



Microwave-Assisted Synthesis of Strontium Tungstate Particles by A Solid-State Metathetic Route

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(Received: 5 March 2011;

Accepted: 25 January 2012)

AJC-11017

Well crystallized strontium tungstate (SrWO_4) particles were formed by a solid-state metathetic (SSM) route assisted by a microwave irradiation, showing a spherical and homogeneous morphology with sizes of 0.5-1 μm . The synthesized SrWO_4 particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The optical properties were investigated by photoluminescence emission and Raman spectroscopy. With excitation at 250 nm, the major peaks are located at the blue wavelength of 425-450 nm. The emission spectra of 4-8 narrow neighbored and sloped shoulders were considered to form by defects structure. The well-resolved Raman spectra for the SrWO_4 particles at 920, 836, 798, 371, 334 and 235 cm^{-1} provide that the synthesized particles are highly crystallized.

Key Words: Strontium tungstate, Microwave-assisted synthesis, Solid-state metathetic route, Luminescence, Raman spectroscopy.

INTRODUCTION

Strontium tungstate (SrWO_4) from the metal tungstates has been widely employed in several industrial applications in photoluminescence, scintillator, photocatalyst and humidity sensors¹⁻³. Strontium tungstate has a Scheelite-type crystal structure with lattice parameters of $a = b = 5.417 \text{ \AA}$ and $c = 11.951 \text{ \AA}$. The shapes and morphology of the metal tungstates would greatly benefit in various fields of optics, electronics, catalysis and medicine. Over the past decade to enhance the applications, metal tungstates have been prepared by a range of processes, such as co-precipitation^{4,5}, a solvothermal method⁶⁻⁸, spray pyrolysis⁹, a reverse micelle system^{10,11}, solution synthesis¹², sol-gel¹³, a mechano-chemical method¹⁴, a molten salt method^{15,16}, a hydrothermal method¹⁷⁻¹⁹, microwave-assisted synthesis²⁰⁻²⁴ and a solid-state metathetic (SSM) reaction^{25,26}. Generally, these methods require expensive and sophisticated equipments, high temperatures with long processing times, expensive precursors and high consumption of energy.

In recent years, Thongtem *et al.*^{20,21} obtained metal tungstate nanoparticles using a solid-state metathetic method assisted cyclic microwave radiation. The microwave synthesis has the advantages of a short reaction time, small particle size, narrow particle size distribution and high purity method for preparing polycrystalline samples. The solid-state metathetic reactions provide convenient route for the synthesis of metal tungstates, which were obtained in the form of loosely con-

nected submicron sized particles at considerably lower temperatures than those usually employed for their synthesis^{23,24}.

In this paper, strontium tungstate particles were synthesized using a solid-state metathetic method assisted by a microwave irradiation. The solid-state metathetic reactions are discussed in detail based on the exothermic reaction accompanying the formation of NaCl. The obtained SrWO_4 particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The optical properties were examined by photoluminescence emission and Raman spectroscopy.

EXPERIMENTAL

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ of analytic reagent grade were used to prepare the SrWO_4 compound. The preparation of SrWO_4 was carried out by reacting well-ground mixtures of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ at a molar ratio of 1:1. The sample mixtures were dried at 100 $^\circ\text{C}$ for 12 h, placed into crucibles and exposed to domestic microwaves (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 10 min. The working cycle of the microwave oven was set between 60 s on and 30 s off. The samples were treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove the sodium chloride reaction by-product. The samples were dried at 100 $^\circ\text{C}$ in an oven. Heat-treatment of the samples was performed at 600 $^\circ\text{C}$ for 3 h.

The phase existings in the particles after the solid-state metathetic reactions and heat-treatment were identified by XRD (D/MAX 2200, Rigaku, Japan). FTIR (Nicolet IR200, Thermo Electron corporation, USA) was used to examine the thermal-decomposition behaviour of the solid-state metathetic reaction and the obtained particles over the frequency range, 4000-400 cm^{-1} . The microstructure and surface morphology of the SrWO_4 particles were observed by SEM (JSM-5600, JEOL, Japan). The photoluminescence spectra were recorded using a spectrophotometer (Perkin-Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using a LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as excitation source, the power was kept at 0.5 mW on the sample.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the microwave-assisted solid-state metathetic synthesized SrWO_4 particles followed by heat-treatment at 600 °C for 3 h. All XRD peaks could be assigned to a tetragonal phase SrWO_4 with a Scheelite-type structure, which is in good agreement with the crystallographic data of SrWO_4 (JCPDS: 08-0490). This means that the tetragonal phase SrWO_4 can be prepared using this solid-state metathetic reaction assisted by a microwave irradiation. The formation of the SrWO_4 crystalline phase requires heat treatment at 600 °C for 3 h. The SrWO_4 formed had a Scheelite-type crystal structure with lattice parameters of $a = b = 5.417 \text{ \AA}$ and $c = 11.951 \text{ \AA}$. This suggests that solid-state metathetic synthesis is suitable for the growth of SrWO_4 crystallites and the development of the strongest intensity peaks at (112), (200) and (312) planes, which were the major peaks of the SrWO_4 , with some preferred orientation^{12,14,21}.

