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Microwave-assisted synthesis, characterization and photoluminescence of shuttle-like $BaMoO_4$ microstructure

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Shuttle-like $BaMoO_4$ microstructure has been successfully synthesized from $Ba(NO_3)_2{\cdot}4H_2O$ and $Na_2MoO_4{\cdot}2H_2O$ as starting materials in ethylene glycol solvent containing 20 mL 5 M NaOH by microwave radiation at 180 W for 30 min. The as-synthesized $BaMoO_4$ product was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectrophotometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy. XRD patterns revealed that the products was tetragonal $BaMoO_4$ phase. SEM and TEM characterization showed that the product had a shuttle-like $BaMoO_4$ microstructure. PL of the shuttle-like $BaMoO_4$ microstructure showed a maximum emission at 466 nm excited by 280 nm wavelength.

Keywords: *$BaMoO_4$; shuttle-like particles; luminescence*

1. Introduction

Recently, alkaline earth molybdate materials with a scheelite-type structure have attracted much interest because of their luminescent behavior, electro-optical properties, structural properties and potential applications [1–3]. The green luminescence properties of molybdate of relatively large bivalent cations (Ca, Ba, Pb and Sr with ionic radii $>$0.99 Å) have attracted much attention of many researchers due to their applications in electro-optical industries [2, 4]. Among the molybdate materials, $BaMoO_4$ with a scheelite structure is an important material in electro-optics, due to its production of blue, green and orange luminescence, and in electro-optical applications, including solid-state lasers and optical fibers [3, 5, 6].

In this research, the shuttle-like $BaMoO_4$ microstructures have been synthesized by microwave method. The phase, morphologies and optical properties of the products were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy.

2. Experiment

In this research, barium nitrate tetrahydrate (99 % $Ba(NO_3)_2{\cdot}4H_2O$), sodium molybdate dihydrate ($\geqslant$99 % $Na_2MoO_4{\cdot}2H_2O$) and ethylene glycol (99 % $C_2H_6O_2$) were purchased from Sigma-Aldrich Co. and Fisher Scientific Inc., and were used without further purification.

To synthesize the shuttle-like $BaMoO_4$ microstructure, 0.005 M barium nitrate tetrahydrate

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and 0.005 M sodium molybdate dihydrate were dissolved in 100 mL ethylene glycol under continuous stirring at room temperature for 30 min. 20 mL of 0 to 5 M NaOH solutions were added to each of the solutions subjected to 30 min stirring. Then, each of the mixtures was transferred into an electric microwave oven at a time, and heated at 180 W for 30 min. Finally, light precipitates were synthesized, separated by filtration, washed with distilled water for removal of ionic remains from the final products, washed with ethanol to help in evaporation and dried at 80 °C in an electric oven for 24 h.

The phase, morphologies and atomic vibrations were characterized with a Philips X'Pert MPD X-ray diffractometer (XRD) using CuKα radiation with a graphitic monochromator and a Ni filter at a scanning angle of 2θ in the range of 15 to 60°. The FT-IR and Raman spectra were analyzed by a Bruker Tensor 27 Fourier transform infrared (FT-IR) spectrometer and by a HORIBA JOBIN YVON T64000 Raman spectrometer using 50 mW Ar green laser with 514.5 nm wavelength. SEM and TEM images were recorded by a JEOL JSM 6335F scanning electron microscope (SEM) at an acceleration voltage of 20 kV and a JEOL JEM-2010 transmission electron microscope (TEM) at 200 kV. Photoluminescence (PL) properties were recorded by a Perkin Elmer luminescence spectrophotometer model LS 50B.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of the as-synthesized products. All the peaks can be well indexed to the tetragonal phase of $BaMoO_4$ which is in good agreement with JCPDS Card No. 29-0193 [7]. No other peaks of impurities were detected, indicating that the products had high purity. In addition, the strong and sharp diffraction peaks confirmed high crystallinity of the $BaMoO_4$ products.

