

Luminescence property of Y-doped ZnWO₄ powders

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Y-doped ZnWO₄ powders have been synthesized by reaction between ZnCl₂, Y(NO₃)₃ and Na₂WO₄ aqueous solutions and following calcinations. XRD analysis indicated that the average particle size and intensity of XRD peaks of the powders were vary with calcining schedules. SEM micrograph indicated that powders had uniform grain size about 20-500 nm, which increases with increasing calcining temperature and time. Compared with the ZnWO₄ powders prepared with same method, Y-doped ZnWO₄ powders show less crystallinity and grain size and more dispersive morphology. The luminescence experiments indicated that the powders show a similar broad blue-green emission bands compared to the ZnWO₄ powder. The luminescence intensity of the Y-doped powders is nearly equal to that of undoped powders at calcining temperature of 500°C for 1h, and decreases with increasing crystallinity and grain size, as opposite to the ZnWO₄ powders. The Y-doped powders with less grain size and more dispersive morphology are more suitable for applications.

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1. Introduction

Sanmartinite ZnWO₄ have been widely studied as photocatalyst^[1-5], microwave dielectric ceramics[6], photo-stimulated photoluminescent[7-12]. The luminescence property of the ZnWO₄ powder has been improved by using various substitutions and synthesis processes in recent year. However the synthesis and property of the Y-doped ZnWO₄ nanocrystals was rarely reported previously.

The ZnWO₄ 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[14], et al.

In this work we reported (i) synthesis of ZnWO₄ and Y-doped ZnWO₄ nanocrystal with chemical reaction-calcination process under different calcining schedules; (ii) the comparison in the luminescent properties between the Y-doped ZnWO₄ nanocrystals and the ZnWO₄ powder; and (iii) the variation of the luminescence property with the calcining schedule.

2. Experimental procedure

The ZnWO₄ and Y-doped ZnWO₄ powders were prepared by a method based on an approach previously used for fabrication of 3D metal tungstates (MWO₄, M=Mn,

Co, Ni and Cu)[14]. For the ZnWO₄ powders equimolecular ZnCl₂ and Na₂WO₄ were respectively dissolved in distilled water, two solutions were then slowly mixed with constant stirring, respectively. For the Y-doped ZnWO₄ powders 1mol% ZnWO₄ was substituted by Y(NO₃)₃. The white precipitations were fast formed. The precursors were filtered and washed repeatedly with distilled water. The precipitations were then dried at 100°C for 4h and calcined at different schedules.

The phase identification of two powders and the films was conducted at room temperature using X-Ray diffractometer (XRD, CuK_{α1}, λ=0.15406nm, Model No. D/Max-2200PC, Rigaku, Japan). The crystalline phases and the particle size of powders were determined with the Jade5 analysis software and the data were collected by a X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analyze the morphology of the powders. The luminescent properties of the nanocrystals were measured on the luminescent spectrophotometer (Modal No: F-4500, Japan).

3. Results and discussion

The XRD patterns of the ZnWO₄ powders are shown in Fig. 1, which indicated that the powders was a sanmartinite ZnWO₄ phase. It can be observed from the XRD patterns that remarkable increases in intensity of XRD peaks of the ZnWO₄ powders were produced by

increasing calcining temperature, which corresponds to a large increase in crystallinity of the powders. The average crystalline sizes determined from the width of the strong peak (111) in the XRD were 23.5nm and 26.3nm for the powders calcined at 400°C and 500°C respectively. The lattice constant a , b and c of the ZnWO_4 powders were calculated from XRD data analyses, which were varied with calcining temperature. The Y-doped ZnWO_4 powders calcined at 400°C for 1h show pale grey color. As it is seen from XRD patterns (Fig. 2) the ZnWO_4 with a sanmartinite structure was a main phase of the Y-doped powder. The peak at $\sim 29.00^\circ$ was identified as yttrium tungstates. It is believed in some literatures[15-17] that this XRD peak was belong to that of sanmartinite ZnWO_4 . The XRD peaks was obviously lower for Y-doped ZnWO_4 powders than for the ZnWO_4 powders, indicating crystallinity were decreased by the Y-substitution. The particle sizes of the Y-doped ZnWO_4 powders determined from the XRD strong peak (111) at $\sim 30.68^\circ$ were 13.3 nm and 13.9 nm for the powders calcined at 500°C for 1h and 1.5h and respectively, and 14.9 nm for the powder preheated at 400°C for 1h and calcined at 700°C for 1h, which are less than that of the undoped powders. These may be attributed to the suppression of the crystalline growth of the powders by the Y-substitution. The lattice constant a , b and c of the ZnWO_4 and Y-doped ZnWO_4 powders were calculated from XRD data analyses and are summarized in Table 1. The lattice constants of the ZnWO_4 powders increased by the Y-substitution, when the variation with the calcining parameters is taken into account. This could indicate the Y^{3+} enter ZnWO_4 lattice by substituting the Zn^{2+} due to larger ionic radius of Y^{3+} (0.93 Å) compared with Zn^{2+} (0.72 Å).

