



Improved red emission by codoping Li⁺ in ZnWO₄:Eu³⁺ phosphors



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ABSTRACT

ZnWO₄:Eu³⁺ and ZnWO₄:Eu³⁺/Li⁺ phosphors have been synthesized successfully by a microwave-assist hydrothermal process. The phase, morphology and luminescent properties are investigated carefully. The XRD and FTIR results indicate that ZnWO₄:Eu³⁺ and ZnWO₄:Eu³⁺/Li⁺ phosphors have the monoclinic phase. The SEM images indicate that ZnWO₄:Eu³⁺ and ZnWO₄:Eu³⁺/Li⁺ phosphors are cubes with average particle size about 1 μm. Under the excitation at 395 nm, ZnWO₄:Eu³⁺ and ZnWO₄:Eu³⁺/Li⁺ phosphors show emission bands originating from the ⁵D₀ → ⁷F_j (j = 0, 1, 2 and 3) transitions of Eu³⁺ ions. The Li⁺ ion acts as charge compensator and results in the enhancement of emission intensity.

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1. Introduction

Metal tungstates are studied widely as electro-optic materials due to their potential application in some technological fields, such as electro-optic devices [1], high-energy physics applications [2], optical fibers [3], phosphors [4] and scintillator materials [5]. ZnWO₄ is a wolframite metal tungstate with d¹⁰s²-d¹⁰ electronic configuration [6], which exhibits promising applications in optical fibers [3], photocatalysts [7], light emitting diodes [8], photo-electrode [9], sensors [10] and radiation detection [11]. ZnWO₄ belongs to the monoclinic syngony with the space-group of P2/c, which are fundamentally built by units of WO₆ and ZnO₆ octahedrons. The ZnO₆ octahedron has a structural distortion, in which two bond lengths are 1.2 times of the other four bonds [12]. In recent years, more and more attention has been paid to the luminescent materials because of their potential applications in light emitting diodes. ZnWO₄ and rare earth ions doped ZnWO₄ nano/micro particles have been synthesized by various methods since ZnWO₄ is a kind of self-activating phosphor and a good host lattice for rare earth ions [8,12–15].

It is well known that Eu³⁺ is a kind of important activators for many inorganic materials producing pure red or reddish orange light due to its ⁵D₀ → ⁷F_j (j = 1, 2, 3, 4, 5) transitions [16]. Also, it has

been reported that the emission intensity of CaMoO₄:Eu³⁺ is increased if the alkali ion is codoped into the CaMoO₄ matrix [17]. The oxidation state of alkali ions and ionic radii are lower than those of Eu³⁺, which modifies the crystal field of Eu³⁺ in the host and accordingly increases the emission intensity. In this work, we present the fabrication and luminescent properties of ZnWO₄:Eu³⁺ and ZnWO₄:Eu³⁺/Li⁺ phosphors. The effect of Eu³⁺ and Li⁺ doping on luminescent properties of obtained samples has been investigated carefully.

2. Materials and methods

A series of ZnWO₄:xmol%Eu³⁺ (x = 1, 3, 5, 7, 8, 9 and 10) and ZnWO₄:9mol%Eu³⁺/ymol%Li⁺ (y = 2, 4, 6, 8, 9 and 10) phosphors were fabricated by a microwave-assist hydrothermal method. ZnWO₄·6H₂O (99.95%), Na₂WO₄·2H₂O (99.95%), LiNO₃ (99.95%) and Eu₂O₃ (99.99%) were chosen as starting materials. Polyvinyl pyrrolidone (PVP, M_w = 90000) was used as the additive. All chemicals were directly used as received. Deionized water was used as solvent. For the obtaining of Eu(NO₃)₃, Eu₂O₃ was dissolved in dilute nitric acid under continuous heating.

