PH-CONTROLLED MICROWAVE-ASSISTED SYNTHESIS OF LUMINESCENT $SrWO_4$ MICROCRYSTALS

GUIZHEN WANG[a,b*], GENGPING WAN[a,b], SHIWEI LIN[a]

[a]*Key Laboratory of Ministry of Education for Application Technology of Chemical Materials in Hainan Superior Resources, The College of Materials and Chemical Engineering, Hainan University, Haikou 570228, P. R. China*

[b]*Key Laboratory of Chinese Education Ministry for Tropical Biological Resources, Hainan University, Haikou 570228, P. R. China*

$SrWO_4$ microcrystals with different morphologies, such as rod-like, flower-like, and spindle-like, have been successfully synthesized by adjusting pH value via a simple microwave-assisted method. The as-prepared products have been characterized by X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy and field-emission scanning electron microscopy. A possible mechanism to illustrate the formation of the $SrWO_4$ structures at different pH values was discussed. The examination of photoluminescence (PL) property reveals that the PL intensity has a biggish improvement with the increase of pH value, which can be relative to various morphologies and crystallinity prepared at different pH values. These interesting properties of $SrWO_4$ microcrystals may have many potential applications.

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Keywords: $SrWO_4$; pH control; Optical properties; Microwave radiation

1. Introduction

Recently, $SrWO_4$ have received great attention because of predicted and confirmed to be perspective for Raman converters, lasers, and amplifiers by the study of spontaneous Raman spectroscopy and also verified to be an excellent Raman medium for the frequency conversion of the high-energy nanosecond laser pulses [1, 2]. Various techniques have been developed to synthesize $SrWO_4$, such as the sonochemical method [3], microemulsion method [4, 5], cyclic microwave irradiation [6, 7], solvothermal-mediated microemulsion method [8], and hydrothermal method [9,10].

Microwave radiation has become an important tool in chemistry for its applications in the synthesis and modification of both organic and inorganic materials. When microwave radiation is supplied to chemical solutions, one or more of the components dissolving in the solutions is capable of coupling with the radiation. It can lead to higher heating rate than that achieved by conventional method. Microwave radiation can solve the problems of temperature and concentration gradients [11]. As a result, this has provided the possibility to synthesize tungstate materials in a short time [12, 13].

Herein, we report a simple and fast microwave-assisted route for preparing $SrWO_4$ microcrystals at different pH values with controlled morphologies and propose a possible mechanism to illustrate the formation of the $SrWO_4$ microstructures. We also studied the

*Corresponding author: wangguizhen0@hotmail.com (G. Wang)

luminescence performance of the as-synthesized $SrWO_4$ microcrystals because of its well-known photoluminescent properties.

2. Experimental

$Sr(NO_3)_2$, $Na_2WO_4{\cdot}2H_2O$, NaOH, and cetyltrimethylammonium bromide (CTAB) were of analytical grade and used as receivedwithout any further purification. In a typical experimental procedure, solution A was prepared by dissolving 1.0 mmol of CTAB in 100 mL of 5 mM $Sr(NO_3)_2$ aqueous solution under magnetic stirring. Solution B was prepared by dissolving 1.0 mmol of CTAB in 100 mL of 5 mM $Na_2WO_4{\cdot}2H_2O$ aqueous solution under magnetic stirring. The pH was adjusted to a specific value using NaOH (4 mol/L) or acetic acid solution (1 mol/L). Two solutions were mixed quickly under magnetic stirring at room temperature. The mixture was placed in the center of an improved household microwave oven (Galanz WP750, 2450 MHz, 750 W) with a refluxing system outside. 60% (450 W) of the microwave-heated power was used to irradiate the mixture for 6min. Then, the microwave heating was terminated, and the solution was cooled to room temperature. The products was separated by centrifugation, washed with distilled water and absolute ethanol respectively three times, and dried at 45 $^{\circ}$C in vacuum.