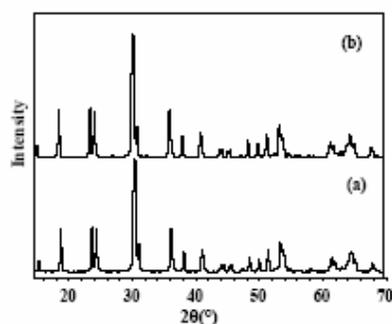


Fig. 1. XRD patterns of (a) the dried precipitation and the ZnWO_4 powders calcined at (a) 400°C, and (b) 500°C for 1h respectively.

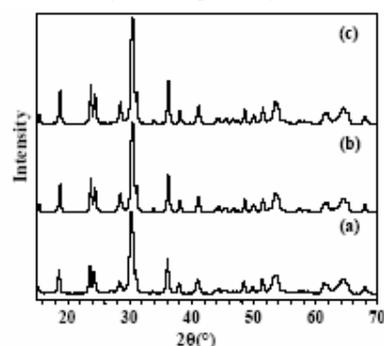


Fig. 2. XRD patterns of the Y-doped ZnWO_4 powders (a) and (b) calcined at 500°C for 1h and 1.5h respectively, and (c) preheated at 400°C for 1h and then calcined at 700°C for 1h.

Table 1. The particle size (D) and lattice parameter of the ZnWO_3 and Sm-doped ZnWO_3 powders prepared in various calcining conditions, determined by XRD data analysis, and the particle size* determined from SEM micrographs.

Sample	Calcining schedule	Lattice parameter			Average particle size	
		$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$D(\text{nm})$	
ZnWO_3	400 °C 1h	4.6965	5.7286	4.9531	23.5	20-100*
	500 °C 1h	4.7014	5.7321	4.9589	26.3	40-200*
Y-doped ZnWO_3	500 °C 1h	4.7058	5.7325	4.9591	13.3	20-100*
	500 °C 1.5h	4.7067	5.7331	4.9601	13.9	20-105*
	400 °C 1h + 700 °C 1h	4.7072	5.7346	4.9608	14.9	30-120*

The SEM micrographs of the ZnWO_4 and Y-doped ZnWO_4 powders are shown in Fig. 3. They indicate that the ZnWO_4 powders have particle size about 10-150 nm, and increases with increasing calcining temperature and calcining time but decreases by the Y-substitution.

This is consistent with the XRD analysis. The morphology of the particle is uniform and near to spherical configuration for all powders.

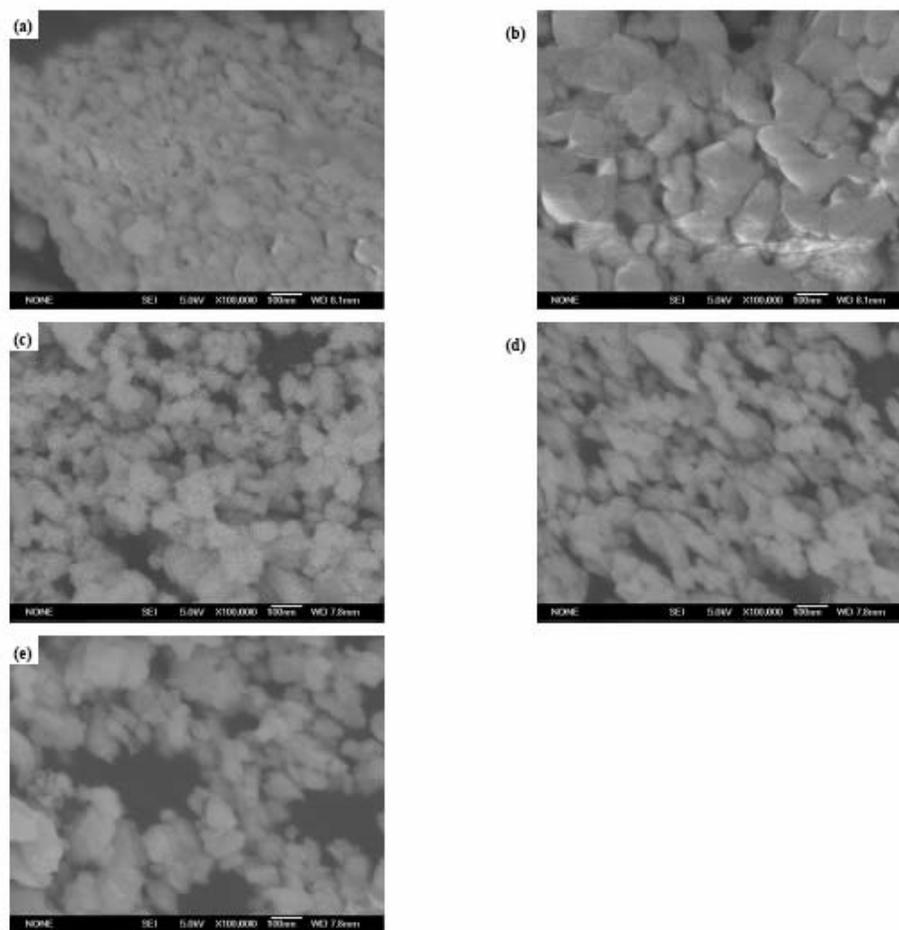


Figure 3. SEM micrographs of the ZnWO₄ powders (a) calcined at 400°C for 1h (b) calcined at 500°C for 1h, and Y doped ZnWO₄ powders (c) and (d) calcined at 500°C for 1h and 1.5h respectively and (e) preheated at 400°C for 1h and then calcined at 700°C for 1h.

