



## Solid-State Metathetic Synthesis and Photoluminescence of BaMoO<sub>4</sub> Assisted by Cyclic Microwave Irradiation†

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A solid-state metathetic route assisted by microwave irradiation was used to synthesize BaMoO<sub>4</sub> particles under environmentally friendly conditions. Well crystallized BaMoO<sub>4</sub> particles were formed at 400-600 °C for 3 h, showing fine and homogeneous morphologies with particle sizes of 1-2 μm. The synthesized BaMoO<sub>4</sub> 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.

**Key Words:** BaMoO<sub>4</sub>, Microwave-assisted synthesis, Solid-state metathesis, Luminescence, Raman spectroscopy.

### INTRODUCTION

Metal molybdates exhibit blue or green luminescent spectra, which are based on a radiative transition within the tetrahedral [MoO<sub>4</sub>]<sup>2-</sup> groups. Metal molybdates with large bivalent cations (*e.g.*, Ca, Ba, Pb and Sr) tend to have a Scheelite-type tetragonal structure, whereas small cationic radii (*e.g.*, Zn, Fe, Mn, Co and Ni) favour the formation of a Wolframite-type monoclinic structure. They have attracted considerable interest for a number of researchers, due to their promising technological importance in a wide range of applications. Currently, metal molybdates have attracted considerable attention for potential applications in photoluminescence, scintillators, photocatalyst hosts for lanthanide-activated lasers and humidity sensors<sup>1,2</sup>. The physical, chemical and photochemical properties of metal molybdates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of BaMoO<sub>4</sub> prepared by a range of processes, such as coprecipitation<sup>3</sup>, a solvothermal method<sup>4</sup>, spray pyrolysis<sup>5</sup>, wet chemical method<sup>6</sup>, a mechano-chemical method<sup>7</sup>, a molten salt method<sup>8</sup>, a hydrothermal method<sup>9</sup>, microwave synthesis<sup>10</sup> and a solid-state metathetic reaction<sup>11</sup>.

Microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction. Microwave energy is delivered directly to the material through molecular

interactions with an electromagnetic field<sup>12,13</sup>. Solid-state metathetic route is a simple and cost-effective method that provides a high yield with easy scale up and is emerging as a viable alternative approach for the synthesis of high-quality novel inorganic materials in short time periods. The solid-state metathetic synthesis of the BaMoO<sub>4</sub> could provide well defined particles with a controlled morphology to fabricate the products in a green manner without the generation of solvent waste under environmentally friendly conditions<sup>14,15</sup>. For practical applications of BaMoO<sub>4</sub> particles in photoluminescence, hosts materials for lasers, photocatalysis and humidity sensors, well-defined particle features with homogeneous particle size distribution and morphology of the BaMoO<sub>4</sub> particles are required. The solid-state metathetic synthesis of the BaMoO<sub>4</sub> could provide well defined particles with a controlled morphology to fabricate the products in a green manner without the generation of solvent waste under environmentally friendly conditions.

In the present study, BaMoO<sub>4</sub> particles were synthesized using a solid-state metathetic route assisted by the cyclic microwave irradiation. The characteristics of the solid-state metathetic reaction of BaMoO<sub>4</sub> particles are discussed in detail based on the formation of a high lattice energy by-product of NaCl. The synthesized BaMoO<sub>4</sub> particles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The optical properties were examined by photoluminescence (PL) emission and Raman spectroscopy.

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## EXPERIMENTAL

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  of analytic reagent grade were used to prepare the metal molybdate compound. The preparation of  $\text{BaMoO}_4$  was carried out by reacting well-ground mixtures of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  at a molar ratio of 1:1, respectively. 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 40 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-treatments of the samples were performed at 400, 500 and  $600^\circ\text{C}$  for 3 h.

The existing phases in the particles after the solid-state metathetic reactions and heat-treatments were identified by powder XRD ( $\text{CuK}\alpha$ , Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the thermal-decomposition behaviour of the solid-state metathetic reaction and heat-treated particles over the frequency range,  $4000\text{--}400\text{ cm}^{-1}$ . The microstructure and surface morphology of the  $\text{BaMoO}_4$  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 LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as the excitation source, the power was kept at 0.5 mW on the samples.

## RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of the  $\text{BaMoO}_4$  particles after solid-state metathetic reaction followed by further heat-treatment at  $600^\circ\text{C}$  for 3 h. All XRD peaks could be assigned to tetragonal phases of  $\text{BaMoO}_4$  with a Scheelite-type structure, which are in good agreement with the crystallographic data of  $\text{BaMoO}_4$  (JCPDS: 29-01930). This means that the tetragonal phases of  $\text{BaMoO}_4$  can be prepared using this solid-state metathetic reaction assisted by cyclic microwave irradiation. The formations of  $\text{BaMoO}_4$  crystalline phases require heat-treatment at  $600^\circ\text{C}$  for 3 h. The  $\text{BaMoO}_4$  formed had the same crystal structure with lattice parameters  $a = b = 5.573\text{ \AA}$  and  $c = 12.786\text{ \AA}$ . These suggest that solid-state metathetic synthesis is suitable for the growth of  $\text{BaMoO}_4$  crystallites and development of the strongest intensity peaks from the (112), (200) and (312) planes, which were the major peaks of the  $\text{BaMoO}_4$ , with some preferred orientation.

