

Solid-state metathetic synthesis of BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) assisted by microwave irradiation

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BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles were synthesized successfully using a solid-state metathetic route assisted by a cyclic microwave irradiation. Well-crystallized BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles were formed at 400–600 °C for 3 h, showing fine and homogeneous morphologies with particle sizes of 1–2 μm . The synthesized BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) 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: BaMO_4 ($\text{M} = \text{W}, \text{Mo}$), Microwave, Solid-state metathesis, Luminescence, Raman spectroscopy.

Introduction

Metal tungstates and molybdates have attracted considerable attention for potential applications in photoluminescence, scintillators, photocatalyst hosts for lanthanide-activated lasers and humidity sensors [1, 2]. The physical, chemical and photochemical properties of metal tungstates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) prepared by a range of processes, such as co-precipitation [3], a solvothermal method [4], spray pyrolysis [5], wet chemical method [6], a mechano-chemical method [7], a molten salt method [8], a hydrothermal method [9], microwave synthesis [10] and a solid-state metathetic reaction [11]. Among these methods, solution-based chemical synthetic methods play a key role in the design and production of fine ceramics and have been successful in overcoming many of the limitations of traditional solid-state, high-temperature methods. In addition, the use of solution chemistry can eliminate major problems, such as a long diffusion path, impurities and agglomeration, which result in products with improved homogeneity. Wet chemical methods have disadvantages, such as complicated synthetic steps, the use of expensive equipment, high synthesis temperatures and long sintering times. On the other hand, solid-state reactions require complex apparatus and techniques, which are becoming gradually unpopular due to excessive energy consumption.

Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, a small particle size, a narrow particle size distribution, and is a

high purity method for preparing polycrystalline samples. 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. Heat can be generated through volumetric heating because microwaves can penetrate the material and supply energy [12]. Therefore, it is possible to achieve rapid and uniform heating of thick materials. Solid-state synthesis of materials by the 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.

Metal tungstates and molybdates exhibit blue or green luminescent spectra, which are based on a radiative transition within the tetrahedral $[\text{MO}_4]^{2-}$ group. However, the study of solid state metathetic (SSM) synthesis assisted by a microwave irradiation and luminescent properties of BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles have not been published previously. Therefore, the precise nature of the optical properties and SSM synthesis assisted by the microwave irradiation of BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles is required for a wide range of applications. In this study, BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles were synthesized using a SSM route assisted by the cyclic microwave irradiation. The characteristics of the SSM reaction of BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) particles are discussed in detail based on the formation of a high lattice energy by-product of NaCl. The synthesized BaMO_4 ($\text{M} = \text{W}, \text{Mo}$) 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

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 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 metal molybdate was carried out by reacting well-ground mixtures of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ for BaWO_4 , and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ for BaMoO_4 at a molar ratio of 1 : 1, respectively. The sample mixtures were dried at 100 °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 minutes. 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 °C in an oven. Heat-treatments of the samples were performed at 400, 500 and 600 °C for 3 h.

The existing phases in the particles after the SSM 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 behavior of the SSM reaction and heat-treated particles over the frequency range, 400 to 4000 cm^{-1} . The microstructure and surface morphology of the BaMoO_4 ($M = \text{W}, \text{Mo}$) particles were observed by SEM (JSM-5600, JEOL, Japan). The PL 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 and Fig. 2 show XRD patterns of the BaWO_4 and BaMoO_4 particles heat-treated at 600 °C for 3 h. All XRD peaks could be assigned to tetragonal phases of

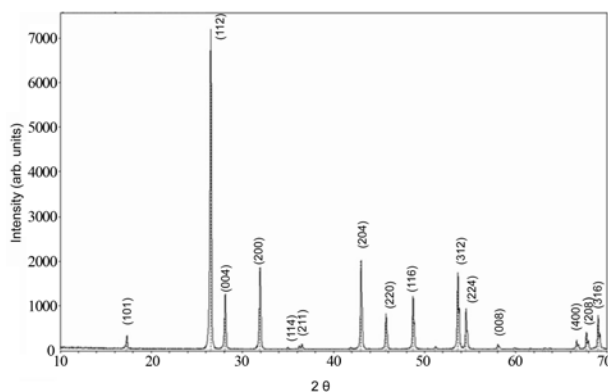


Fig. 1. XRD patterns of the BaWO_4 particles heat-treated at 600 °C for 3 h.

