

# Synthesis and luminescent property of ZnWO<sub>4</sub> powders by aqueous reactions

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ZnWO<sub>4</sub> powders have been synthesized by reaction between ZnCl<sub>2</sub> and Na<sub>2</sub>WO<sub>4</sub> aqueous solutions and following calcinations at final temperature of 700°C. XRD analysis indicated that single phase ZnWO<sub>4</sub> powders were formed above calcining temperature of 400°C, the ZnWO<sub>4</sub> powders had a monoclinic sanmartinite structure, and particle size and intensity of XRD peak of the powders were change with change of calcining schedules. SEM micrograph indicated that powders had uniform and grain size about 20-500nm which increased with increasing calcining temperature. The powders showed a broad blue-green emission bands. Little shift in the peaks of excitation and luminescence and change in its intensities were observed as related to the changes of intensity of XRD peaks and grain size and morphology of the powders. The ZnWO<sub>4</sub> powders possessed of very high luminescent efficiency.

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**Keywords:** ZnWO<sub>4</sub>, powders, Synthesis, Luminescence

## 1. Introduction

Sanmartinnite ZnWO<sub>4</sub> have been widely studied as photocatalyst [1-5], microwave dielectric ceramics<sup>[6]</sup>, photo-stimulated photoluminescent [7-12]. ZnWO<sub>4</sub> nanocrystals have been prepared 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 [13], spray pyrolysis [11], aqueous salt metathesis reaction<sup>[14]</sup>, et al. The nanomaterials and nanostructures are of a great interest for the modern science and technology. The properties and phenomena of these materials and structures are mainly due to the quantum confinement (QC), which is determined by the sizes of 10 – 20 interatomic distances, and to the surface/interface effects, which are amplified by the enormous surface/volume ratio( $10^8$ - $10^9$ m<sup>-1</sup>). Luminescent property of ZnWO<sub>4</sub> nanocrystal may be dependent on the character of the ZnWO<sub>4</sub> powders which was found to depend on the synthesis process and processing parameters, such as, reaction temperature, pH, etc. [9].

In this work we report (i) synthesis of ZnWO<sub>4</sub> nanocrystal with chemical reaction-calcination process under different calcining schedules which may influence the character of the powder and (ii) the luminescent properties of the ZnWO<sub>4</sub> nanocrystals.

## 2. Experimental Procedure

The ZnWO<sub>4</sub> powders were prepared by a method based on an approach previously used for fabrication of 3D metal tungstates (MWO<sub>4</sub>, M=Mn, Co, Ni and Cu) [14]. Equimolecular ZnCl<sub>2</sub> and Na<sub>2</sub>WO<sub>4</sub> were respectively dissolved in distilled water, two solutions was then slowly mixed with constant stirring, respectively. The pale yellow precipitation was fast formed. The precursor was filtered

and washed repeatedly with distilled water. The precipitation was then dried at 100 °C for 4h and calcined at different temperatures from room temperature to 700 °C. To investigate the effect of preheating on character of the powders, the precursor calcined at 400 °C was grinded and further calcined at 600 °C and 700 °C for 1h respectively.

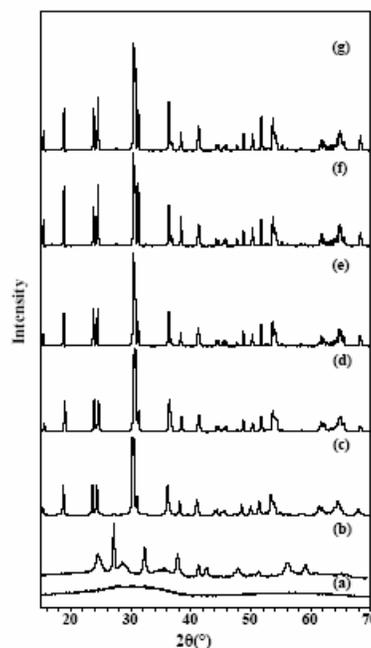


Fig. 1. XRD patterns of (a) the dried precipitation and the ZnWO<sub>4</sub> powders (b), (c) and (d) calcined at 300°C, 400°C, and 500°C for 1h respectively, (e) and (f) preheated at 400°C for 1h and then calcined at 600°C and 700°C for 1h respectively, (g) calcined at 700°C for

1.5h

The phase identification of the powders was conducted at room temperature using 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 X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analyze the particle morphology and the agglomeration of the powders. The luminescent properties of the  $\text{MnWO}_4$  nanocrystals were measured on the luminescent spectrophotometer (Modal No: LS-55, PE, US).

