lattice structure of ZnWO_4 . The framed part represents the unit cell.

Fig. 2. XRD patterns of the ZnWO_4 : Pr^{3+} and Li-doped ZnWO_4 : Pr^{3+} phosphors.

(a)

(b)

Fig. 3. Typical SEM images of (a) $\text{Zn}_{0.997}\text{WO}_4: \text{Pr}^{3+}_{0.003}$, and (b) $\text{Zn}_{0.994}\text{WO}_4: \text{Pr}^{3+}_{0.003}, \text{Li}^{+}_{0.003}$ phosphors.

Fig. 4. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of $\text{Zn}_{0.997}\text{WO}_4:\text{Pr}^{3+}_{0.003}$ and $\text{Zn}_{1-x-y}\text{WO}_4:\text{Pr}^{3+}_x, \text{Li}^+_y$ phosphors.

Fig. 5. Fluorescence decay times of 607 nm emission of $\text{Zn}_{0.994}\text{WO}_4:\text{Eu}^{3+}_{0.003}, \text{Li}^{+}_{0.003}$ under excitation into the $^3\text{H}_4$ at 490 nm.

Fig. 6. CIE average chromaticity diagram for Pr single-doped or Pr, Li co-doped ZnWO_4 phosphors

Graphical Abstract

Figure. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of $Zn_{0.997}WO_4: Pr^{3+}_{0.003}$ and $Zn_{1-x-y}WO_4: Pr^{3+}_x, Li^+_y$ phosphors.