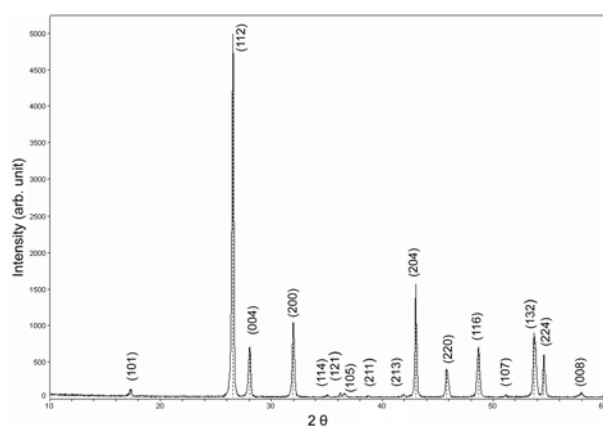


Fig. 2. XRD patterns of the BaMoO_4 particles heat-treated at 600 °C for 3 h.

BaWO_4 and BaMoO_4 with a scheelite-type structure, which are in good agreement with the crystallographic data of BaWO_4 (JCPDS : 43-0646) and BaMoO_4 (JCPDS : 29-01930). This means that the tetragonal phases of BaWO_4 and BaMoO_4 can be prepared using this SSM reaction assisted by a cyclic microwave irradiation. The formations of BaWO_4 and BaMoO_4 crystalline phases require heat treatment at 600 °C for 3 h. The BaWO_4 formed had a scheelite-type crystal structure with lattice parameters of $a = b = 5.613 \text{ \AA}$ and $c = 12.720 \text{ \AA}$ [1], and the BaMoO_4 formed had the same crystal structure with lattice parameters $a = b = 5.573 \text{ \AA}$ and $c = 12.786 \text{ \AA}$ [12]. These suggest that SSM synthesis is suitable for the growth of BaWO_4 and BaMoO_4 crystallites and development of the strongest intensity peaks from the (112), (200) and (312) planes, which were the major peaks of the BaWO_4 and BaMoO_4 , with some preferred orientation.

Fig. 3 shows SEM images of the BaWO_4 particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h, and BaMoO_4 particles after heat-treatment at (d) 400 °C for 3 h, (e) 500 °C for 3 h and (f) 600 °C for 3 h. The SEM image of BaWO_4 in Fig. 3(c) shows a well-defined and homogeneous morphology with particle sizes of 1-2 μm , while the SEM image of BaMoO_4 in Fig. 3(d-f) show well-defined octahedron-like morphologies with particle sizes of 1-2 μm . The structures of the samples prepared at 600 °C in Fig. 3(c) and Fig. 3(f) were much crystallized than that of the samples prepared at 400 and 500 °C in Fig. 3(a, b, d, e). After SSM reaction assisted by the microwave irradiation, the reactants are needed to heat at temperatures at 400, 500, 600 °C for 3 h. The SSM reaction assisted by the microwave irradiation and post heat-treatment are interdependently essential procedure to synthesize the BaWO_4 and BaMoO_4 particles employed for the solid state reactions. These results indicate that the well-defined crystallization depends on the heat-treatment temperatures of the BaWO_4 and BaMoO_4 particles. It is noted that the post heat-treatment plays an important role in the well-defined crystallized morphology.

The SSM reaction assisted by the microwave irradiation

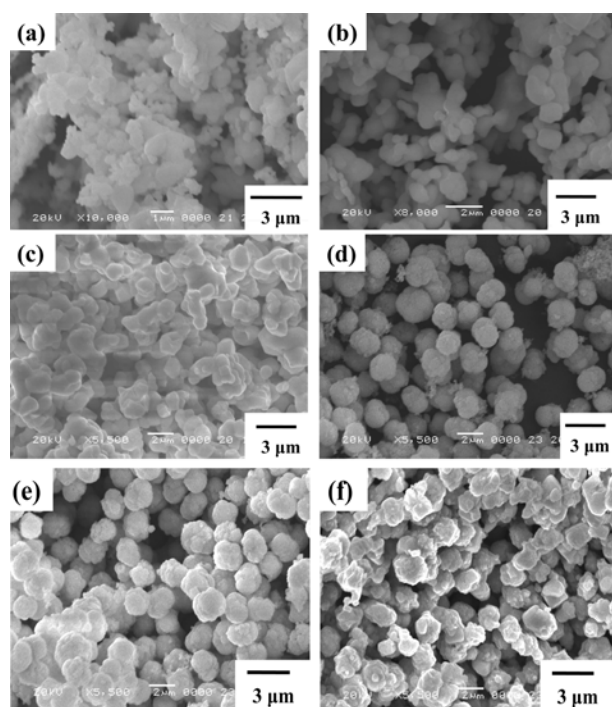


Fig. 3. SEM images of the BaWO₄ particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h, and BaMoO₄ particles after heat-treatment at (d) 400 °C for 3 h, (e) 500 °C for 3 h and (f) 600 °C for 3 h.

