Functional Materials 20, No.4 (2013)

Microwave hydrothermal synthesis and luminescent properties of $ZnWO_4$ nanoparticles

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Received August 19, 2013

Nanosized crystals of zinc tungstate were synthesized by microwave-hydrothermal method under different conditions of temperature and pH of initial solutions. Emergence of the nanophase was established in temperature range of the microwave processing from 120°C to 200°C. Change in the morphology of the crystallites synthesized at 120–200°C and $6 \le pH \le 10$ units were considered. Transformation of the nanograins (size of 10 nm to 40 nm) to nanorods (length of 50 nm to 200 nm) and their enlargement occurs when temperature of the microwave processing and pH of the initial solutions rise. The relation between luminescent parameters of the nanocrystals and their morphological features was investigated.

Гидротермально-микроволновым методом получены наноразмерные кристаллы вольфрамата цинка при варьировании температуры микроволновой обработки и pH маточного раствора. Установлено зарождение и формирование нанокристаллической фазы в температурном диапазоне микроволновой обработки от 120°C до 200°C. Рассмотрено изменение морфологии кристаллитов, синтезированных при 120–200°C и $6 \le pH \le 10$ единиц. Трансформация нанозерен (размером от 10 до 40 нм) в наностержни (длиной от 50 до 200 нм) и их укрупнение происходит при повышении температуры микроволновой обработки и pH маточного раствора. Исследована связь морфологических особенностей нанокристаллитов и их люминесцентных параметров.

Гідротермально-мікрохвильовий синтез і люмінесцентні властивості наночастинок $ZnWO_4$. *А.Якубовська, І.Туніцина, Д.Сафронов*, О.Вовк*, К.Катрунов, А.Жуков, В.Баумер*, А.Андрющенко.*
Гідротермально-мікрохвильовим методом отримано нанорозмірні кристали вольфрамату цинку при варіюванні температури мікрохвильової обробки та pH маточного розчину. Встановлено зародження і формування нанокристалічної фази у температурному діапазоні мікрохвильової обробки від 120°C до 200°C. Розглянуто зміну морфології кристалітів, синтезованих при 120–200°C і $6 \le pH \le 10$ одиниць. Трансформація нанозерен у наностержні та їх укрупнення відбувається при підвищенні температури мікрохвильової обробки і pH маточного розчину. Досліджено зв'язок морфологічних особливостей нанокристалітів та їх люмінесцентних параметрів.

1. Introduction

Zinc tungstate ($ZnWO_4$) single crystals are scintillation materials for detecting and spectrometric systems used in nuclear physics and nuclear energetic for radiation monitoring and digital radiography, as well as for registration of rare events [1–5]. The scintillation material based on $ZnWO_4$ at-

tracts particular attention because its scintillation parameters are close to those of cadmium tungstate while it has a low level of intrinsic radioactivity and toxicity [4].

Modern requirements to scintillators stimulate the search for new materials to create the new generation of detectors. Usage of nanocrystalline materials allows providing qualitatively new devices including scintillators with the required functional characteristics (radiation stability, sensitivity, spatial, temporal and energy resolution) [6–8]. The properties of the nanomaterials depend significantly on the size and morphology of their particles [9, 10].

Several synthesis methods for obtaining nanoparticles of alkaline-earth metals tungstates were introduced earlier: sol-gel [11], hydrothermal [12, 13], solvotermal [14], molten salt methods [15] and others. Multistep method of uniform $ZnWO_4$ nanoparticles production by the sol-gel technology was proposed by J.H.Ryu et al. [16]. In this case, the MW treatment was used only to obtain a polymerized metal-citrate complex. This substance then was heated to 600°C by traditional way. Formation of $ZnWO_4$ nanocrystalline phase was completed at temperature range 550–600°C (according to the DTA and the spectra of FT-IR).

The divalent metal tungstates nanoparticles have been synthesized in a microwave-assisted oven at 100°C and 150°C and corresponding autogenous water vapor pressure within a time frame from 30 min to 2 h [17]. The submicrometer crystals formed equidimensional and needlelike crystals. Morphology of the synthesized particles depended on both temperature and duration of the microwave treatment.

MWH synthesis of all divalent metal tungstates with either the scheelite or the wolframite structure has many advantages over conventional techniques [17–19]. Among others: quick and homogenous heating of the reaction mixture, high speed of interaction, inverse temperature gradients, sharp-cut control of reaction conditions. In addition, under the autogenous water vapor pressure the boiling point of solvent raises consequently speeding up phase formation and lowering the temperature (up to 200°C) of dispersed phase formation. The dispersion and phase composition of the product could be controlled by varying the synthesis conditions.