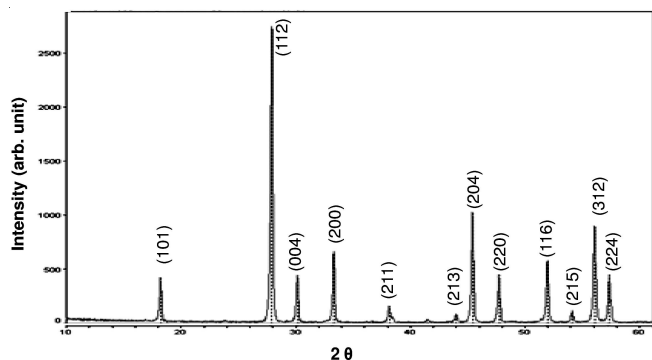


Fig. 1. XRD patterns of the SrWO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

Fig. 2 shows a SEM image of the SrWO_4 particles and shows a spherical and homogeneous morphology with particle sizes of 0.5-1 μm . The microwave-assisted solid-state metathetic resulted in fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste, because the microwave radiation provides the exothermic energy to synthesize metal tungstates. It assisted to heat the bulk of the material uniformly. Solid-state metathetic reactions, such as $\text{SrCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{SrWO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, where the driving force is the exothermic reaction

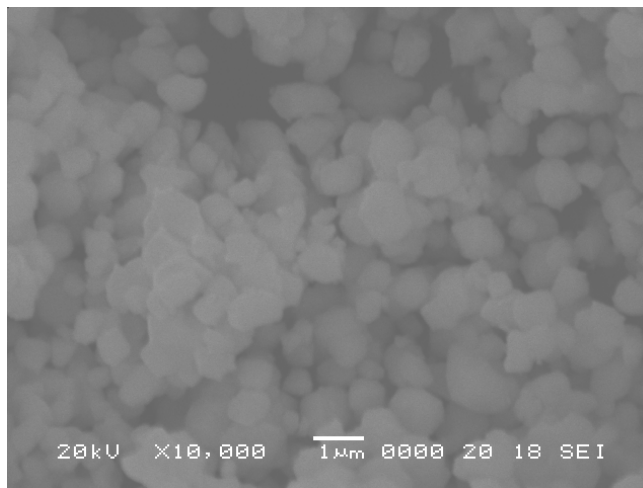


Fig. 2. A SEM image of the SrWO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

accompanying the formation of NaCl with high lattice energy^{23,24}. The enthalpy change favours the solid-state metathetic and is the driving force accompanying the formation of NaCl ^{25,26}. The solid-state metathetic provides a convenient route for the synthesis of metal tungstates, which were obtained in the form of loosely connected submicrometre sized particles at considerably lower temperatures than those usually employed for their synthesis. For tungstate materials to be used for practical applications, control of the particle size distribution and morphology of the particles is needed. The well-defined particle features of the SrWO_4 particles synthesized by solid-state metathetic reactions have control over the morphology of the final particles and can be used for such technological applications.

Fig. 3 shows FTIR spectrum of the obtained SrWO_4 particles at the wavenumber range of 4000-480 cm^{-1} . The stretching vibration was detected as a strong W-O stretch in the $[\text{WO}_4]^{2-}$ tetrahedrons at 823 cm^{-1} . The $[\text{WO}_4]^{2-}$ is constituted by four internal modes [$\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$] specified as an anti-symmetric stretching vibration²². All modes are Raman active, but $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ are IR active.