$BaMoO_4$ belongs to a scheelite-type structure with $I4_1/a$ space group. The MoO_4^{2-} ion has a tetrahedral symmetry and is represented as $\Gamma = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$, where $A_1(\nu_1)$ and $E(\nu_2)$ are Raman active and $F_2(\nu_3)$ and $F_2(\nu_4)$

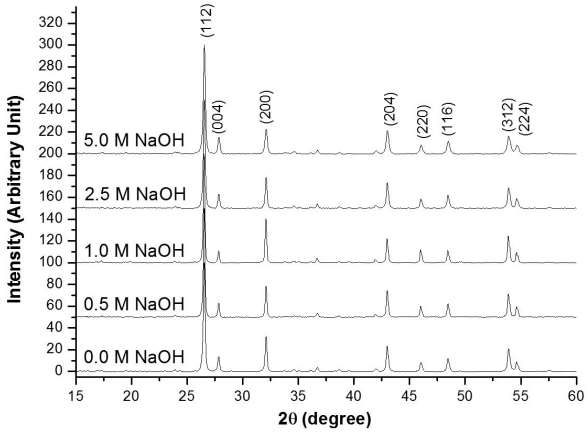

Fig. 1. XRD patterns of $BaMoO_4$ products synthesized in solutions with different contents of NaOH.

are infrared (IR) active. The $F_2(\nu_3)$ vibrations are antisymmetric stretching vibrations, whereas the $F_2(\nu_4)$ vibrations are bending vibrations [8]. Fig. 2a shows the FT-IR spectrum of $BaMoO_4$ with wavenumber of 400 to 4,000 cm^{-1}. It exhibits a board band at about 810 cm^{-1} corresponding to the $F_2(\nu_3)$ antisymmetric stretching vibrations in consistency with that of $BaMoO_4$ [8–10]. This peak could be originated from the Mo–O stretching vibrations of the MoO_4 tetrahedrons.

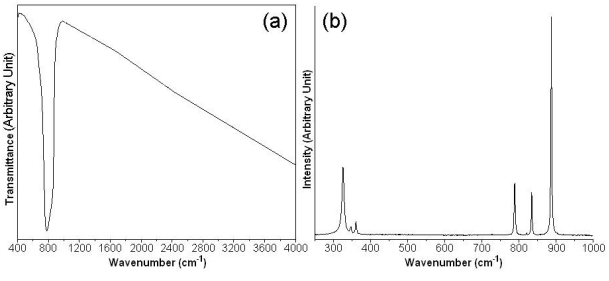

Fig. 2. (a) FT-IR and (b) Raman spectra of $BaMoO_4$ synthesized in a solution containing 20 mL of 5 M NaOH.

$BaMoO_4$ belongs to the scheelite structured family with two formula units per primitive cell and with $I4_1/a$ space group. The group theoretical analysis predicts that phonon vibrations belong to irreducible representations for the C_{4h} point group. The $3N = 36$ degrees of freedom for 12 atoms of $BaMoO_4$ primitive cells are divided into 26

vibrational modes: $\Gamma = 3A_g + 5B_g + 5E_g + 5A_u + 3B_u + 5E_u$. The internal vibration is associated with displacement inside the MoO_4 molecular units. The external or lattice phonons correspond to the motion of cationic Ba and the rigid molecular unit (translational modes) [9, 11, 12]. Raman peaks of $BaMoO_4$ at 325, 346, 360, 789, 834 and 887 cm^{-1} (Fig. 2b) are assigned as the internal modes arising from $\nu_2(B_g)$, $\nu_4(E_g)$, $\nu_4(E_g)$, $\nu_3(E_g)$, $\nu_3(B_g)$ and $\nu_1(A_g)$, respectively [9, 12–14].

The morphology of the as-synthesized $BaMoO_4$ product was examined by SEM. Fig. 3 shows the images of the $BaMoO_4$ microcrystals synthesized in the solution containing 5 M NaOH at low and high magnifications. It can be seen that the product consists of a large quantity of relatively uniform shuttle-like crystals with two sharp tips at both ends and four symmetrically grown protrusions at the middle. A single shuttle-like $BaMoO_4$ microstructure is 40 to 60 μm long and 5 to 10 μm wide at the middle section.