It was reported in [12, 14] that increasing of the hydrothermal synthesis temperature in aqueous medium and in non-aqueous solvents leads to increasing of $ZnWO_4$ nanoparticle sizes. It was also indicated the influence of pH of the stock solution on the size of $ZnWO_4$ particles under hydrothermal conditions [14]. However, authors of this work have not investigated the effect of synthesis temperature on the nature of the transition from amorphous to nanocrystalline phase at varying pH values.

Therefore, in this paper, we report the synthesis of $ZnWO_4$ nanoparticles by MWH method and investigation of the influence of synthesis conditions on morphological and luminescent properties of the nanoparticles.

2. Experimental

We used the following starting materials: $Na_2WO_4 \cdot 2H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ and $NH_3 \cdot H_2O$ of analytical grade purity (98 %) and HNO_3 ($\rho = 1.40$) (Merk, GR for analysis). All solutions were prepared in distilled water without further purification of precursors.

The synthesis was carried out in two stages. Initially, amorphous $ZnWO_4$ was prepared by co-precipitation of 25 ml of 0.1 M aqueous solutions of $Zn(NO_3)_2$ and Na_2WO_4 at the room temperature with vigorous stirring. pH of solutions was adjusted by adding dilute aqueous 69 % HNO_3 or 30 % $NH_3 \cdot H_2O$ solutions. The MWH synthesis was carried out on microwave installation MARS (CEM Corporation Matthews, USA) at 120, 160 and 200°C (maximal temperature for a given set of synthesis) and the frequency of 2.45 GHz for 30 min. Upon completion of the synthesis the white precipitate was filtered, washed with distilled water and dried at 70°C in air for 3 h.

Morphology of the nanocrystals was determined by transmission electron microscopy using a microscope EM-125 (SELMA, Ukraine). Electron accelerating voltage was 125 kV, the survey was carried out in the bright field mode, the image was recorded by CCD matrix. We used thin carbon films coated with water suspension of the investigated powders for electron microscopy.

Phase purities of the samples were characterized by X-ray powder diffraction (XRD) on Siemens D 500 powder diffractometer (radiation $CuK\alpha$, nickel filter, Bragg-Brentano geometry). Diffraction patterns were measured in the angular range $10 < 2\theta < 70°$ with increments of 0.02° and accumulation time of 2 seconds at each point. Search of the phases was executed on

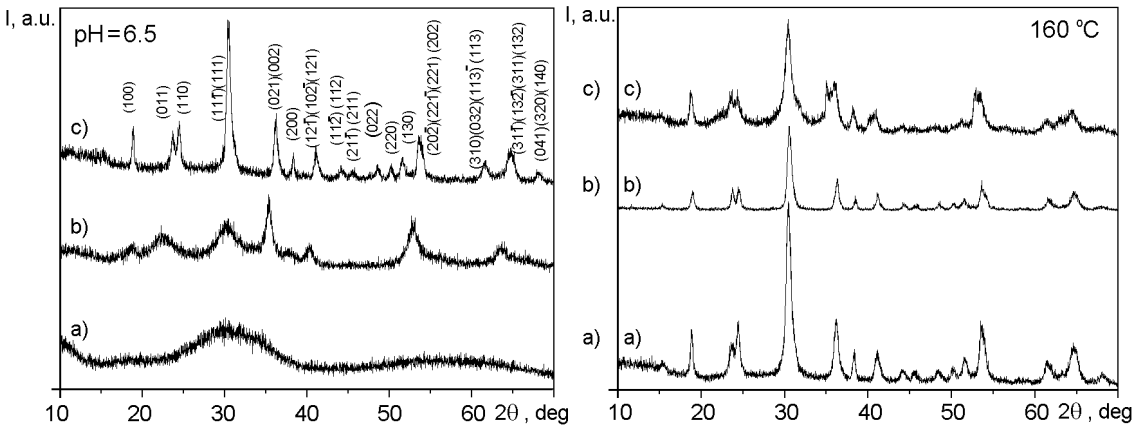

Fig. 1. $ZnWO_4$ XRD patterns. The samples were prepared at pH = 6.5: a — precursor (room temperature), b — 120°C, c — 200°C; at 160°C: a — pH = 6, b — pH = 8.5, c — pH = 9.5.

the catalog PDF-1 [20] using the software EVA and SEARCH, included in the diffractometer.

X-ray luminescence spectra were measured by spectrophotometric complex KSVU-23. X-ray source REIS ($U\alpha \leq 40$ kV, $ia \leq 50$ μA) was used as an excitation [21].