The fabrication process was as following. Firstly, 0.045 mmol of Eu₂O₃ was dissolved in 10 mL of dilute nitric acid. Secondly, 0.87 mmol of Zn(NO₃)₂·6H₂O and 0.04 mmol of LiNO₃ were dissolved in 20 mL of deionized water and mixed with the above Eu(NO₃)₃ solution under constant stirring for 10 min. Thirdly, 0.4 g of PVP and 1 mmol of Na₂WO₄·2H₂O was dissolved in 20 mL of

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deionized water under continuous stirring for 10 min. Finally, the two solutions were mixed under continuous stirring and transferred into a high-pressure autoclave containing a magnetic stirrer. The high-pressure autoclave was heated up to 180 °C and kept at this temperature for 30 min by a Microwave Synthesizer (Nova Microwave Synthesizer, Shanghai, China). The system then naturally cooled to room temperature. After that, the production was collected, separated, washed and dried.

The X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-RA X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. The scan was in stepwise scanning mode with step size of 0.05° and counting time of 1 s per step. FTIR spectra were measured by a Perkin-Elmer 580B infrared spectrophotometer in the range of $4000\text{--}400 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} using the KBr pellet technique. The morphology was inspected by an FESEM-4800 field emission scanning electron microscope (SEM, Hitachi). Excitation and emission spectra were measured on a Fluorescence Spectrophotometer (Hitachi F-7000) equipped with a 150W xenon lamp as excitation source. Both the excitation and emission slits were set at 1 nm. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 presents the XRD patterns of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$ phosphors. Diffraction peaks according with the JCPDS No. 15-0774 are observed, indicating the formation of monoclinic ZnWO_4 phase. All of other samples have the same XRD patterns. These results suggest that $\text{ZnWO}_4:\text{Eu}^{3+}$ and $\text{ZnWO}_4:\text{Eu}^{3+}/\text{Li}^+$ phosphors with good crystallinity are synthesized successfully under the current synthesis condition. This result indicates that microwave-assist hydrothermal synthesis can accelerate the crystallization kinetics and the reaction rate, and thus reduces energy consumption and reaction time, which is according with earlier report [18]. The ionic radiuses of Zn^{2+} , W^{6+} in six-fold coordination, Eu^{3+} and Li^+ are 0.74 \AA , 0.62 \AA , 0.95 \AA and 0.68 \AA , respectively. Considering to the element chemical states and ionic radiuses, Eu^{3+} ions prefer to occupy Zn^{2+} sites. Li^+ ions also replace the Zn^{2+} ions and possess the site in ZnWO_4 .

Fig. 2 shows the FTIR spectra of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$ phosphors. The peaks at 465 cm^{-1} , 618 cm^{-1} and 705 cm^{-1} associate with bending and stretching of

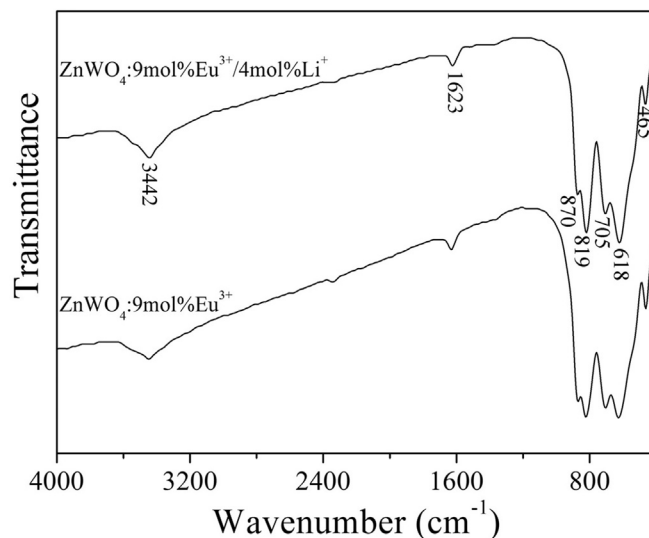


Fig. 2. FTIR spectra of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$.

