

Synthesis and luminescence property of Fe-doped ZnWO_4 powders with aqueous solution reaction

H. HE*, J. HUANG, L. CAO, J. WU

College of Materials Science and Engineering, Shaanxi University of Science and Technology, 710021 China

Fe-doped ZnWO_4 powders have been synthesized with low-cost reaction between sodium tungstates and chloride aqueous solutions and following calcinations. The powders were characterized with XRD, SEM, and luminescence analysis. XRD analysis indicated that the powders were a monoclinic sanmartinite. SEM micrograph indicated that powders were of a grain size about 20-500 nm which increased with increasing calcining temperature. The powders exhibit a broad blue-green emission band. The Fe-substitution results in the decrease of the crystallinity, grain size and luminescence intensity, but different character of luminescence band. The deep blue and blue emission appear more intense, and blue-green and yellow-green emission appear weaker, for the Fe-doped powders than for the undoped powders. The experimental results also revealed a red emission near 590-680 nm for the Fe-doped powders.

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1. Introduction

Sanmartinite ZnWO_4 have been widely studied as photocatalyst [1-5], microwave dielectric ceramics [6], photo-stimulated photoluminescent [7-12]. The luminescence property of the Fe-doped ZnWO_4 single crystals had been widely studied for the scintillator applications [13-19]. Their luminescence property compared with undoped one has been investigated with different methods. However, the synthesis and property of Fe-doped ZnWO_4 nanocrystal have not been found in current literature. The polycrystalline product with a desirable property can be conveniently prepared by sintering powder with a low cost, and have replaced many single crystals, such as transparent garnet. The Fe-doped ZnWO_4 nanocrystal can be used to produce a polycrystalline material.

The ZnWO_4 nanocrystals have been prepared currently via various processes including co-precipitated process [1], hydrothermal [2,3,5,9], molten salt method [7], a standard ceramic route [6], the polymerized complex method [20], spray pyrolysis [11], aqueous salt metathesis reaction [21] etc.. In this work we focus on (i) synthesis of ZnWO_4 and Fe-doped ZnWO_4 nanocrystal with chemical reaction-calcination process under different calcining schedules which may influence the character of the powder and (ii) the luminescent properties of Fe-doped ZnWO_4 nanocrystals and pure ZnWO_4 powder.

2. Experimental procedure

The ZnWO_4 and Fe-doped ZnWO_4 powders were prepared by a method based on an approach previously used for fabrication of metal tungstates (MWO_4 , $\text{M}=\text{Mn}$, Co , Ni and Cu) [14]. For the ZnWO_4 powders, equimolecular ZnCl_2 and Na_2WO_4 were separately dissolved in distilled water. The two solutions were then

slowly mixed with constant stirring. For the Fe-doped ZnWO_4 powders, 1mol% ZnCl_2 was substituted by FeCl_3 . In the mixing processes, the white precipitates were formed. The mixed precursors were filtered and washed repeatedly with distilled water. The precipitates were dried at 100°C for 4h, and then calcined at different temperatures from room temperature up to 700 °C.

The phase identification of two powders was conducted at room temperature using an X-ray diffractometer (XRD, $\text{CuK}_{\alpha 1}$, $\lambda=0.15406\text{nm}$, Model No. D/Max-2200PC, Rigaku, Japan). The phase and the particle sizes of powders were determined with the Jade5 analysis software that was provided with the X-ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analyze the morphology of the powders. The luminescence properties of the nanocrystals and films were measured on the luminescence spectrophotometer (Model No: LS-55, PE, US) at 27 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnWO_4 powders. As-dried precipitations is amorphous. Crystallization of the ZnWO_4 powders begin at 300°C. The crystallized powders have a monoclinic sanmartinite structure. Similarly, ZnWO_4 powders were also prepared with aqueous salt metathesis reaction by Montemayor [14], who reported that tungstates were obtained from solution as amorphous hydrated materials that crystallized between 400°C and 500°C. To synthesis the ZnWO_4 powders higher temperatures were required with other processes except for hydrothermal [1-13]. The crystalline size and the XRD peaks intensities of the ZnWO_4 powders vary with calcining temperature. It can be observed from the XRD patterns that remarkable increases in intensity of

