Research Article

Characterization of Donut-Like SrMoO_4 Produced by Microwave-Hydrothermal Process

Surangkana Wannapop,¹ Titipun Thongtem,^{2,3} and Somchai Thongtem^{1,3}

¹ Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

² Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

³ Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Correspondence should be addressed to Titipun Thongtem; ttphongtem@yahoo.com
and Somchai Thongtem; schthongtem@yahoo.com

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SrMoO_4 hierarchical nanostructures were successfully produced by a one step of 270 W microwave-hydrothermal process of one of the solutions containing three strontium salts [$\text{Sr}(\text{NO}_3)_2$, $\text{Sr}(\text{CH}_3\text{CO}_2)_2$, and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$] and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ for different lengths of time. The as-produced products were characterized by X-ray diffraction, electron microscopy, and spectroscopy. In this research, they were primitive tetragonal structured donut-like SrMoO_4 , with the main 881 cm^{-1} $\nu_1(\text{A}_g)$ symmetric stretching vibration mode of $[\text{MoO}_4]^{2-}$ units and 3.92 eV energy gap.

1. Introduction

Alkaline earth scheelite structured molybdate has been very attractive material for a wide variety of applications such as scintillating materials, laser-host materials, cryogenic detectors, heterogeneous catalysts, photoluminescence, optical fibers, solid-state optical masers, and electrochromic materials [1, 2]. One of them is SrMoO_4 which is very attractive for using as optoelectronic and electrochromic materials. It was produced by different methods: irregular aggregates of particles and microdisks by an electrochemical process [1], films of micrograins by a nonreversible galvanic cell method [2], hierarchical crystallites by simple precipitation [3], round nanoparticles with uniform sizes by coprecipitation at room temperature [4], spheres and dumbbells by simple aqueous mineralization [5], nanocrystals by microwave-assisted synthesis [6], nanostructured material by solvothermal-mediated microemulsion [7], and powders by coprecipitation and microwave-hydrothermal combination [8].

In this research, hierarchical nanostructures of SrMoO_4 with donut shape were produced by microwave-hydrothermal method for different lengths of time without using

surfactants, complexing agents, and other additives. The process is very simple, attractive, and novel for large scale synthesis.

2. Experimental Procedures

To produce donut-like SrMoO_4 , 5 mmol each of strontium salts [$\text{A} = \text{Sr}(\text{NO}_3)_2$, $\text{B} = \text{Sr}(\text{CH}_3\text{CO}_2)_2$, and $\text{C} = \text{SrCl}_2 \cdot 6\text{H}_2\text{O}$] and 5 mmol ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ were separately dissolved in 25 mL distilled water to form strontium and molybdenum solutions, which were mixed, stirred for 10 min at room temperature, and processed by a 270 W microwave-hydrothermal method for 5, 15, 30, and 90 min (encoded as 1, 2, 3, and 4 in sequence) to form precipitates. In this research, the products were encoded as A1, A2, A3, A4, B1, B2, B3, C1, C2, and C3. The A2 product implied that it was produced from $\text{Sr}(\text{NO}_3)_2 + (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ for 15 min, the C3 product from $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} + (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ for 30 min, and similarly for other products.

The products were characterized by an X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV and 15 mA

FIGURE 1: XRD patterns of (a) A1, A2, and A3; (b) B1, B2, and B3; and (c) C1, C2, and C3.

FIGURE 2: Simulated XRD pattern and crystal structure of SrMoO_4 .

to create $\text{Cu-K}\alpha$ line for the analysis; a scanning electron microscope (SEM, JEOL JSM-6335F) operating at 15 kV; a transmission electron microscope (TEM, JEOL JEM-2010), high resolution transmission electron microscope (HRTEM), and selected area electron diffractometer (SAED) operating at 200 kV; a Raman spectrometer (HORIBA Jobin Yvon T64000) using a 50 mW and 514.5 nm wavelength Ar green laser; and a UV-visible spectrometer (PerkinElmer Lambda 25) using a UV lamp with the resolution of 1 nm.