3. Results and discussion

According to X-ray structural analysis the precursor $ZnWO_4$ prepared by co-precipitation of zinc and tungstate salts solutions at the room temperature was amorphous substance (Fig. 1). XRD of the product synthesized in MW field with varying the synthesis temperature and pH of the medium showed that the nucleation of nanocrystalline monoclinic phase of $ZnWO_4$ with wolframite structure (JCPDS No.15-0774) starts at 120°C and continues at higher temperatures of the synthesis (Fig. 1). The XRD patterns of $ZnWO_4$ powders prepared from the initial solutions with various pH under the same other conditions (160°C) have different form of structural peaks because of their dependence on size and morphology of the particles. The peak shapes on the X-ray reflection spectra become more narrow when temperature of the synthesis increases at constant pH value. This may point that the length of nanorods increases with the increase of the temperature. It was confirmed by studies of the particle morphology by the method of transmission electron microscopy.

Dispersion and morphology of the particles of $ZnWO_4$ obtained under different conditions are shown in Fig. 2–4.

Formation of the particles in the form of grains of average size of 10 nm was observed at the temperature of 120°C of the MWH synthesis (Fig. 2). The effect of pH of the solution on the particle size at this temperature was negligible.

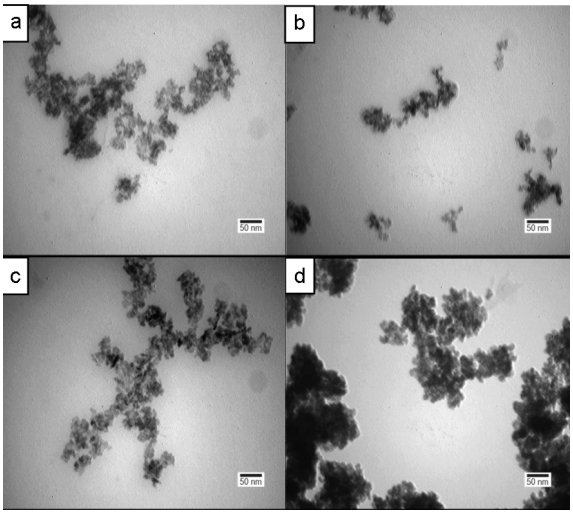

Fig. 2. Transmission electron microscope images of $ZnWO_4$ samples obtained by MWH synthesis at 120°C for 30 min at pH 5.5 (a), 6.7 (b), 8.5 (c) and 9.5 (d).

Formation of two types of the particles was observed when the MWH synthesis temperature was raised to 160°C: grains in the range of 20–40 nm (Fig. 3a, b, c) and the rods with length of 50–60 nm and diameter of 4–6 nm (Fig. 3d). The formation of the particles with a granular structure was observed in a wide pH range of 5.6–8 units and the nanorods at pH above of 9 units.

Formation of the two types of the particles: the grain of 25 nm (Fig. 4a, b) and rods with length of up to 100–200 nm and diameter of 5–10 nm (Fig. 4c, d), was observed at 200°C. A significant factor influ-

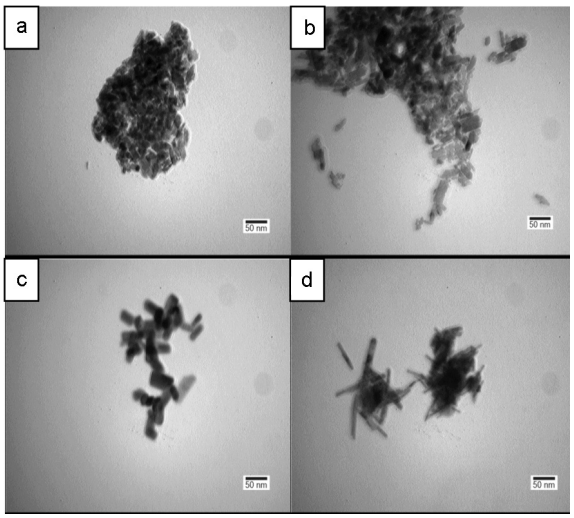

Fig. 3. Transmission electron microscope images of $ZnWO_4$ samples obtained by MWH synthesis at 160°C for 30 min at pH 5.6 (a), 6.2 (b), 8 (c) and 9.5 (d).

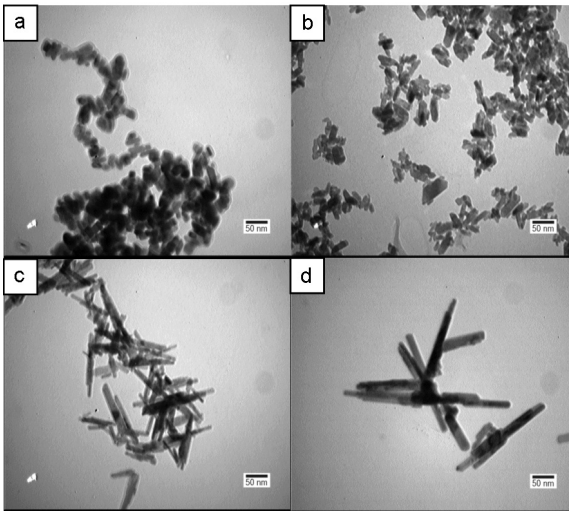

Fig. 4. Transmission electron microscope images of $ZnWO_4$ samples obtained by MWH synthesis at 200°C for 30 min at pH 5.5 (a), 6.2 (b), 8 (c) and 9.5 (d).

encing the shape of the particles is pH of the initial solution. The grain structure formation was observed in the pH range of 5.5–6.2 and rod-shape — when pH was increased above 8 units.