### 3. Results and discussion

The XRD patterns of the  $\text{ZnWO}_4$  powders are shown in Fig. 1. As-dried powder was amorphous. Crystallization of the  $\text{ZnWO}_4$  powders was detected at 300 °C and entirely completed at a temperature of 400 °C for 1h, which had a monoclinic sanmartinite structure. Similarly,  $\text{ZnWO}_4$  powders were also prepared with aqueous salt metathesis reaction by Montemayor<sup>[14]</sup>, who reported that tungstates were obtained from solution as amorphous

hydrated materials which crystallized between 400 and 500 °C. To synthesis the  $\text{ZnWO}_4$  powders higher temperatures were needed with other processes except for hydrothermal [1-13]. Changes of crystalline size and increases in intensity of the XRD peaks of the  $\text{ZnWO}_4$  powders were produced by increasing calcining temperature to 700 °C. It can be observed from the XRD patterns that remarkable increases in intensity of XRD peaks of the  $\text{ZnWO}_4$  powders were produced by increasing calcining temperature and calcining time, which corresponds to a large increase in crystallinity of the powders. It is worth noted that (110) and (001) preferred orientation were observed in the XRD peaks of the  $\text{ZnWO}_4$  powders preheated at 400 °C and then calcined at 700°C for 1h although (111) peak was not enhanced compared to that of the powder calcined at 600 °C. The average crystalline sizes determined with strong peak (111) in the XRD were 23.5-35.0nm, which was increased from 23.5 nm to 35.0 nm with increasing calcining temperature from 400 °C to 700 °C but decreased to 32.6 nm at 700 °C for 1.5h, as summarized in Table 1. The lattice constant  $a$ ,  $b$  and  $c$  of the  $\text{ZnWO}_4$  powders were calculated from XRD data analyses, which were also changed with calcining temperature and calcining time, as also summarized in Table 1.

Table1. The particle size (D) and lattice parameter of the  $\text{ZnWO}_3$  powders prepared at different calcining schedule, determined with the XRD data analysis.

calcining schedule	lattice parameter			particle size
	a(Å)	b(Å)	c(Å)	D(nm)
400 °C1h	4.6965	5.7286	4.9531	23.5
500 °C1h	4.7014	5.7321	4.9589	26.3
400 °C1h +600 °C1h	4.6963	5.7180	4.9468	34.2
400 °C1h +700 °C1h	4.7061	5.7124	4.9530	35.0
700 °C1.5h	4.6962	5.7146	4.6308	32.6

The SEM micrographs of the  $\text{ZnWO}_4$  powders are shown in Fig. 2, which indicated that the  $\text{ZnWO}_4$  powders were of particle size about 20-500nm, which increased remarkably with calcining temperature and calcining time. The morphology of the particle were uniform spherical in calcining temperature range of 400°C to 600°C, but become to platelike at calcining temperature of 700°C for 1h, and tetragonal (monoclinic) at calcining temperature of 700°C for 1.5h.

The luminescence properties of the  $\text{ZnWO}_4$  nanocrystals were measured on the luminescent spectrophotometer and are shown in figure 3. The powders showed a broad excitation band and a broad deep blue-green emission band. The excitation band of the  $\text{ZnWO}_4$  powders calcined at 500 °C for 1h was consisted of three bands at 200.0 nm (6.20 eV), 237.0nm (5.23 eV) and 251.5.0 nm (4.93 eV) with a broad shoulder band until ~300 nm in the wavelength range used in this measurement, its emission band was centered at 450.0 nm (2.76 eV) consisted of four strong bands at 424.0 nm (2.92 eV), 450.5 nm (2.75 eV), 458.5 nm (2.70 eV) and 486.5 nm (2.55 eV)and one weak bands at 531.1 nm (2.33 eV).