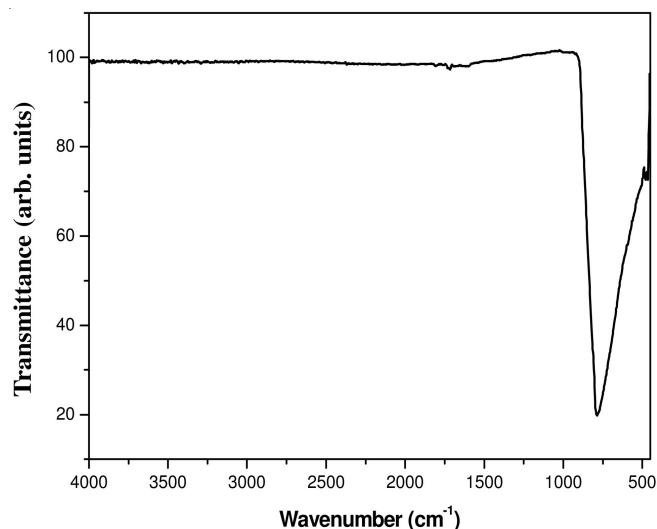


Fig. 3. FT-IR spectra of the obtained SrWO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

Fig. 4 presents room-temperature photoluminescence emission spectrum of the SrWO₄ particles. It is generally assumed that the measured emission spectrum of metal tungstates are mainly attributed to the charge-transfer transitions within the [WO₄]²⁻ complex^{27,28}. With excitation at 250 nm, the spectra show rugged peaks, which are composed of three kinds of groups. The first major peaks are located at the blue wavelength 450-425 nm, the second neighbored shoulders at 490-460 and the third sloped shoulders at 550-530 nm. The emission spectra of 4-8 narrow neighbored and sloped shoulders, namely the spread-eagle-shape, at approximately 460-550 nm are considered to form by defect structures²⁹. Generally, the presence of Gaussian components indicates that the electronic levels corresponding to relaxed excited state of an emission centre belong to a degenerate excited state influenced by some perturbation, *e.g.* local low symmetry crystal field³⁰. Such emission peaks can be explained by the influence of the Jahn-Teller effect^{31,32} on the degenerated excited state of [WO₄]²⁻ tetrahedron.

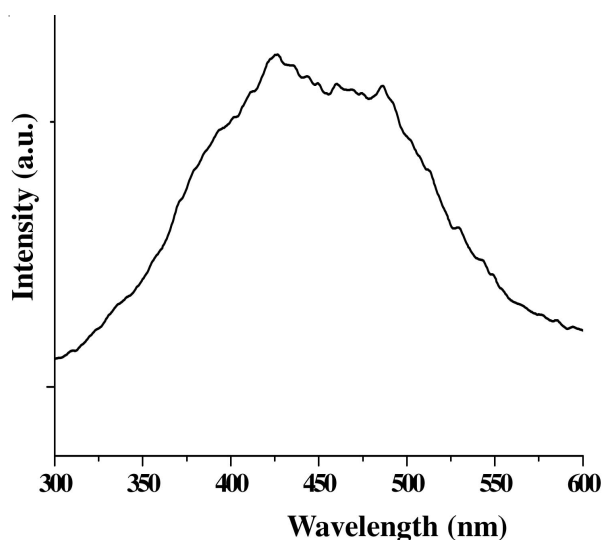


Fig. 4. Photoluminescence emission spectra of the SrWO₄ particles excited at 250 nm at room temperature

Fig. 5 shows a schematic diagram of the crystal-field of the Jahn-Teller splitting effect and hybridization of the [WO₄]²⁻ complex on the spread-eagle-shapes. The ground state of the system corresponds to the filling of all one-electron states below the band gap, resulting in a many-electron state of ¹A₁ symmetry. The lowest excited states involve one hole in the t₁ (primarily O 2pπ) states and one electron in the e (primarily W4d) states, corresponding to the many electron states, ¹T₁, ³T₁, ¹A₂ and ³A₂. Of these states, only the ¹A₁ → ¹T₂ transition is a dipole-allowed transition. However, it is the lower ³T₁ or ³T₂ states that account for the intrinsic luminescence by a spin-forbidden transition to the ground ¹A₁ state in optically detected electron paramagnetic resonance experiments on metal tungstates³². Both ¹A₁ → ¹T₁, ¹T₂ and ¹A₁ → ³T₁, ³T₂ transitions, causing at room temperature a radiating transition from the triple levels ³T₁, ³T₂ → ¹A₁ at the lowest transition energy, were detected in the luminescent spectra³³. The directions of the principal axes of the fine structure and tensors support the idea that the effect results from the

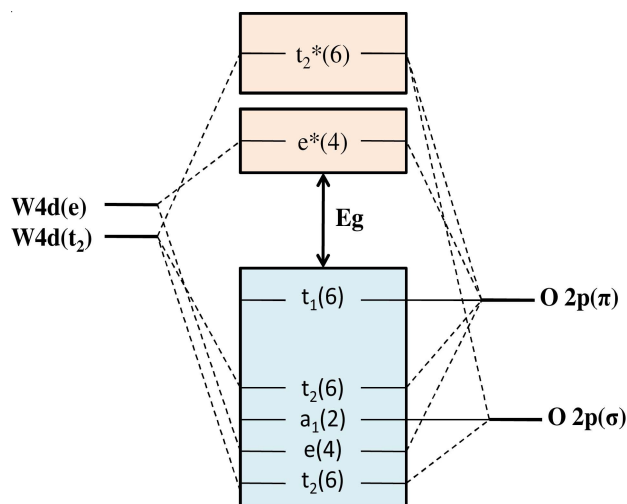


Fig. 5. Schematic diagram of the crystal-field of the Jahn-Teller splitting effect and hybridization of the [WO₄]²⁻ complex on the spread-eagle-shapes