3. Results and Discussion

Comparing XRD patterns (Figure 1) to the JCPDS no. 85-0586 [9], they were specified as primitive tetragonal scheelite structured SrMoO_4 [1–3, 5]. No other characteristic peaks of impurities were detected. The Sr^{2+} cations were mixed with $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions to form intermediate complexes at room temperature. Upon processing the complexes by the microwave-hydrothermal combination, they were gradually transformed for a few steps into SrMoO_4 precipitates.

The XRD peaks became sharpened with the increase in the length of time, including the crystalline degree being much improved and the crystals being enlarged. The longer processing time was used, the larger crystallite size and the better crystalline degree would be. Calculated crystallite sizes of the A3, B3, and C3 products [10] were 34.7, 64.7, and 83.2 nm, respectively. They seemed to be influenced by different intermediates, which led to form crystals with different sizes.

XRD peaks of the purified SrMoO_4 produced in the solution containing $\text{Sr}(\text{NO}_3)_2$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ by the microwave-hydrothermal reaction for 30 min were compared with that obtained by simulation [11] (Figure 2). The 2θ Bragg angles and peak intensities obtained from the experiment, simulation, and JCPDS database were in good accordance. Crystal growth rates along the x -, y -, and z -directions could be different. The simulated scheelite-type tetragonal structured SrMoO_4 (Figure 2) belongs to $I4_1/a$ space group with two SrMoO_4 formula units with inversion centers per primitive unit cell. The Sr and Mo sites have S_4 point symmetry. The O sites have only a little symmetry and reside as almost tetrahedral coordination surrounding each of the Mo sites, composing as $[\text{MoO}_4]^{2-}$ tetrahedral configuration. Each Sr atom shares corners with eight adjacent O atoms of $[\text{MoO}_4]^{2-}$ tetrahedrons. Sr^{2+} cations form bond with $[\text{MoO}_4]^{2-}$ anions to produce SrMoO_4 crystal structure with $\alpha \rightarrow 2$, including the $[\text{MoO}_4]^{2-}$ units with strong Mo–O covalent bonds [4, 5, 8].

SEM images (Figure 3) show some examples of the hierarchical architectures of SrMoO_4 produced using different strontium salts and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ by microwave-hydrothermal reactions for different lengths of time. The hierarchical architectures with donut-like or flower-like shape were composed of a number of SrMoO_4 nanosheets with 2–3 nm thickness for the products produced using $\text{Sr}(\text{NO}_3)_2$ or $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and of SrMoO_4

FIGURE 3: Donut-like SrMoO_4 colonies of the (a–h) A1, A3, A4, B1, B2, B3, C1, and C3 products, respectively.

FIGURE 4: (a, b) TEM and HRTEM images and (c, d) SAED and simulated patterns of the A3 product.

nanorods with 100–150 nm length for the product produced using $\text{Sr}(\text{CH}_3\text{CO}_2)_2$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Different morphologies seemed to be obtained from different intermediate complexes, influenced by different anions of Sr salts. They were continuously enlarged and densely populated and their sizes were increased with the increase in the processing time. At these stages, the nanosheets and nanorods were squeezed and their shapes lack symmetry, due to the stress developed inside.

The donut-like product was confirmed by the TEM image (Figures 4(a) and 4(b)) of the A3 product, appeared as dark spherical area around the middle white one. A number

of the (112) planes with 0.322 nm apart were detected. An ED pattern (Figure 4(c)) with electron beam in the $[0 - 1 0]$ direction belongs to the SrMoO_4 crystalline nanosheet. This interpreted pattern was in good accordance with the simulated one (Figure 4(d)), although some spots of the simulated pattern did not appear on the interpreted one. To simulate the pattern, intensity and size of the spots (planes) were mutually related. The stronger intensity was used, the larger size was achieved. The intensity and size of the spots were limited by a saturated intensity used for simulation. Thus the spots of the simulated pattern with low intensity were absent from the interpreted one.