X-ray powder diffraction (XRD) analysis was performed on a BRUKER AXS D8 Advance diffractometer with Cu Kα radiation (λ=1.54178 Å) using a 40 kV operation voltage and 40 mA current. Scanning electron microscopy (SEM) was recorded on a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM). Fourier transform infrared (FTIR) spectra were determined on a TENSOR 27 spectrophotometer using KBr pressed disk. The Raman spectra of the products were obtained by Raman spectrometer (HORIABA Jobin Yvon T64000) with a radiation of 514.5 nm from an argon ion laser. The photoluminescence (PL) was studied on a Hitachi F-7000 fluorescence spectrophotometer with Xe lamp at room temperature. The resulting products were dispersed in water and measured in a standard quartz cuvette.

3. Results and discussion

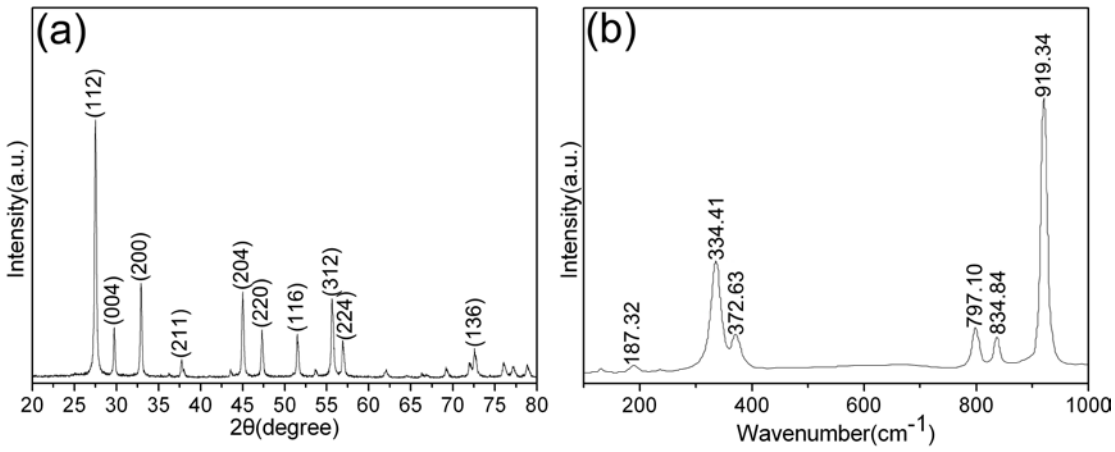

Fig. 1. (a) XRD pattern and (b) Raman spectrum of the as-prepared $SrWO_4$ products at pH 7.0.

Fig. 1(a) shows typical XRD pattern of the as-prepared $SrWO_4$ products. All diffraction peaks of the products can be indexed to pure scheelite-type tetragonal $SrWO_4$ phase with space group $I4_1/a$, in agreement with the respective JCPDS (Joint Committee on Powder Diffraction Standards) card No. 08-0490. The Raman spectrum of the $SrWO_4$ product is shown in Fig. 1(b). It is seen that six different vibrations are detected on Raman spectrum of the products. Among them, $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(B_g)$, $\nu_2(A_g)$, and $\nu_{f.r.}(Ag)$ are at 919.34, 834.84, 797.10, 372.63, 334.41 and 187.32 cm^{-1}, respectively. The vibration modes are in accord with Raman vibrations analyzed by other researchers [5-7, 14]. No peaks in the XRD or Raman spectra from other impurities were detected. This result shows that the microwave irradiation method can accelerate the formation of crystalline $SrWO_4$ with low heat treatment temperature and reduced processing time than the conventional methods.