of various metal tungstates and molybdates helps to overcome the energy barrier. It helped to heat the bulk of the material uniformly resulting in fine particles with a controlled morphology, and to fabricate the product in a green manner without the generation of solvent waste. The SSM reactions, such as $\text{BaCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{BaWO}_4 + 2\text{NaCl}$ and $\text{BaCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{BaMoO}_4 + 2\text{NaCl}$ involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of NaCl with a high lattice energy [12]. SSM reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The SSM reactions provide a convenient route for the synthesis of metal tungstates and 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 tungstate and 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 BaWO₄ and BaMoO₄ particles synthesized by SSM reactions have a control over the morphology of the final particles, and can be used for technological applications.

Fig. 4 shows FT-IR spectra of the (a) BaWO₄ and (b) BaMoO₄ particles after heat-treatment at 600 °C for 3 h in the wavenumber range, 480–4000 cm⁻¹. A stretching vibration for BaWO₄ in Fig. 4(a) was detected as a strong W-O stretch in the [WO₄]²⁻ tetrahedra at 816 cm⁻¹. Similar characteristics absorption bands of metal tungstates for

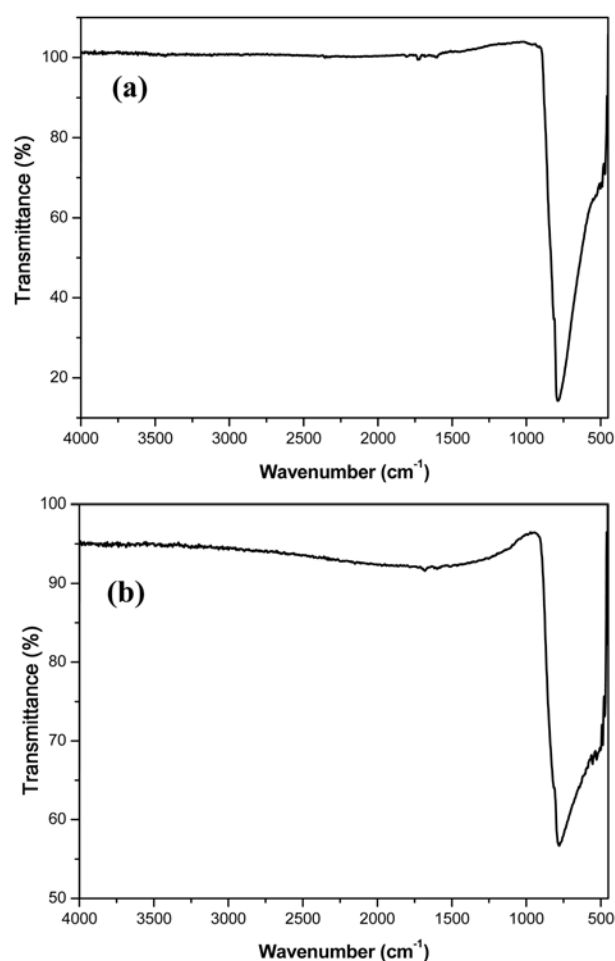


Fig. 4. FT-IR spectra of the (a) BaWO₄ and (b) BaMoO₄ particles after heat-treatment at 600 °C for 3 h.

the scheelite oxides having S₄ site symmetry in this region have been reported in the literature [6]. A stretching vibration for BaMoO₄ in Fig. 4(b) was detected as a strong Mo-O stretch in the [MoO₄]²⁻ tetrahedrons at 742–901 cm⁻¹. The [WO₄]²⁻ and [MoO₄]²⁻ are constituted by four internal modes ($\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$) specified as symmetric stretching, symmetric bending, asymmetric stretching and asymmetric bending modes. All these modes are Raman active, whereas only $\nu_3(F_2)$ and $\nu_4(F_2)$ are IR active.