Fig. 2 shows SEM images of the  $\text{BaMoO}_4$  particles after solid-state metathetic reaction followed by further heat-treatment at (a)  $400^\circ\text{C}$  for 3 h, (b)  $500^\circ\text{C}$  for 3 h and (c)  $600^\circ\text{C}$  for 3 h. The SEM images of  $\text{BaMoO}_4$  in Fig. 2(a-c) show well-defined octahedra-like morphologies with particle sizes of 1-2  $\mu\text{m}$ . The structure of the samples prepared at  $600^\circ\text{C}$  in Fig. 3(c) was much crystallized than that of the samples prepared at 400 and  $500^\circ\text{C}$  in Fig. 3(a,b). After solid-state metathetic reaction assisted by the microwave irradiation, the

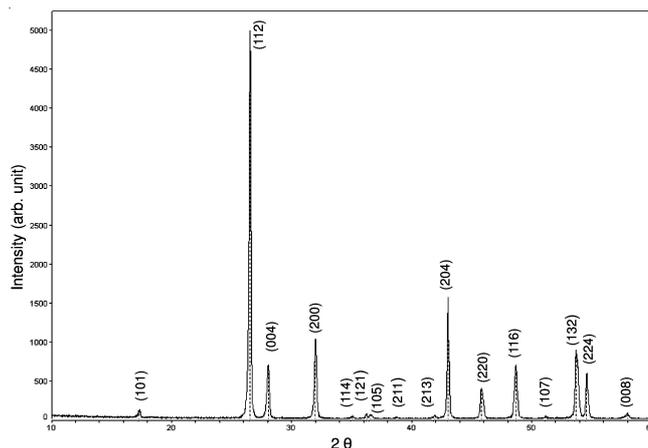


Fig. 1. XRD patterns of the  $\text{BaMoO}_4$  particles after solid-state metathetic reaction followed by further heat-treatment at  $600^\circ\text{C}$  for 3 h

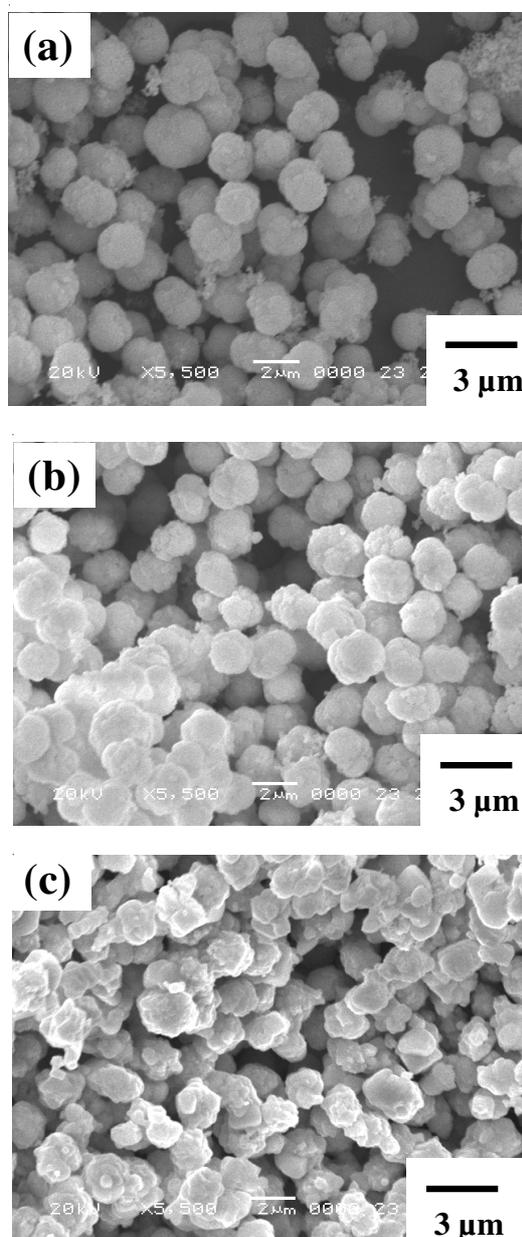
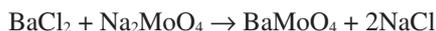


Fig. 2. SEM images of the  $\text{BaMoO}_4$  particles after solid-state metathetic reaction followed by further heat-treatment at (a)  $400^\circ\text{C}$  for 3 h, (b)  $500^\circ\text{C}$  for 3 h and (c)  $600^\circ\text{C}$  for 3 h

reactants are needed to heat at temperatures at 400, 500, 600 °C for 3 h. The solid-state metathetic reaction assisted by the microwave irradiation and post heat-treatment are interdependently essential procedure to synthesize the BaMoO<sub>4</sub> particles employed for the solid state reactions. These results indicate that the well-defined crystallization depends on the heat-treatment temperatures of the BaMoO<sub>4</sub> particles. It is noted that the post heat-treatment plays an important role in the well-defined crystallized morphology.