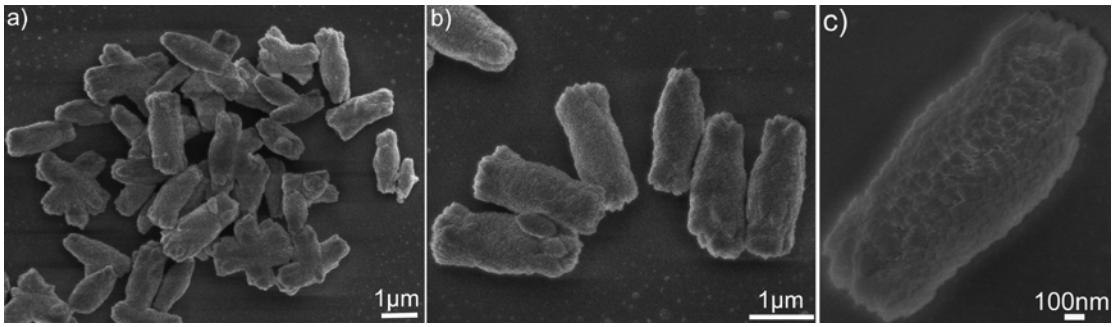

Fig. 2. SEM images of the as-prepared $SrWO_4$ products at pH 7.0.

The typical FE-SEM images of the as-prepared $SrWO_4$ products are shown in Fig. 2. It can be seen that the product represents a rod-like morphology with width of about 700 nm and length of about 2 μm. Single microrod shown in Fig. 2c indicates that the $SrWO_4$ rod have a rough surface and is composed of self-assembled $SrWO_4$ nanoparticles.

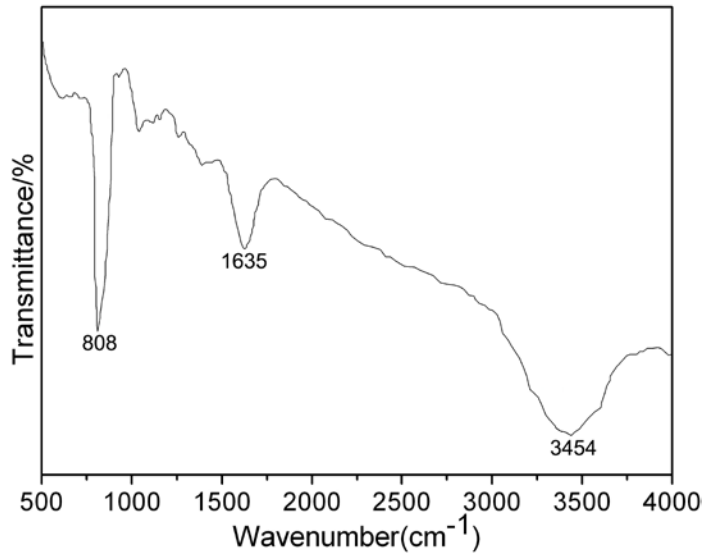

Fig. 3. FTIR spectrum of the as-prepared $SrWO_4$ products at pH 7.0.

Fig. 3 shows FTIR spectrum of the as-prepared $SrWO_4$ products. For T_d symmetry, $\nu_3(F_2)$ and $\nu_4(F_2)$ are IR active and correspond to stretching and bending modes, respectively [15, 16]. The spectrum of $SrWO_4$ shows a characteristic band at 808 cm^{-1} corresponded to W-O stretching vibration. It is one of the internal modes specified as $\nu_3(F_2)$ antisymmetric stretching vibration [15]. The broad band (3600-3000 cm^{-1}) centered at 3454 cm^{-1} can be assigned to hydrogen bonded O-H stretching vibration arising from crystal water. The absorption band at 1635 cm^{-1} on spectrum refers to the vibration of remainder H_2O in present samples.