Fig. 5 and Fig. 6 show the PL emission spectra of the BaWO₄ and BaMoO₄ particles after 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 tungstates and molybdates are due mainly to charge-transfer transitions within the [WO₄]²⁻ and [MoO₄]²⁻ complex [13, 14]. With excitation at 250 nm, BaWO₄ particles in Fig. 5 exhibit major PL emissions in the blue wavelength range of 390–420 nm. The emission spectra of four narrow shoulders at approximately 490, 510, 520 and 600 nm are considered to form by defect structures. With excitation at 250 nm, BaMoO₄ particles in Fig. 6 exhibit PL emission in the blue wavelength range

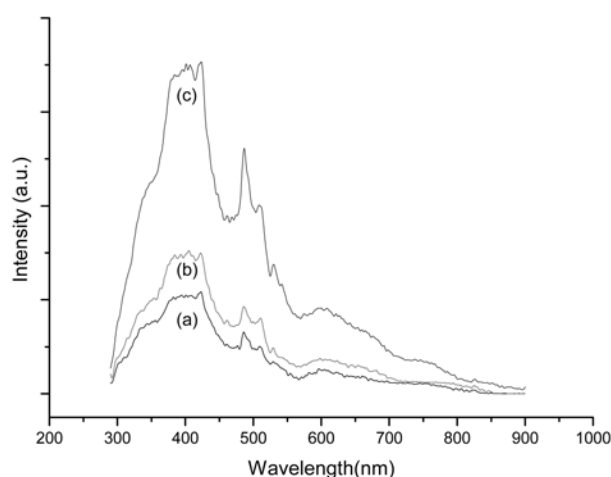


Fig. 5. PL emission spectra of the BaWO_4 particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h excited at 250 nm at room temperature.

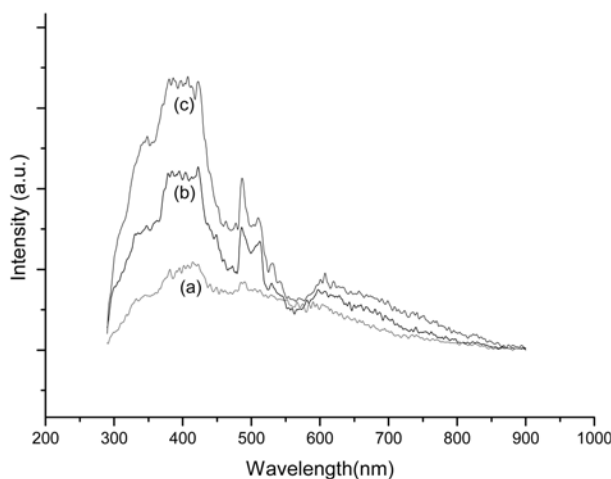


Fig. 6. PL emission spectra of the BaMoO_4 particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h and (c) 600 °C for 3 h excited at 250 nm at room temperature.

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 All spectra show broad peaks on which is superimposed considerable several fine structures. The explanation of the narrow shoulders in Fig. 5 and Fig. 6 is proposed considering the Jahn-Teller splitting effect [15, 16] on excited states of $[\text{WO}_4]^{2-}$ and $[\text{MoO}_4]^{2-}$ anion in the BaWO_4 and BaMoO_4 . This is similar to that reported by Zhan *et al.* [17]. The Jahn-Teller splitting effect essentially determines the emission shape of the MMoO_4 ($M = \text{Ba}, \text{Ca}$) particles. The additional emission bands can be interpreted by the existence of Frenkel defect structures (oxygen ion shifted to the interposition with the simultaneous creation of vacancies) in the surface layers of the BaWO_4 and BaMoO_4 particles [18, 19]. Despite of the somewhat different shapes of the spectra due to the different heat-treatment temperatures, common spectral features can be found. The PL spectra of the BaWO_4 and BaMoO_4 prepared from 400 to 600 °C

had same peak positions. The PL intensities of the samples prepared at 600 °C for the BaWO_4 and BaMoO_4 particles are much stronger than that of the samples prepared at 400 and 500 °C. These results indicate that the PL intensity depends on crystallinity of the BaWO_4 and BaMoO_4 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 PL intensity with the heat-treatment temperature up to 600 °C is due to the increment of crystallinity.