Zn-O and W-O bonds in WO_6 and ZnO_6 octahedrons, respectively, while the bands centered at 819 cm^{-1} and 872 cm^{-1} relate to the bending and stretching vibrations in Zn-W-O bond [19]. The absorption band peaking at 1623 cm^{-1} is induced by the bending vibration of H-O-H bond. The absorption band peaking at 3442 cm^{-1} comes from the stretching vibration of O-H bond. These two absorption bands result from the absorbed water on the surface of phosphors. The FTIR results support the result of the XRD analysis by the absorption bands ranging from 450 cm^{-1} to 1000 cm^{-1} .

The morphologies of the obtained phosphors have been investigated by SEM. Fig. 3 shows the morphology of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ (A) and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$ (B) phosphors. Both of them present the homogenous cubes, whose average particle sizes are about $1 \mu\text{m}$. Moreover, all of other samples have the same morphology and particle sizes, demonstrating that the Eu^{3+} and Li^+ doping will not change the growing interface and final morphology. Herein, PVP has obvious influence on the obtaining of cubic $\text{ZnWO}_4:\text{Eu}^{3+}$ and $\text{ZnWO}_4:\text{Eu}^{3+}/\text{Li}^+$ phosphors. PVP is used widely in the controllable synthesis of nano/microparticles as one of stabilizing and structure-directing agents. In the microwave-assist hydrothermal process, the absorbing PVP molecules on the surface of growing nanoparticles can weaken the energy consumption of crystal growth and facilitate the development of uniform ZnWO_4 phase through the Ostwald ripening. The preferential adsorption of PVP will lead to the isotropic growth of $\text{ZnWO}_4:\text{Eu}^{3+}$ and $\text{ZnWO}_4:\text{Eu}^{3+}/\text{Li}^+$ crystals and modulate the morphologies of the final samples.

Fig. 4 gives the excitation spectra of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$ phosphors by monitoring the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} at 620 nm . The two emission spectra contain the broad band centered at 286 nm and some sharp bands in the range of $350\text{--}500 \text{ nm}$. According to the data calculated through Jorgensen's equation, the charge transfer band of Eu^{3+} locates at 238 nm [17]. Therefore, the broad band peaking at 286 nm should correspond to the $\text{W}^{6+} \rightarrow \text{O}^{2-}$ charge transfer transition. The other sharp bands peaking at 361 nm , 376 nm , 382 nm , 395 nm , 417 nm and 466 nm can be ascribed to the $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{G}_1$, $^7\text{F}_0 \rightarrow ^5\text{L}_7$, $^7\text{F}_0 \rightarrow ^5\text{L}_6$, $^7\text{F}_0 \rightarrow ^5\text{D}_3$ and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transitions of Eu^{3+} . Moreover, the codoping Li^+ can enhance the excitation intensity of excitation bands for $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$ phosphors.

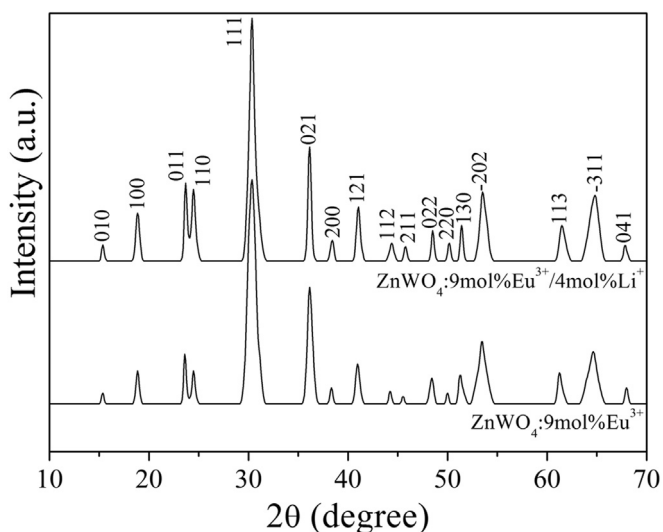


Fig. 1. XRD patterns of $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}$ and $\text{ZnWO}_4:9\text{mol}\%\text{Eu}^{3+}/4\text{mol}\%\text{Li}^+$.

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