The solid-state metathetic reaction assisted by the microwave irradiation of various metal molybdates helps to fabricate the product in a green manner without the generation of solvent waste. The solid-state metathetic reactions, such



involve the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of NaCl with a high lattice energy<sup>12</sup>. Solid-state metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The solid-state metathetic reactions provide a convenient route for the synthesis of metal molybdates, which were obtained in the form of loosely connected submicrometer sized particles at considerably lower temperatures than those usually employed for their synthesis. For molybdate 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 BaMoO<sub>4</sub> particles synthesized by solid-state metathetic reactions have a control over the morphology of the final particles and can be used for technological applications.

Fig. 3 shows FT-IR spectra of the BaMoO<sub>4</sub> particles after solid-state metathetic reaction and followed by further heat-treatment at 600 °C for 3 h in the wavenumber range, 4000-480 cm<sup>-1</sup>. A stretching vibration for BaMoO<sub>4</sub> was detected as a strong Mo-O stretch in the [MoO<sub>4</sub>]<sup>2-</sup> tetrahedrons at 901-742 cm<sup>-1</sup>. The [MoO<sub>4</sub>]<sup>2-</sup> 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 symmetric stretching, symmetric bending, asymmetric stretching and asymmetric bending modes. All these modes are Raman active, whereas only  $\nu_3(\text{F}_2)$  and  $\nu_4(\text{F}_2)$  are IR active.

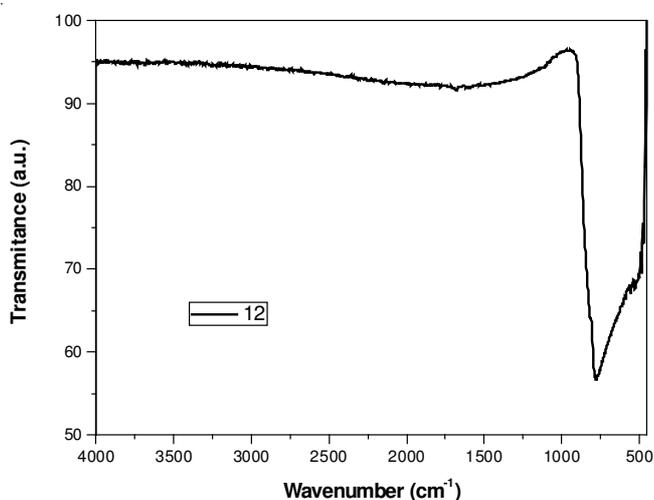


Fig. 3. FT-IR spectra of the BaMoO<sub>4</sub> particles after solid-state metathetic reaction followed by further heat-treatment at 600 °C for 3 h

Fig. 4 shows the photoluminescence emission spectra of the BaMoO<sub>4</sub> particles after solid-state metathetic reaction followed by further heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h excited at 250 nm at room temperature. The emission spectra of metal molybdates are due mainly to charge-transfer transitions within the [MoO<sub>4</sub>]<sup>2-</sup> complex<sup>13,14</sup>. With excitation at 250 nm, BaMoO<sub>4</sub> particles exhibit photoluminescence emission in the blue wavelength range of 390-420 nm. The emission spectra of four narrow shoulders at approximately 490, 510, 520 and 610 nm are considered to form by defect structures. The spectra show broad peaks on which is superimposed considerable several fine structures. The explanation of the narrow shoulders is proposed considering the Jahn-Teller splitting effect<sup>15,16</sup> on excited states of [MoO<sub>4</sub>]<sup>2-</sup> anion in the BaMoO<sub>4</sub>. This is similar to that reported by Zhan *et al.*<sup>17</sup>. The Jahn-Teller splitting effect essentially determines the emission shape of the MMoO<sub>4</sub> (M = Ba, Ca) particles. The additional emission bands can be interpreted by the existence of Frenkel defect structures (oxygen ion shifted to the inter-position with the simultaneous creation of vacancies) in the surface layers of the BaMoO<sub>4</sub> particles<sup>18,19</sup>. Despite of the somewhat different shapes of the spectra due to the different heat-treatment temperatures, common spectral features can be found. The photoluminescence intensities of the samples prepared at 600 °C for the BaMoO<sub>4</sub> particles are much stronger than that of the samples prepared at 400 and 500 °C. These results indicate that the photoluminescence intensity depends on crystallinity of the BaMoO<sub>4</sub> particles. It is noted that the high crystallinity plays an important role in the improvement of luminescent efficiency. Therefore, it can be considered that the enhancement of photoluminescence intensity with the heat-treatment temperature up to 600 °C is due to the increment of crystallinity.