XRD peaks of the ZnWO₄ powders are produced by increasing calcining temperature and calcining time, which corresponds to a large increase in crystallinity of the powders. The (100), (110), and (020) peaks in Fig. 1 appear relative intense. Their ratios of intensity of diffraction peaks equal to $I_{(100)}/I_{(111)}=0.648$, $I_{(110)}/I_{(111)}=0.658$, and $I_{(020)}/I_{(111)}=0.682$, which are larger than the standard powder diffraction data of $I_{(100)}/I_{(111)}=I_{(110)}/I_{(111)}=0.35$ and $I_{(020)}/I_{(111)}=0.25$. This could demonstrate *a*- and *b*-orientation growth of the ZnWO₄ powder calcined at 700 °C. The average crystalline sizes determined with strong peak (111) in the XRD are 23.5 and 34.2 nm for the calcining temperatures of 500 °C and 700 °C, as summarized in Table 1.

Table 1. The particle size (*D*) and lattice parameter of the ZnWO₃ powders prepared at different calcining schedule, determined with the XRD data analysis.

Calcining schedule		Lattice parameter			Particle size <i>D</i> (nm)
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
ZnWO ₃	500 °C 1h	4.7014	5.7321	4.9589	26.3
	400 °C 1h +700 °C 1h	4.7061	5.7124	4.9530	35.0
ZnWO ₃ : Fe	500 °C 1h	4.6868	5.7333	4.9310	27.8
	400 °C 1h +700 °C 1h	4.6886	5.7169	4.9208	32.5

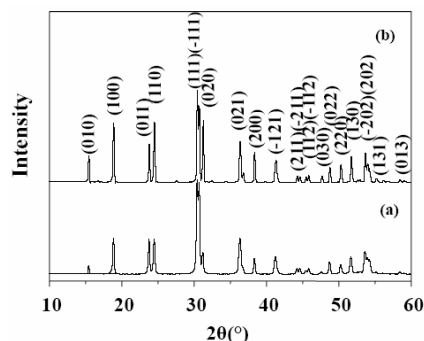


Fig. 1. XRD patterns of the ZnWO₄ powders (a), calcined at 500°C for 1h (b) preheated at 400°C for 1h and then calcined at 700°C for 1h.

The Fe-doped ZnWO₄ powders preheated at 400 °C and then calcined at 600 °C and 700 °C for 1h show hazel color and had a monoclinic sanmartinite structure as seen from XRD patterns (Fig. 2). The XRD peaks are obviously weaker for Fe-doped ZnWO₄ powders than for the ZnWO₄ powders, indicating the Fe³⁺ cation poisoned the crystallization of the powder. The average crystallite sizes of the Fe-doped ZnWO₄ powders determined with strong peak (111) at ~30.46 °C are 27.8 nm and 32.5 nm for the calcining temperatures of 600 °C and 700 °C, respectively (Table 1). The poison effect of the Fe³⁺ cation on the crystallization can also explain this smaller amount of the sizes. The lattice constant *a*, *b* and *c* of the ZnWO₄

and the Fe-doped ZnWO₄ powders were calculated from XRD data. The lattice constants of the powders decrease by the Fe-substitution (Table 1). This would indicate that the Fe³⁺ entered the ZnWO₄ lattice due to the less ionic radius of Fe³⁺ (0.64 Å) compared with Zn²⁺ (0.74 Å).