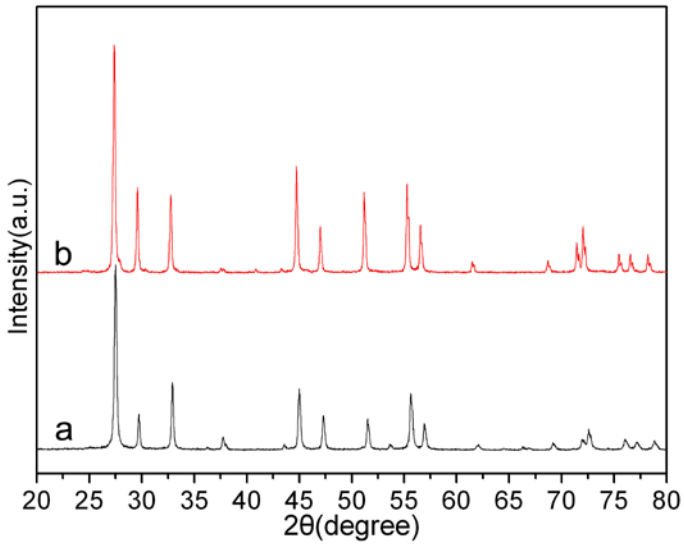

Fig. 4. XRD patterns of $SrWO_4$ products prepared at pH values of (a) 5.0 and (b) 9.0.

The XRD patterns of $SrWO_4$ samples prepared at different pH values are shown in Fig. 4. The reflection peaks of both the two products can be indexed as a pure tetragonal scheelite structure with a lattice constant (α=5.416Å and c=11.95 Å), which are in good agreement with JCPDS No. 08-0490. It can be considered that phase-pure tetragonal structure $SrWO_4$ with good crystallinity had been successfully synthesized under a wide range of conditions via the present microwave-assisted method.

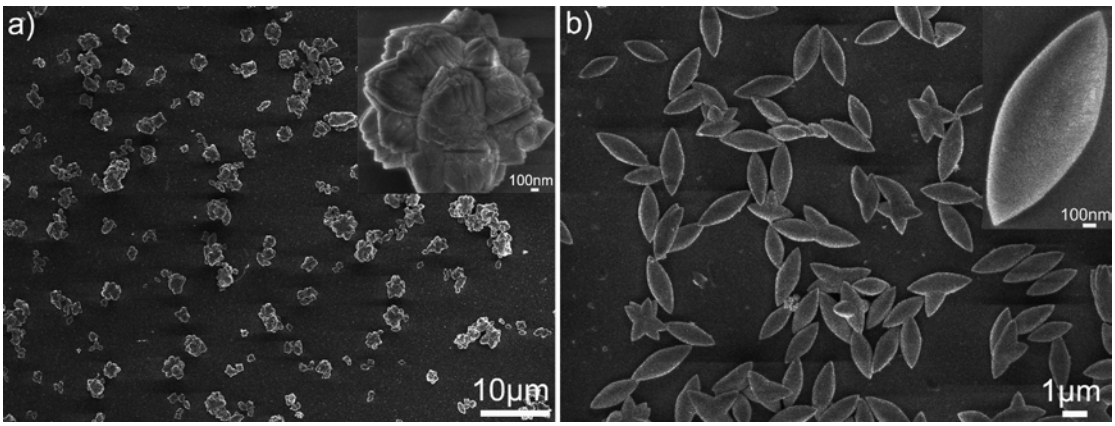

Fig. 5. SEM images of $SrWO_4$ products prepared at pH values of (a) 5.0 and (b) 9.0.

In the present work, it is found that the pH value of reaction system has great influence on the morphologies of the obtained samples. When the other conditions were the same, Fig. 5 presents SEM images of $SrWO_4$ with different morphologies including flower-like and spindle-like products obtained at different pH values. Fig. 5a shows that the products prepared at pH 5.0 are flower-like structures with an approximate dimension of 2.0-3.5 μm. A high-magnification SEM image inset to Fig. 5a shows that a flower-like $SrWO_4$ microcrystal has a great deal of horns which aggregate to form a ball-flower. When the reaction was performed at pH 9.0, the SEM image (Fig. 5b) shows that the products are composed of uniform spindle-like structures $SrWO_4$. Single $SrWO_4$ spindle shown inset to Fig. 5b indicates that it has a smooth surface with a wide length of ca. 800 nm and a length of ca. 2.5 μm.