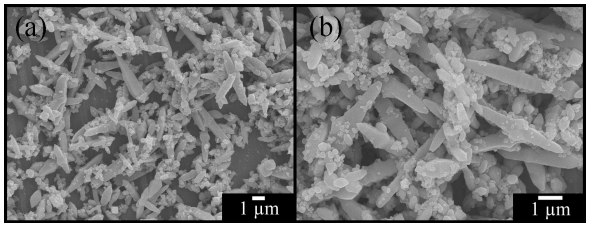

Fig. 3. SEM images of shuttle-like $BaMoO_4$ microstructures synthesized in a solution containing 20 mL of 5 M NaOH at low and high magnifications.

The concentration of NaOH contained in the precursor solution, which influenced the shape and size of the $BaMoO_4$ microcrystals, was investigated by TEM (Fig. 4). For NaOH free solution, the TEM image clearly shows highly uniform $BaMoO_4$ nanoparticles with particle size of about 20 to 30 nm. When 0.5 M NaOH was added into the precursor solution, $BaMoO_4$ nanoparticles gradually transformed into octahedral particles. Their shape became more clear with the size of about 930 nm long and 450 nm wide (at the middle) upon the addition of 1 M NaOH. With increasing the amount of NaOH, the size of $BaMoO_4$ crystals increased. When the NaOH concentration was increased to 5 M, a large number of shuttle-like $BaMoO_4$ microstructures with the length less than 3 μm and middle section of 0.8 μm width were detected. The shuttle-like $BaMoO_4$ microcrystals were composed of very long central stems with four perpendicular branches at the middle. When the concentration of NaOH was increased to 5 M, all of the nanoparticles developed into the shuttle-like microstructures.

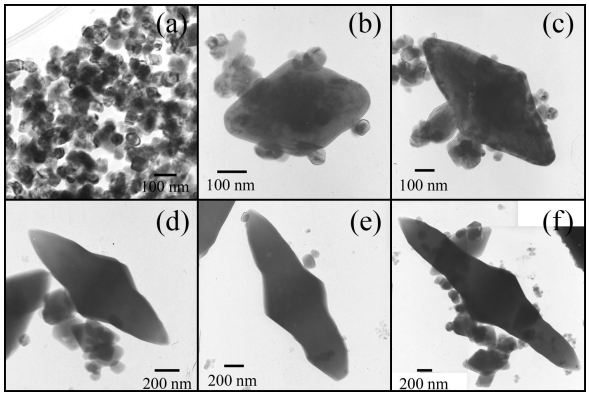

Fig. 4. TEM images of $BaMoO_4$ products synthesized in solutions containing (a) 0.0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 2.5 and (f) 5.0 M of NaOH.

The characteristic photoluminescence (PL) of the shuttle-like $BaMoO_4$ microstructures was analyzed in an absolute ethanol solution in the wavelength range of 350 to 650 nm using the excitation wavelength of 280 nm as shown in Fig. 5. The PL emission of the shuttle-like $BaMoO_4$ microstructures was caused by charge transfer in the $[MoO_4]^{2-}$ complexes with the T_d symmetry groups or self-trapping electron states. Molecular orbital calculations for the $[MoO_4]^{2-}$ ions disclosed one ground state ($A_{1(1)}$) and four single excited states as $T_{1(1)}$, $T_{2(1)}$, $T_{1(3)}$ and $T_{2(3)}$ [12, 15]. PL spectra of the shuttle-like $BaMoO_4$ microstructures showed an emission spectrum at 466 nm which was mainly attributed to the charge transition of the $[MoO_4]^{2-}$ complexes. Moreover, the shoulder in emission band might be explained by the Jahn-Teller effect or Jahn-Teller distortion which describes the geometrical distortion of molecules and ions associated with certain electron configurations, which influenced the $[MO_4]^{2-}$ (M = Mo and

W) complex anions with slightly distorted tetrahedral symmetry, leading to a structured emission for the $T_{2(1)} \rightarrow A_{1(1)}$ transition [12, 13].