The luminescence properties of the powders were measured on the luminescent spectrophotometer and are shown in Fig. 4 for the ZnWO₄ powders and Fig. 5 for the Y-doped ZnWO₄ powders. They were monitored at 470 nm and excited at 280 nm. The spectrum exhibits a broad excitation band and a broad deep blue-green emission band. The excitation band of the ZnWO₄ powders calcined at 400°C for 1h is centered at 266.8 nm (4.65 eV), its emission band was centered at 466.2 nm (2.66 eV). Similarly, the excitation band of the ZnWO₄ powders calcined at 500°C for 1h was centered at 278.9nm (4.45 eV), its emission band was centered at 470.2 nm (2.64 eV). The intensity of excitation and luminescence peaks increase with increasing calcining temperature from 400°

C to 500°C for 1h, which can be attributed to increase in crystallinity and grain size of the ZnWO₄ powders. The excitation band and emission band of the Y-doped ZnWO₄ powders calcined at 500° C for 1h were respectively centered at 282.8 nm (4.38 eV) and 473.1 nm (2.62 eV). Similarly the excitation band and emission band of the Y-doped ZnWO₄ powders calcined at 500°C for 1.5 h are respectively centered at 283.08 nm (4.38 eV) and 473.4 nm (2.62 eV). For the Y-doped ZnWO₄ powders preheated at 400° C for 1h and then calcined at 700° C for 1 h, the center of the excitation band and emission band are, respectively, shifted to 282.6 nm (4.38 eV) and 472.0 nm (2.62 eV). The blue-green emission near 470 nm may arise from the WO₄²⁺ group.

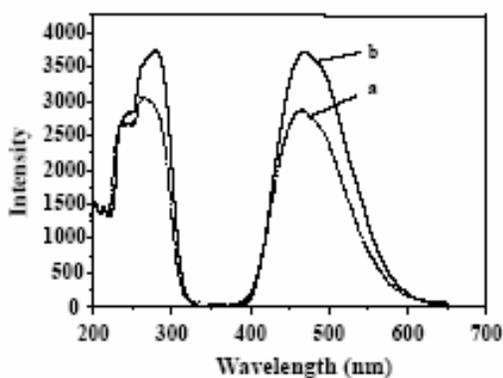


Fig. 4. The luminescence spectra of the ZnWO_4 powders calcined (a) and (b) at 400°C and 500°C for 1h.

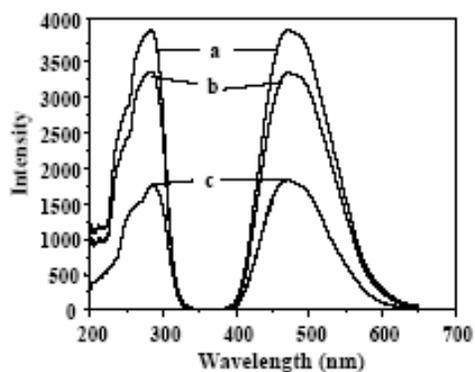


Fig. 5. The luminescence spectra of the Y-doped ZnWO_4 powders calcined at (a) and (b) 500°C for 1h and 1.5h respectively, and (c) preheated at 400°C for 1h and then calcined at 700°C for 1h. Monitored at 470nm, excited at 280nm.

By comparison, it is obvious that the Y-substitution results in red shift of the luminescence and the luminescence intensity is nearly equal for the two powders calcined at 500°C for 1 h. The intensities of luminescence peaks of the doped powders decrease with increasing calcining temperature and calcining time, which is opposite to the case of the undoped powders. Regarding the quantum-size effect, luminescence intensity may increase with decreasing grain size of luminescence powder. Nevertheless the stronger light diffusion of the luminescence powder with a smaller size generally results in lower intensity of the luminescence. The Y-substitution here would decreased this light diffusion of the powder.

4. Conclusions

Ultrafine Y-doped ZnWO_4 and ZnWO_4 powders has been successfully synthesized by aqueous reaction process at lower temperature. The crystallinity and grain size of the powders increase with increasing calcining temperature but decrease by Y-substitution. The ZnWO_4 and Y-doped ZnWO_4 powders show a broad excitation band and broad deep blue-green emission band. The Y-substitution results in a red shift of the luminescence peaks. The luminescence intensity increases for undoped powder but decreases for the doped powder with increasing crystallinity and grain size of the powders. The luminescence intensity is nearly equal for the two powders calcined at 500°C for 1h. The Y-doped powders with lower grain size and dispersive morphology would be suitable for applications.

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