Fig. 7 shows Raman spectra of the (a) BaWO_4 and (b) BaMoO_4 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 tungstates and molybdates are classified into two groups, internal and external. The internal vibrations are related to the $[\text{WO}_4]^{2-}$ and $[\text{MoO}_4]^{2-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Ba^{2+} cation and rigid molecular units. In free space, $[\text{WO}_4]^{2-}$ and $[\text{MoO}_4]^{2-}$ tetrahedra show T_d -symmetry. The Raman modes for the BaWO_4 particles in Fig. 7(a) 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 925, 831, 795, 352, 344 and 332 cm^{-1} , respectively, which provide evidence of a scheelite structure. The free rotation

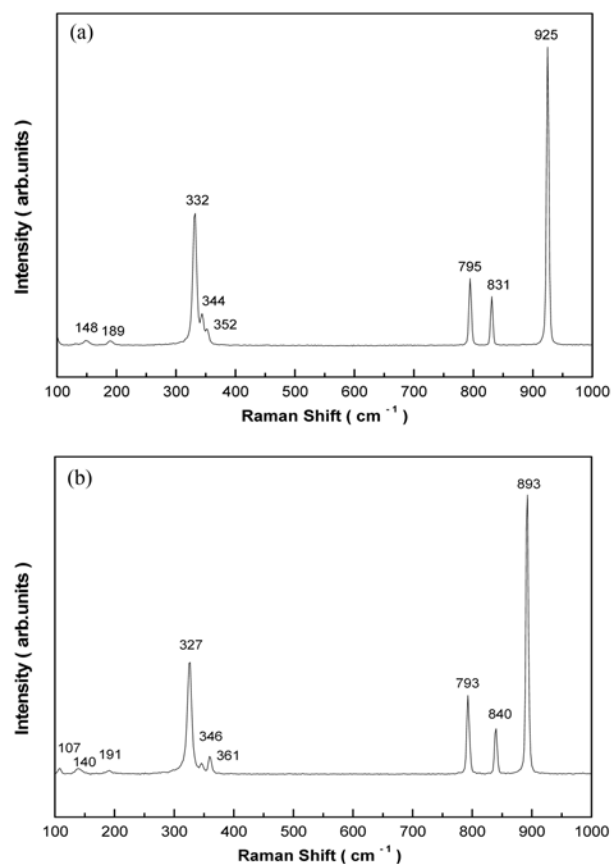


Fig. 7. Raman spectra of the (a) BaWO_4 and (b) BaMoO_4 particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples.

mode was detected at 189 cm^{-1} and the external modes were localized at 148 cm^{-1} . The Raman modes for the BaMoO_4 particles in Fig. 7(b) 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 cm^{-1} , respectively, which provide evidence of a scheelite structure. The free rotation mode was detected at 191 cm^{-1} and the external modes were localized at $140\text{--}107\text{ cm}^{-1}$. The well-resolved sharp peaks for the BaWO_4 and BaMoO_4 particles indicate that the synthesized particles are highly crystallized. The type of cations (Ca^{2+} , Sr^{2+} , Ba^{2+}) can influence on the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect [20]. There is an essential dependence of the bandwidth of the $\nu_1(A_g)$ Raman mode on the peculiarities of the crystal lattice and the type of Me^{2+} cation in the series of MWO_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$) crystals with a scheelite structure. Moving in the series of tungstates Ca^{2+} Sr^{2+} Ba^{2+} increases the unit cell and interionic distance inside the molecular group. The degree of covalent bond between the cation and molecular group usually decreases within the series Ca^{2+} Sr^{2+} Ba^{2+} .

Conclusions

BaWO_4 and BaMoO_4 particles synthesized using a SSM method assisted by a cyclic microwave irradiation were well crystallized at 600°C , showing a fine and homogeneous morphology with particle sizes of $1\text{--}2\text{ }\mu\text{m}$. With excitation at 250 nm , the BaWO_4 and BaMoO_4 particles exhibit major PL emissions in the blue wavelength range of $390\text{--}420\text{ nm}$, accompanying four narrow shoulders considered to form by defect structures. The PL intensities of the BaWO_4 and BaMoO_4 particles prepared at 600°C were much stronger than that of the samples prepared at 400 and 500°C . The Raman modes for the BaWO_4 particles were detected at 925, 831, 795, 352, 344 and 332 cm^{-1} , the free rotation mode was detected at 189 cm^{-1} and the external modes were localized at 148 cm^{-1} . The Raman modes for the BaMoO_4 particles were detected at 893, 840, 793, 361, 346 and 327 cm^{-1} , respectively, the free rotation mode was detected at 191 cm^{-1} and the external modes were localized at $140\text{--}107\text{ cm}^{-1}$.

Acknowledgement

This study was supported by Research Program through the Campus Research Foundation funded by Hanseo University in 2011 (111Gonghang06).

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