



Characterization of ZnMoO₄ nanofibers synthesized by electrospinning–calcination combinations

Yanee Keereeta^a, Titipun Thongtem^{b,*}, Somchai Thongtem^a

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

^b Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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ABSTRACT

ZnMoO₄ nanofibers were synthesized by electrospinning–calcination combinations. In the present research, anorthic structured ZnMoO₄ was detected by X-ray diffraction (XRD) and confirmed by simulation and selected area electron diffraction (SAED). Morphology was confirmed by scanning and transmission electron microscopy (SEM, TEM) and atomic force microscopy (AFM). Vibrations were detected by Fourier transform infrared (FTIR) and Raman spectroscopy. By using photoluminescence (PL) and UV–visible spectroscopy, the PL emission was found to be in the same range as the indirect energy gap (E_g). A formation mechanism was proposed according to the experimental results.

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1. Introduction

ZnMoO₄, a semiconducting material, exists as anorthic and monoclinic structures [1]. It contains non-heavy elements and Mo as high as 42.58 wt%. It is nontoxic, and also is very attractive for its properties of luminescence, scintillation and photocatalysis, and for its use in battery electrodes and drug delivery systems [2–6]. Previously, ZnMoO₄ with rhombus sheet or flower-like structure, α -ZnMoO₄, and needle-like ZnMoO₄·0.8H₂O were successfully synthesized by simple hydrothermal crystallization reactions of (NH₄)₆Mo₇O₂₄·4H₂O and Zn(NO₃)₂·6H₂O solutions containing citric acid [4]. AMoO₄ with scheelite (A = Ca, Sr, Ba) and wolframite (A = Mg, Mn, Zn) structures were synthesized by conventional mixed oxide calcination method [2]; nanocrystalline wolframite-structured MMoO₄ (M = Ni, Zn) phosphors by a modified citrate complex route assisted by microwave irradiation [3]; ZnMoO₄ hollow microspheres by yeast-directed hydrothermal synthesis of Zn(AC)₂ and Na₂MoO₄ in aqueous solution [5]; and ZnBO₄ (B = W, Mo) single crystals by the Czochralski method [6]. In the present research, anorthic ZnMoO₄ nanofibers were successfully synthesized by electrospinning–calcination combinations. To the best of our knowledge, no ZnMoO₄ nanofibers have ever been synthesized by the present processes. This success may lead to large-scale production in the near future.

2. Experiment

To synthesize ZnMoO₄ nanofibers, 0.003 mol Zn(CH₃COO)₂·2H₂O, 0.003 mol (NH₄)₆Mo₇O₂₄·4H₂O, and 1.5 g poly (vinyl alcohol) (PVA) with the molar mass of 72,000 g/mol were dissolved in 30 ml deionized water, and vigorously stirred at 80 °C for 30 min. The mixture was electrospun through a horizontal hollow needle, biased with +15 kV direct voltage to synthesize a fibrous web on a grounded aluminum foil. These fibers were subsequently calcined at 300, 400, 519, and 600 °C for 3, 6, and 9 h, for further different analyses. For convenience, ZnMoO₄-PVA fibers before calcination were symbolized as PBF. The fibers after calcination at 400 °C for 3 h were as P4003, at 519 °C for 3 h as P5193, and similarly for other products.

3. Results and discussion

3.1. Phase analysis

A comparison of XRD patterns (Fig. 1a) to those of JCPDS No. 35–0765 [1] revealed that they corresponded to anorthic (triclinic [7]) structured ZnMoO₄ with P-1 space group. Some PVA seemed to remain in the P4003 product. The PVA peak at 2θ of 22.5° [8] could be covered by the peaks of ZnMoO₄; but for the P5193, P5196 and P5199, no PVA was in existence on the products [8]. The nanofibers were the best crystal quality, with their atoms residing in a perfect crystal lattice. The lengths of calcination time did not have strong influence on the degree of crystallinity. Calculated crystal axes (8.3600, 9.7000 and 6.9690 Å) and angles (106.880, 102.010 and 96.859°) [9] were in accordance with those of the JCPDS database [1]. XRD patterns of purified ZnMoO₄ were compared with that obtained by simulation

* Corresponding author. Tel.: +66 53 943344; fax: +66 53 892277.

E-mail addresses: ttphongtem@yahoo.com, ttphongtem@gmail.com (T. Thongtem).