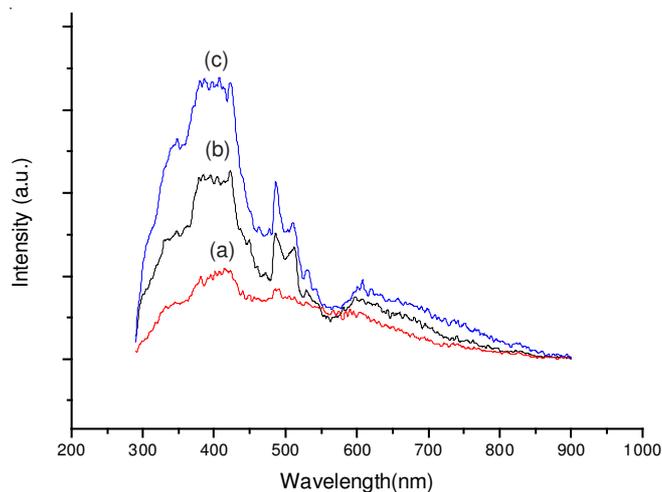


Fig. 4. Photoluminescence emission spectra of the BaMoO<sub>4</sub> particles after solid-state metathetic reaction followed by further heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h excited at 250 nm at room temperature

Fig. 5 shows Raman spectra of the BaMoO<sub>4</sub> particle excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the samples. The vibration modes in the Raman spectra of molybdates are classified into two groups, internal and external. The internal vibrations are related to the [MoO<sub>4</sub>]<sup>2-</sup>

molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the  $\text{Ba}^{2+}$  cation and rigid molecular units. In free space,  $[\text{MoO}_4]^{2-}$  tetrahedra show  $T_d$ -symmetry. The internal Raman mode for the  $\text{BaMoO}_4$  particles in Fig. 5 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 893, 840, 793, 361, 346 and 327  $\text{cm}^{-1}$ , respectively. The free rotation mode was detected at 191  $\text{cm}^{-1}$  and the external modes were localized at 140-107  $\text{cm}^{-1}$ . The well-resolved sharp peaks for the  $\text{BaMoO}_4$  particles indicate that the synthesized particles are highly crystallized.

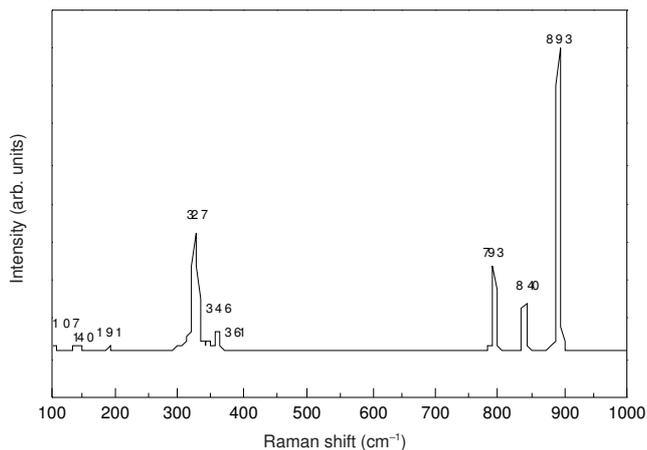


Fig. 5. Raman spectra of the  $\text{BaMoO}_4$  particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples

## Conclusion

$\text{BaMoO}_4$  particles synthesized using a solid-state meta-  
thetic method assisted by a cyclic microwave irradiation were well crystallized at 600  $^{\circ}\text{C}$ , showing a fine and homogeneous morphology with particle sizes of 1-2  $\mu\text{m}$ . With excitation at 250 nm, the  $\text{BaMoO}_4$  particles exhibit major photoluminescence emissions in the blue wavelength range of 390-420 nm, accompanying four narrow shoulders considered to form by defect structures. The photoluminescence intensities of the  $\text{BaMoO}_4$  particles prepared at 600  $^{\circ}\text{C}$  were much stronger than that of the samples prepared at 400 and 500  $^{\circ}\text{C}$ . The Raman

modes for the  $\text{BaMoO}_4$  particles were detected at 893, 840, 793, 361, 346 and 327  $\text{cm}^{-1}$ , respectively, the free rotation mode was detected at 191  $\text{cm}^{-1}$  and the external modes were localized at 140-107  $\text{cm}^{-1}$ .

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