On the basis of above results, it is clear that the morphology of the final product can be controlled by adjusting the pH value of the solution. The mechanism of $SrWO_4$ have a changeful morphologies in the presence of CTAB at different pH values is studied. It is assumed that the influence of the different pH values on the growth of the crystals may lie in affecting the adsorption of CTAB to different facets. Because of the faces of $SrWO_4$ particles showing different polarity pattern and average interface energy at different pH values, the CTAB molecules absorbed and desorbed the $SrWO_4$ particles with different velocity, which lead to an anisotropic growth and directional self-arranged growth of $SrWO_4$ crystals [17, 18]. In addition, the microwave irradiation is also responsible for the formation of $SrWO_4$. Microwave heating leads to a high heating rate and a rapid increase in temperature during the nucleation process, which is important for fast nucleation and growth of crystals.

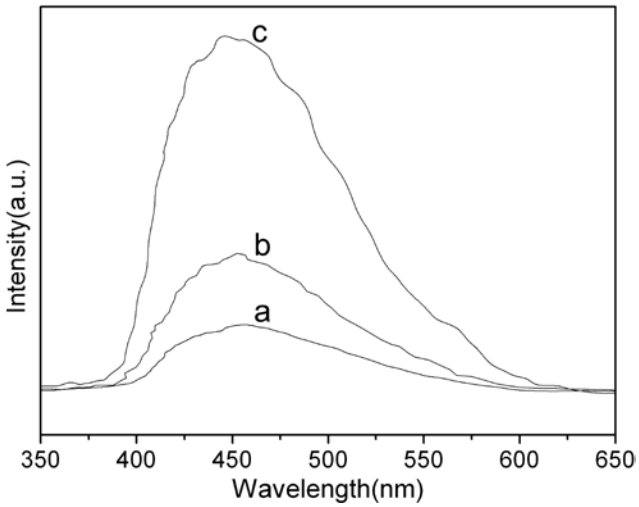

Fig. 6. PL spectra of the products prepared at pH values of (a) 5.0, (b) 7.0, and (c) 9.0.

Room-temperature PL properties of the $SrWO_4$ samples were also studied. Fig. 5 shows the PL spectra of the different $SrWO_4$ microcrystals were measured from 350 to 650 nm using the same excitation line of 270 nm. The spectra show that all of the three samples exhibited typical emission peaks at ca. 456 nm considered to be from the $^1T_2 \rightarrow {}^1A_1$ transition of electrons within $[WO_4]^{2-}$ anions [19-21]. The shoulders are from some defects and/or impurities, and interpreted as extrinsic transitions. It is easily found that the PL intensity have a biggish improvement with the increase of pH value. The possible explanation is that the samples with spindle-like structure (pH 9.0) have a more uniform morphology and better crystallinity, which is responsible for the stronger emission and fine light-collection efficiency. The samples prepared at pH 7.0 and 5.0 show weaker

crystallization than the one made at pH 9.0, so the relative intensities of the PL peaks seem closely related to the morphology and crystallinity, and the crystallinity may play a more important role. Based on these properties, the $SrWO_4$ microcrystal materials may be promising for applications in photoelectric materials.

4. Conclusions

In summary, we have developed a microwave-assisted route for the morphology-controlled synthesis of $SrWO_4$ microcrystals. $SrWO_4$ with rod-like, flower-like, and spindle-like morphologies have been obtained by adjusting the pH values. Room-temperature PL properties of $SrWO_4$ samples also have been investigated, and the results reveal that luminescence properties of $SrWO_4$ are very sensitive for its morphology and crystallinity. The luminescence performance observed in the prepared microstructure may have significant technological applications in the inorganic scintillating field.

Acknowledgements

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