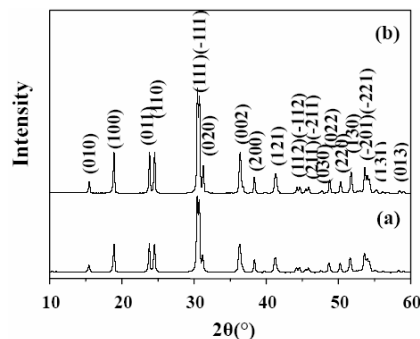
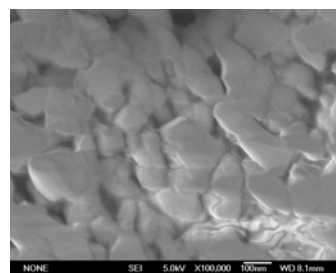
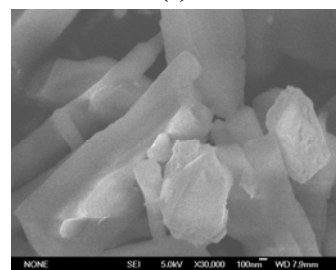


Fig. 2. XRD patterns of the Fe-doped ZnWO₄ powders(a), calcined at 500 °C for 1h (b) preheated at 400 °C for 1h and then calcined at 700°C for 1h.

Fig. 3 and Fig. 4 illustrate the SEM micrographs of the ZnWO₄ and Fe-doped ZnWO₄ powders. The ZnWO₄ powders calcined at 500 °C and the powder preheated at 400 °C for 1h and then calcined at 700 °C have average particle sizes about 20-500 nm. The average grain sizes of the Fe-doped powders are about 50-200 nm which are between the grain sizes of the two ZnWO₄ powders. This is consistent with the XRD analysis. The morphology of the particles are closed pseudo-tetragonal (monoclinic) morphology except for the ZnWO₄ powder calcined 700 °C for 1h which shows a large platelike morphology. This platelike morphology would associates with the *a*- and *b*-orientations of the powder.

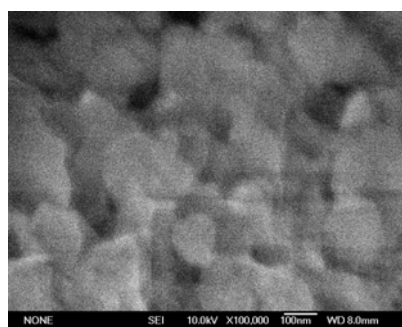


(a)

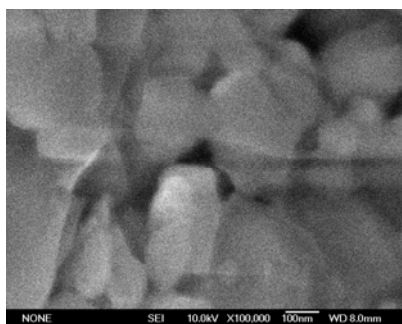


(b)

Fig. 3 (a and b). SEM micrographs of the ZnWO₄ powders (a) calcined at 500°C (b) preheated at 400°C for 1h and then calcined at 700°C for 1h.



(a)



(b)

Fig. 4 (a and b). SEM micrographs of the Fe-doped ZnWO_4 powders (a) calcined at 500 °C (b) preheated at 400 °C for 1h and then calcined at 700 °C for 1h.

The luminescence properties of the ZnWO_4 nanocrystals were measured on the luminescence spectrophotometer and are shown in Fig. 5. The excitation was monitored at 470 nm. The emission was excited at 280 nm. The powders show a broad excitation band and a broad deep blue-green emission band. The excitation band is consisted of three bands at 200.0 nm (6.20 eV), 237.0 nm (5.23 eV) and 251.5.0 nm (4.93 eV) for calcining temperature of 500 °C for 1h, its emission band is centered at 450.0 nm (2.76 eV) and consisted of four strong bands at 424.0 nm (2.92 eV), 450.5 nm (2.7 5eV), 458.5 nm (2.70 eV) and 486.5 nm (2.55 eV) and one weak bands at 531.1 nm (2.33 eV). At calcinations temperature of 700 °C, the excitation band is consisted of three bands at 200.0 nm (6.20 eV), 238.0 nm (5.21 eV) and 252.5.0 nm (4.91 eV), the emission band is centered at 451.0 nm (2.75 eV) and consisted of five bands at 425.0 nm (2.92 eV), 451.0 nm (2.75 eV), 459.0 nm (2.70 eV), 487.0 nm (2.55 eV), and 531.5 nm (2.33 eV). The intensities in the peaks of excitation and luminescence increase with increasing calcination temperature from 500 °C to 700 °C for 1h, which can be attributed to increases in crystallinity and grain size of the ZnWO_4 powders.