Similarly, the excitation band of the  $\text{ZnWO}_4$  powders preheated at 400 °C for 1h and then calcined at 600°C for 1h was at 205.5nm (6.03 eV) with two weak bands at 220.0 nm (5.64 eV) and 237.5nm (5.22 eV) and broad shoulder peak until ~300 nm, its emission band was centered at 449.5 nm (2.48 eV) consisted of three strong bands at 424.0 nm (2.92 eV), 449.5 nm (2.48 eV) and 487.5 nm (2.54 eV) and one weak bands at 531.5 nm (2.69 eV). The excitation band of the  $\text{ZnWO}_4$  powders preheated at 400 °C for 1h and then calcined at 700 °C for 1h was consisted of three bands at 200.0nm (6.20 eV), 238.0nm (5.21 eV) and 252.5.0nm (4.91 eV) with a broad shoulder band until ~300nm in the wavelength range used in this measurement, its emission band was centered at 451.0 nm (2.75 eV) consisted of four strong bands at 425.0 nm (2.92 eV), 451.0 nm (2.75 eV), 459.0 nm (2.70 eV) and 487.0 nm (2.55 eV)and one weak bands at 531.5 nm (2.33 eV). The excitation band of the  $\text{ZnWO}_4$  powders calcined at 700 °C for 1.5h was at 200.0 nm (6.20 eV) with three bands at 219.5nm (5.65 eV), 238.0 nm (5.21 eV) and 275.5 (4.50 eV) followed by broad shoulder peak until ~300nm in the wavelength range used in this measurement,

its emission band was centered at 451.0 nm (2.75 eV) consisted of four strong bands at 427.0nm (2.90 eV), 448.0nm (2.77 eV), 462.5 nm (2.88 eV) and 487.5nm (2.54 eV) and one weak bands at 531.5nm (2.33eV). The increase in intensities in the peaks of excitation and luminescence were observed with increasing calcining temperature from 500 °C to 600 °C for 1h, which can be attributed to increase in crystallinity and grain size of the ZnWO<sub>4</sub> powders. The intensities in the peaks of excitation and emission were decreased when sample preheated at and then calcined at 700 °C for 1h which can explained by preferred orientation and platelike morphology. The intensities in the peaks of excitation and luminescence were remarkably increased when sample calcined at 700 °C for 1.5h which can also explained by largest crystallinity and grain size of the powders. It is obvious that the emission bands at centers are strongest for the four samples, especially for the ZnWO<sub>4</sub> powders calcined at

700°C for 1.5h. The ZnWO<sub>4</sub> powders had also been synthesized with via hydrothermal route by Song et al<sup>[15]</sup>. In their experiment results, the intensities in the peaks of luminescence were increased as increase in crystallinity of the ZnWO<sub>4</sub> powders produced by increasing pH of hydrothermal solution and hydrothermal time up to 12h although they proposed that the formation of rodlike morphology of the powders is main reason of the increase of emission intensity of the ZnWO<sub>4</sub> powders. Similarly, Lou et al [10] reported that the broad band of ZnWO<sub>4</sub> films prepared by a spray pyrolysis was centered at 495 nm (2.51 eV) consisted of three bands at 444 nm (2.80eV), 495 nm (2.51 eV) and 540 nm (2.30 eV). By comparison, the emission bands of the powders in this work are obvious shifted to shorter wave-length, which would be attributed to the quantum-size effect resulted from smaller particle size of the ZnWO<sub>4</sub> powders compared with that of their powders.