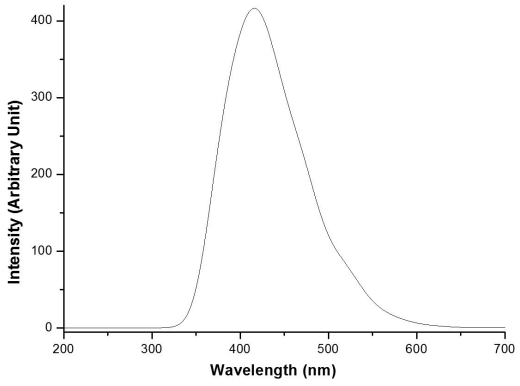

Fig. 5. PL emission of shuttle-like $BaMoO_4$ microstructure excited by 280 nm photonic wavelength.

4. Conclusions

Shuttle-like $BaMoO_4$ microstructures were successfully synthesized by a novel microwave radiation method. X-ray diffraction patterns presented the body-primitive tetragonal $BaMoO_4$ structure. By using FT-IR and Raman analysis, the strongest stretching modes of $[MoO_4]^{2-}$ tetrahedrons were detected. Transmission electron microscopy revealed the presence of the product with shuttle-like microstructure. The PL emission exhibited broad luminescence in the 350 to 650 nm range with the maximum emission at 466 nm excited by the wavelength of 280 nm. The advantage of this technique is its simplicity, low cost and short reaction time.

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References

[1] LUO Z., LI H., SHU H., WANG K., XIA J., YAN Y., *Mater. Chem. Phys.*, 110 (2008), 17.
[2] RANGAPPA D., FUJIWARA T., WATANABE T., YOSHIMURA M., *Mater. Res. Bull.*, 43 (2008), 3155.
[3] LUO Z., LI H., SHU H., WANG K., XIA J., YAN Y., *Cryst. Growth Des.*, 8 (2008), 2275.
[4] WU X., DU J., LI H., ZHANG M., XI B., FAN H., ZHU Y., QIAN Y., *J. Solid State Chem.*, 180 (2007), 3288.
[5] CAVALCANTE L.S., SCZANCOSKI J.C., TRANQUILIN R.L., VARELA J.A., LONGO E., ORLANDI M.O., *Particuology*, 7 (2009), 353.
[6] SUN Y., MA J., FANG J., CAO C., LIU Z., *Ceram. Inter.*, 37 (2011), 683.
[7] *Powder Diffract. File*, JCPDS Internat. Centre Diffract. Data, PA 19073-3273, U.S.A., 2001.
[8] MAO C.J., GENG J., WU X.C., ZHU J.J., *J. Phys. Chem. C*, 114 (2010), 1982.
[9] SCZANCOSKI J.C., CAVALCANTE L.S., MARANA N.L., SILVA R.O., TRANQUILIN R.L., JOYA M.R., PIZANI P.S., VARELA J.A., SAMBRANO J.R., LI M.S., LONGO E., ANDRÉS J., *Curr. Appl. Phys.*, 10 (2010), 614.
[10] YANG P., LI C., WANG W., QUAN Z., GAI S., LIN J., *J. Solid State Chem.*, 182 (2009), 2510.
[11] LONGO V.M., CAVALCANTE L.S., PARIS E.C., SCZANCOSKI J.C., PIZANI P.S., LI M.S., ANDRÉS J., LONGO E., VARELA J.A., *J. Phys. Chem. C*, 115 (2011), 5207.
[12] PHURUANGRAT A., THONGTEM T., THONGTEM S., *Superlattice. Microst.*, 52 (2012), 78.
[13] PHURUANGRAT A., THONGTEM T., THONGTEM S., *J. Phys. Chem. Solids*, 70 (2009), 955.
[14] THONGTEM T., PHURUANGRAT A., THONGTEM S., *Mater. Lett.*, 62 (2008), 454.
[15] THONGTEM T., PHURUANGRAT A., THONGTEM S., *J. Nanopart. Res.*, 12 (2010), 2287.

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