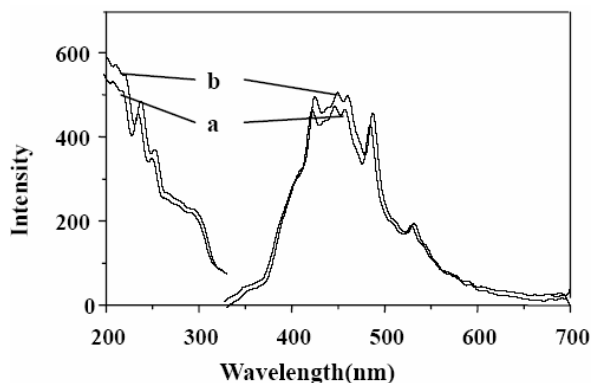


Fig. 5. The luminescence spectra of the ZnWO_4 powders (a) calcined at 500 °C for 1h, (b) preheated at 400 °C for 1h and then calcined at 700 °C for 1h, monitored at 426 nm and excited at 237 nm.

The Fe-doped ZnWO_4 powders calcined at 500 °C for 1h were determined at monitoring wavelength of 425 nm and at exciting wavelength of 247 nm. The excitation band consists in two bands at 200.0 nm (6.20 eV), 237.0 nm (5.23 eV), its emission band is centered at 449.5 nm (2.76 eV) and consisted of four strong bands at 426.0 nm (2.92 eV), 449.5 nm (2.75eV), and 487.0nm (2.55eV) and one weak bands at 529.0nm (2.33eV). The Fe-doped ZnWO_4 powders preheated at 400 °C for 1h and then calcined at 700 °C for 1h were determined at two monitoring wavelengths and at two exciting wavelengths. The excitation bands are consisted of two bands at 208.5 nm (6.20 eV), 236.5 nm (5.21 eV) for monitoring wavelengths of 425 nm and at 203.0 nm (4.91 eV) and 236.5 nm for monitoring wavelengths of 437 nm with a broad shoulder band until ~300 nm in the wavelength range used in this measurement (Fig. 6). When exciting at 208 nm, its emission band is centered at 445.5 nm (2.75 eV) consisted of five strong bands at 407.0 nm, 425.5 nm (2.92 eV), 445.5 nm (2.75 eV), 457.0 nm (2.70 eV) and 487.0 nm (2.55 eV) and one weak bands at 531.0 nm (2.33 eV) (Fig. 7a). When exciting at 239 nm, its emission band is centered at 424.0 nm (2.75 eV) consisted of four strong bands at 405.5 nm (2.92 eV), 424.5 nm (2.75 eV), 447.0 nm (2.70 eV) and 487.5 nm (2.55 eV) and one weak bands at 53150 nm (2.33 eV) (Fig. 7b). The emission band is relative intense at excitation wavelength of 208 nm, comparing with that at 239 nm. However, the short wavelength emission appears relative intense when the sample excited at short wavelength (Fig. 6 and Fig. 8). This is reverse with the emission of tungstate with scheelite structure [22-24]. From the Fig. 5, 6, and 8, it can be observed that the deep blue to blue emissions near short wavelength of 425 nm, 445 nm, 459 nm are stronger, but the blue-green to yellow-green emissions near long wavelength of 487 nm, and 531 nm are weaker, for doped

powders than for the undoped one.

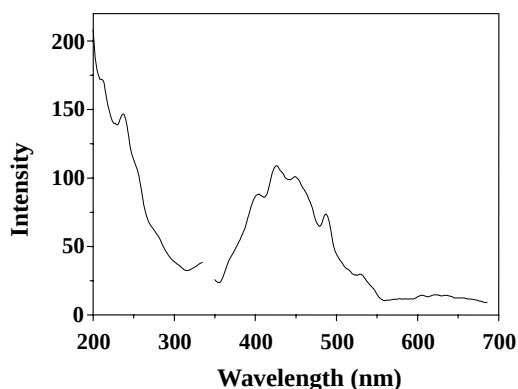


Fig. 6. Luminescence spectra of the Fe-doped ZnWO₄ powders calcined at 500 °C for 1h, monitored at 425 nm and excited at 247 nm.