combined action of the Jahn-Teller instability and the crystal field. The preliminary interpretation of the spectroscopic properties has been carried out on the basis of local atomic and electronic structure of tungsten ions in MWO₄ crystals of Scheelite and Wolframite types³⁴.

Fig. 6 shows a Raman spectrum of the SrWO₄ particle excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the sample. The vibration modes in the Raman spectrum of tungstates are classified into two groups, internal and external^{35,36}. The internal vibrations are related to the [WO₄]²⁻ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated with the motion of the Sr²⁺ cation and rigid molecular units. In the free space, [WO₄]²⁻ tetrahedra show T_d-symmetry. In this case, the vibrations of the [WO₄]²⁻ ions are constituted by four internal modes [$\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$], one free rotation mode [$\nu_{fr}(F_1)$] and one transition mode (F₂). When [WO₄]²⁻ ions are present in a Scheelite-type structure, its point symmetry reduces to S₄. Therefore, all degenerative vibrations are split due to the crystal field effect. For a tetragonal Scheelite primitive cell with a k = 0 wave vector^{22,35}, there are 26 different vibrations ($\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$), as determined by group-theory calculations. Among them, the 3A_g, 5B_g and 5E_g vibrations are Raman-active. Only 4A_u and 4E_u of the 5A_u and 5E_u vibrations are active in the IR frequencies and the remaining (1A_u and 1E_u) are acoustic vibrations. The 3B_u vibration is a silent mode. The Raman modes for the SrWO₄ particles in Fig. 6 were detected as $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 920, 836, 798, 371, 334 and 235 cm⁻¹, respectively. A free rotation mode was detected at 187 cm⁻¹ and external modes were localized at 133 cm⁻¹. The well-resolved sharp peaks for the SrWO₄ particles provide that the synthesized particles are highly crystallized. The internal vibration mode frequencies exhibited a dependence on the lattice parameters and the degree of the partially a covalent bond between the cation and molecular ionic group [WO₄]²⁻. The type of cations (Ca²⁺, Sr²⁺, Ba²⁺) can influence the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect³⁶.

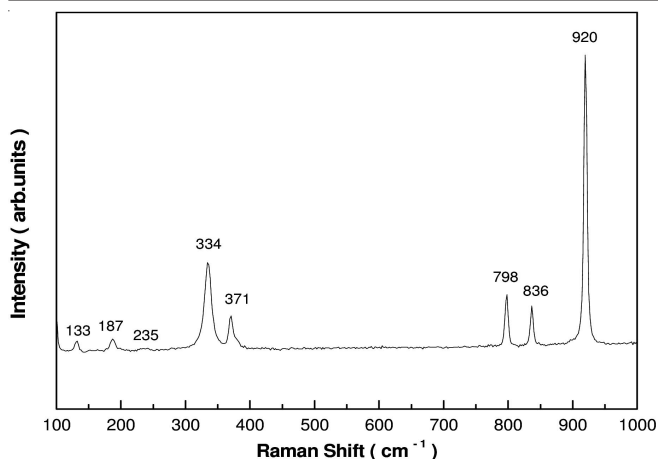


Fig. 6. Raman spectra of the SrWO₄ particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

Conclusion

Strontium tungstate (SrWO₄) particles were well synthesized by the solid-state metathetic route with microwave irradiation, showing a spherical and homogeneous morphology with particle sizes of 0.5-1 μm. The stretching vibration in FTIR was detected as a strong W-O stretch in the [WO₄]²⁻ tetrahedra at 823 cm⁻¹. With excitation at 250 nm, the major peaks are located at the blue wavelength of 425-450 nm. The emission spectrum of 4-8 narrow neighbored and sloped shoulders were considered to form from defect structures, which was explained by the influence of the Jahn-Teller effect. The internal Raman mode for the SrWO₄ particles was detected at 920, 836, 798, 371, 334 and 235 cm⁻¹. A free rotation mode was detected at 187 cm⁻¹ and the external modes were localized at 133 cm⁻¹. The well-resolved sharp peaks for the SrWO₄ particles provide that the synthesized particles are highly crystallized.

ACKNOWLEDGEMENTS

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0026911).

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