At the higher pH the larger rods were formed: at pH 8 the length and diameter of the nanorods were 50–100 nm and 5–7 nm, respectively. At pH 9.5 the length was increased to 150–200 nm and diameter to 10 nm. The anisotropic growth of the particles along (021) direction due to the coalescence process by the Gibbs-Thompson mechanism [5, 17, 22]. The Gibbs-Thomson effect refers to observation that small crystals are in equilibrium with their liquid melt at the lower temperature than large crystals. It is known that pH of Zn^{2+} complete precipitation is equal to 8. pH of solution and precipitate solubility increase then ammonia adding to the solution [23].

Because of ammonia provides very stable complexes with Zn^{2+} the dissolution process can be expressed by equation (1):

$$ZnWO_4 \downarrow + nNH_3 \rightarrow \quad (1)$$
$$\rightarrow Zn(NH_3)_n^{2+} + WO_4^{2-}, \text{ there } n = 2,4.$$

Increase of the zinc ammonia complex concentration facilitates the rate of recrystallization of zinc tungstate and promotes the formation of nanorods.

X-ray luminescence spectra of the nanocrystalline samples with different morphologies prepared at varying temperature of the MWH synthesis and pH of the initial solution were also investigated. All samples

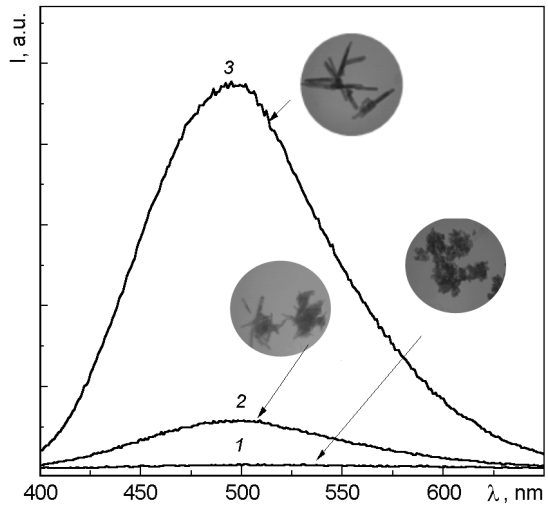

Fig. 5. X-ray luminescence of the $ZnWO_4$ nanocrystals synthesized at varying MWH synthesis temperature and pH: *1* — pH = 9.5 T = 120°C; *2* — pH = 9.5 T=160°C; *3* — pH=9.5 T=200°C.

had the same emission peak at λ_{max} = 500 nm which is almost identical to that of the single crystal. Luminescent properties of $ZnWO_4$ correspond to the transitions within oxyanion complex WO_6^{6-} [24–26].

However, we observed that the luminescent properties of the nanoparticles were determined by their morphology, which in turn depends on temperature of the MWH synthesis and pH of the solution. The most intensive band of X-ray luminescence is typical for the samples which were nanorods with diameter of 10–15 nm and length of

150 nm synthesized at 200°C and pH 9.5 (Fig. 5). Similar effect was observed for the emission spectra under photoexcitation.

4. Conclusions

The nanosized crystals of zinc tungstate were prepared by MWH synthesis with varying temperature of synthesis and pH of the initial solutions.

It is shown that crystallization of the amorphous phase of zinc tungstate to monoclinic structure occurs under the MWH synthesis (frequency 2.45 GHz) for 30 min at temperatures range from 120°C to 200°C.

It is also shown that the morphological characteristics of the particles are mainly influenced by pH of the initial solutions and temperature of the MWH synthesis. Transformation of the nanograins into the nanorods and their integration occurs when temperature of the MWH synthesis and the initial solutions pH increase.

The dependency of luminescence parameters on morphological properties of the nanocrystallites was investigated. With enlargement of the nanograins the intensity of X-ray luminescence grows up. The most intensive luminescence band was observed for the samples which were nanorods with the length of around 150 nm.

Acknowledgements. This work was partly supported by the State Agency on Science, Innovation and Informatization of Ukraine (Contract No.M316.2012) and National Academy of Sciences of Ukraine.

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