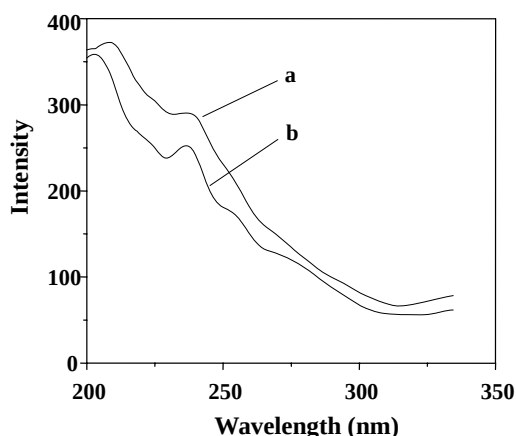


Fig. 7. Excitation spectra of the Fe-doped ZnWO₄ powders preheated at 400 °C for 1h and then calcined at 700 °C for 1h, monitored at (a) 425 nm (b) 437 nm.

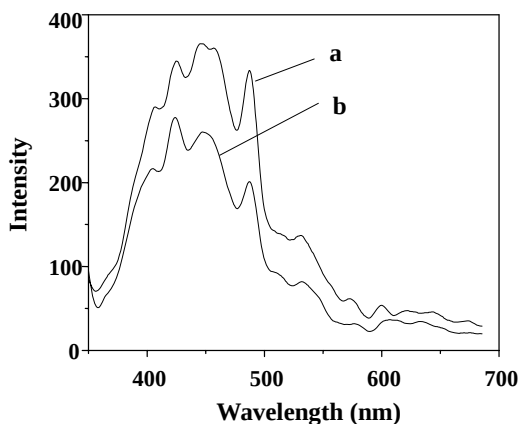


Fig. 8. Emission spectra of the Fe-doped ZnWO₄ powders preheated at 400 °C for 1h and then calcined at 700 °C for 1h, excited at (a) 208 nm, (b) 239 nm.

In addition, a weak broad emission band at 590-680nm are also observed in the emission spectra of the Fe-doped powders (Fig. 6 and 8). It seems that there is energy transfer from the WO₄²⁺ group to Fe³⁺ cation. Nagirnyi and coworkers [18] studied luminescence of Fe³⁺-related centers. They reported that iron centers of different types efficiently promote the formation of crystal defects at low temperatures. Electrons and holes can be trapped near Fe²⁺ or Fe³⁺ ions, and is further revealed in phosphorescence, thermostimulated or photostimulated luminescence. Kornlyo and coworkers [14] also reported a red emission of Fe and Li co-doped ZnWO₄ crystals at 650nm, this red emission would related to the Fe³⁺ cation. By comparison, the center of the red emission bands of the powders in this work are obviously shifted to shorter wave-length than that of the single crystal, which could be explained by the quantum-size effect resulted from small particle size of the Fe-doped ZnWO₄ powders.

4. Conclusions

Ultrafine ZnWO₄ and Fe-doped ZnWO₄ powders have been synthesized by aqueous reaction process. The effect of calcinations schedule on the powder character was studied. The crystallinity and grain size of the powders increased with increasing calcining temperature to 700°C but decreased by Fe-substitution. The powders shown a broad excitation band and broad deep blue-green emission band, which were enhanced with increasing crystallinity and grain size of the powders. The Fe-doped powders shown especially a red emission near 590-680nm. These different luminescence structures and small particle size, together with the advantages of low cost and concise technique, should make the Fe-doped powder can be used for the sintering of the Fe-doped ZnWO₄ polycrystalline that is suitable for the scintillator application and for other luminescence application.

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*Corresponding author: hehy@sust.edu.cn