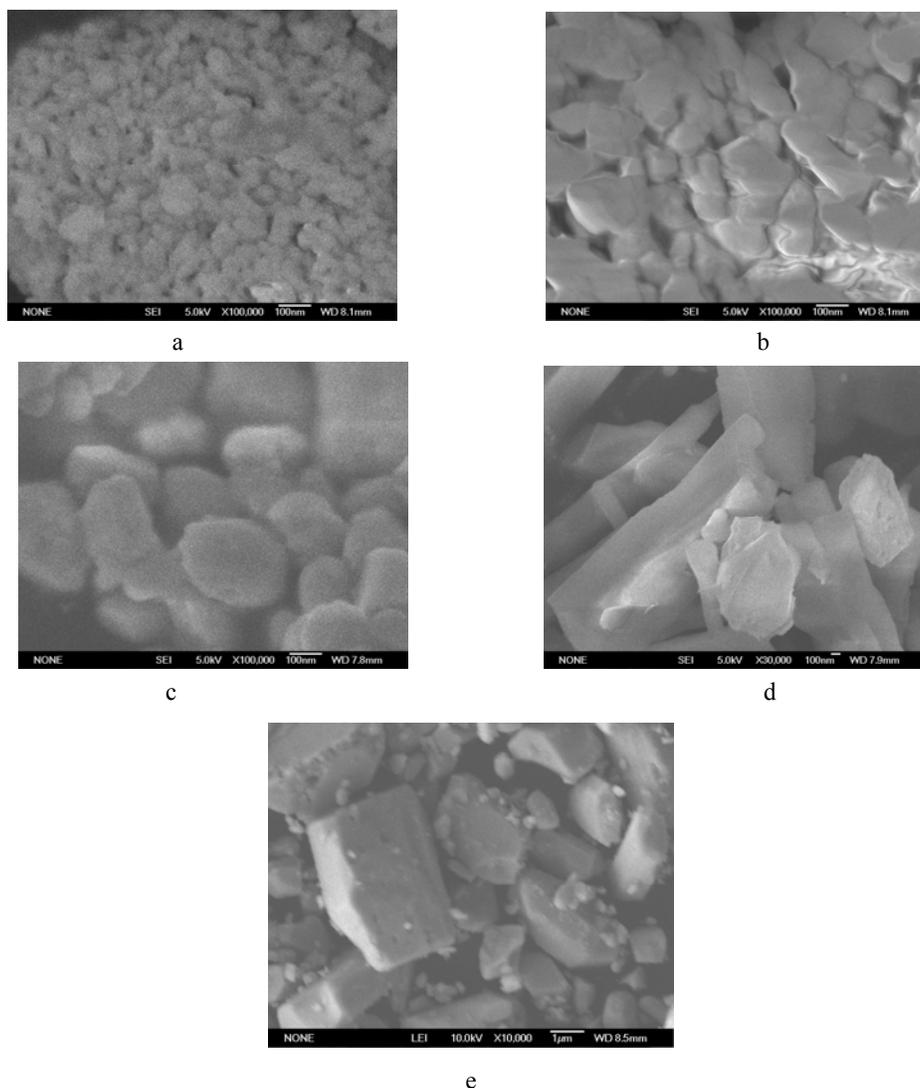


Fig. 2. SEM micrographs of the ZnWO<sub>4</sub> powders (a) calcined at 400°C (b) calcined at 500°C (c) and (d) preheated at 400°C for 1h and then calcined at 600°C and 700°C for 1h respectively, (e) calcined at 700°C for 1.5h

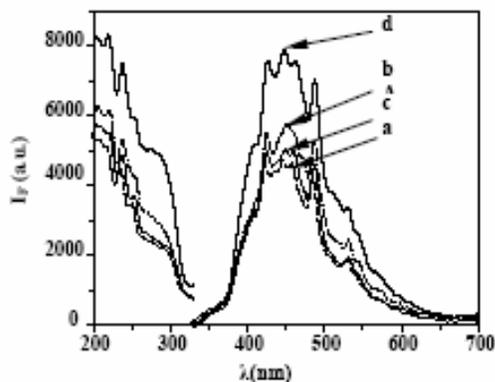


Fig. 3. The luminescence spectra of the  $\text{ZnWO}_4$  powders (a) calcined at  $500^\circ\text{C}$  for 1h, (b) and (c) preheated at  $400^\circ\text{C}$  for 1h and then calcined at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 1h respectively, (d) calcined at  $700^\circ\text{C}$  for 1.5h

In comparison with the emission peak intensity ( $\sim 1200$  a.u.) of the powders prepared with hydrothermal route by Song et al, the powders prepared in this work have very strong emission peak of  $\sim 8000$  a.u., which indicated very high luminescent efficiency of the powders prepared with the aqueous solution reaction -calcination processes.

#### 4. Conclusion

Ultrafine  $\text{ZnWO}_4$  powders has been successfully synthesized by aqueous reaction process at lower temperature. The powder synthesized at room temperature was amorphous, but  $\text{ZnWO}_4$  becomes only XRD detectable phase when sample were heated at  $400^\circ\text{C}$  for 1h. The crystallinity and grain size of the powders was increased with increasing calcining temperature to  $700^\circ\text{C}$ .  $\text{ZnWO}_4$  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. Very high luminescent efficiency can be obtained on the powders prepared with the method mentioned in this work.

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