FIGURE 5: Schematic illustration for the formation of hierarchical architecture of SrMoO_4 .

FIGURE 6: Raman spectra of the A3, B3, and C3 products.

When Sr and Mo solutions were mixed, the intermediate complexes formed. Subsequently, they were processed by the microwave-hydrothermal reaction and gradually transformed for a few steps into hierarchical nanostructures of SrMoO_4 with donut-like or flower-like shape:

SrMoO_4 molecules nucleated and grew to form nanoparticles. Furthermore, these nanoparticles selectively grew to form nanosheet petals for the A1 to A4 and C1 to C3 products and nanorod petals for the B1 to B3 products on top. As the processing time passed, the petals were enlarged and squeezed each other. Some petals were bent and some were broken to release stress energy. The flowers (donuts) became more complete as well. In the end, the particles became completely donut-like shape (Figure 5).

Several different vibrations were detected on Raman spectra of the SrMoO_4 crystals (Figure 6). The Raman peaks at 881 cm^{-1} were specified as the $\nu_1(\text{A}_g)$ symmetric stretching vibration mode of $[\text{MoO}_4]^{2-}$ units. Those at $838\text{--}841$ and $788\text{--}790 \text{ cm}^{-1}$ corresponded to the $\nu_3(\text{B}_g)$ and $\nu_3(\text{E}_g)$

FIGURE 7: UV-visible absorption and the $(\alpha h\nu)^2$ versus $h\nu$ plot of the C3 product.

antisymmetric stretching vibration modes, respectively. The peaks at 368 and $328\text{--}330 \text{ cm}^{-1}$, respectively, corresponded to the $\nu_4(\text{B}_g)$ antisymmetric and $\nu_2(\text{A}_g)$ symmetric bending modes, including the $181\text{--}183 \text{ cm}^{-1}$ to the $\nu_{\text{f.r.}}(\text{F}_1)$ free rotation modes. Those at 118 , 141 , and 163 cm^{-1} were specified as the external vibration modes of Sr^{2+} cations and $[\text{MoO}_4]^{2-}$ units. These vibration modes were very close to those reported by other researchers [3, 5, 8] and provided the evidence of scheelite structure.

UV-visible absorption (Figure 7) of the hierarchical SrMoO_4 architecture of the C3 product synthesized by the 270 W and 30 min microwave-hydrothermal process indicated an exponential decreasing of the UV-visible energy attenuated through the crystalline C3 product. During attenuation, the absorption was controlled by two photon energy ($h\nu$) ranges. For $h\nu < E_g$, the absorption was linearly increased with the increasing of photon energy. The steep inclination of the linear portion of the curve was caused by the UV absorption for charged transition from the topmost occupied state of valence band to the bottommost unoccupied state of the conduction band. For $h\nu < E_g$, the absorption curve became different from linearity, caused by the UV absorption for charged transition relating to defects. Band gap of the product is related to its absorbance and photonic energy. Thus the combination of absorbance and photonic energy was used to determine the photonic band gap. By extrapolating the linear portion curve (tail of the curve) of the $(\alpha h\nu)^2$ versus $h\nu$ plot to zero absorbance, its direct energy gap was determined to be 3.92 eV for the hierarchical architecture of the C3 product. This energy gap was very close to the 3.98 eV of SrMoO_4 powder processed by the microwave-hydrothermal reaction at 413 K for 5 h reported by Sczancoski et al. [8].

4. Conclusions

SrMoO_4 hierarchical nanostructures were successfully produced by the one-step microwave-hydrothermal process. In

this research, the products were tetragonal scheelite crystal with donut-like or flower-like SrMoO_4 . Their main vibration modes were detected at 881 cm^{-1} and the energy gap of 3.92 eV .

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