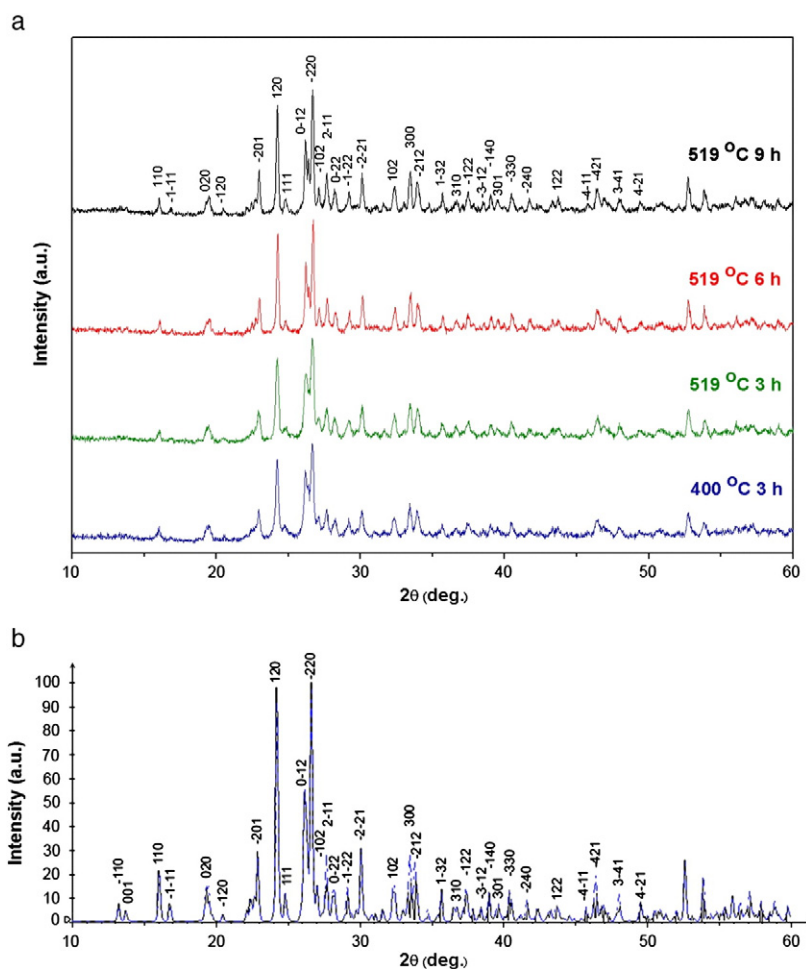


Fig. 1. (a) XRD patterns of P4003, P5193, P5196 and P5199. (b) The simulated pattern.

(Fig. 1b) [10]. The 2θ Bragg angles and peak intensities of the experiment, simulation, and JCPDS database were in good accordance.

The simulated structure (Fig. 2a) contained three non-equivalent units of MoO₄ tetrahedrons with different Mo–O bond lengths. Zn²⁺ ions occupied sites with five- and six-fold coordination. The SAED pattern (Fig. 2b) was indexed [11] and specified as ZnMoO₄ [1].

3.2. Morphologies

Before calcination (Figs. 2c, d and 3a), the product was composed of fibers with smooth surfaces; diameters were in the 110–230 nm range. ZnMoO₄ nuclei blended in the fibers were unable to be detected. Upon calcination at 300, 400 and 519 °C for 3 h (Figs. 2e–g and 3b–d), the fibers became less thick due to the evaporation of PVA. Some PVA was still left on the fibers at 300 and 400 °C, but was no longer left at 519 °C [8]. At these stages, ZnMoO₄ nuclei also grew into nanoparticles. The rate of particle growth became faster at higher temperature. At 300, 400 and 519 °C for 3 h, the evaporation rate of PVA was faster than the growth rate of particles. Thus, at 519 °C and 3 h (Figs. 2e–g and 3d), the fibers were the smallest (nanofibers). At a constant temperature of 519 °C (Fig. 3e and f), the nanofibers were also enlarged with prolonged times (6 and 9 h). The nanofibers seemed to be constant at 100 nm diameter. At 600 °C and 3 h (Fig. 3g), the fibers were the largest. Sometimes the fibers were broken, caused by the internal stress developed inside. On close inspection of a nanofiber of P5193 (Fig. 2g and h), the product was found to consist of faceted nanoparticles. Characterization on a rectangle of Fig. 2h showed that the particle was composed of a number of parallel strips (Fig. 2i), corresponding to the (202) crystallographic planes.

3.3. Formation mechanism

Zn(CH₃COO)₂·2H₂O, (NH₄)₆Mo₇O₂₄·4H₂O and PVA mixture was electrospun through +15 kV to heat up the as-spun fibers. ZnMoO₄ molecules were synthesized, nucleated, blended in PVA template, and deposited as fibers on aluminum foil.



At high-temperature calcination, PVA and residual water evaporated and decomposed. ZnMoO₄ nuclei grew to form nanoparticles, and arranged themselves in lines like nanofibers. In the present research, the reactants could be left inside the fibers after electrospinning. Thus, ZnMoO₄ molecules formed, nucleated, and grew into nanoparticles by high-temperature calcination.

3.4. Vibration modes

Fig. 3h shows FTIR spectra of different products; the major vibrations of PVA were clearly detected. But no ZnMoO₄ was detected in the PBF. Upon calcination at different conditions, PVA evaporated and decomposed. Some trace PVA was still detected in the P4003; however it was no longer detected in the P5193, P5196 and P5199, and the vibrations at 750–960 cm^{−1} became strengthened. Those at 957 cm^{−1} were specified as the ν_1 stretching of Mo–O in bridging Mo–O–Mo linkages. The vibrations at 870 cm^{−1} corresponded to the ν_1 stretching of (MoO₄)^{2−} tetrahedrons, and those at 754 cm^{−1} to the ν_3 stretching of Mo–O [12,13].

Raman vibrations (Fig. 3i) of ZnMoO₄-PVA fibers after calcination at different conditions showed the strongest intensity at 965 cm^{−1},

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