



Solid-State Metathetic Synthesis of Strontium Molybdate Particles Assisted by Microwave Irradiation

WON-CHUN OH, CHONG YEON PARK, JEONG WON JEON and CHANG SUNG LIM*

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, South Korea

*Corresponding author: Tel/Fax: +82 41 660 1445; E-mail: cslim@hanseo.ac.kr

(Received: 5 March 2011;

Accepted: 25 January 2012)

AJC-11016

A solid-state metathetic route was used to synthesize strontium molybdate (SrMoO_4) particles assisted by microwave irradiation under environmentally friendly conditions. The SrMoO_4 particles were synthesized successfully using the solid-state metathetic method with microwave irradiation. Well crystallized SrMoO_4 particles were formed at 600 °C for 3 h, showing a spherical and homogeneous morphology with sizes of 0.5-1 μm . The solid-state metathetic reaction of the SrMoO_4 particles is discussed in detail based on the exothermic reaction. The synthesized SrMoO_4 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: Strontium molybdate, Microwave irradiation, Solid-state metathetic synthesis, Luminescence, Raman spectroscopy.

INTRODUCTION

Metal molybdates exhibit blue or green luminescent spectra, which are based on a radiative transition within the tetrahedral $[\text{MoO}_4]^{2-}$ 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, strontium molybdate (SrMoO_4) particles among the metallic molybdate compound with a Scheelite type structure, which have lattice parameters of $a = b = 5.406 \text{ \AA}$ and $c = 11.988$, have significantly employed in the field of potential applications in photoluminescence, hosts for lanthanide-activated lasers, photocatalysis and humidity sensors¹⁻³.

Several processes have been developed to enhance the applications of metal molybdates prepared by a range of processes, such as co-precipitations^{4,5}, electrochemical techniques⁶⁻⁸, polymerized complex methods⁹, aqueous mineralization processes¹⁰, hydrothermal methods^{11,12}, microwave-hydrothermal preparations¹³⁻¹⁵, microwave-assisted polymerized complex methods¹⁶⁻¹⁹, a pulsed laser ablation²⁰, microwave irradiation²¹⁻²⁴ and solid-state a metathetic synthesis^{25,26}. For practical applications of SrMoO_4 particles in photoluminescence, hosts materials for lasers, photocatalysis and humidity sensors, well-defined particle features with homogeneous

particle size distribution and morphology of the SrMoO_4 particles are required. The solid-state metathetic synthesis of the SrMoO_4 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 present study, we synthesized SrMoO_4 particles using a solid-state metathetic method with microwave irradiation. The characteristics of the solid-state metathetic reaction of SrMoO_4 particles are discussed in detail based on exothermic reaction accompanying the formation of NaCl. The synthesized SrMoO_4 particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The optical properties were examined by photoluminescence emission and Raman spectroscopy.

EXPERIMENTAL

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ at a molar ratio of 1:1. 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 15 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 °C in an oven. Heat-treatment of the samples was performed at 600 °C for 3 h.

The phase existings in the particles after the solid-state metathetic reactions and heat-treatment were identified by XRD (D/MAX 2200, Rigaku, Japan). FTIR (Nicolet IR200, Thermo Electron corporation, USA) was used to examine the thermal-decomposition behaviour of the solid-state metathetic reaction and the obtained particles over the frequency range, 4000 to 400 cm^{-1} . The microstructure and surface morphology of the SrMoO_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 a LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as excitation source, the power was kept at 0.5 mW on the sample.

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of the SrMoO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h. All XRD peaks could be assigned to a tetragonal phase SrMoO_4 with a Scheelite-type structure, which is in good agreement with the crystallographic data of SrMoO_4 (JCPDS: 08-0482). This means that the tetragonal phase SrMoO_4 can be prepared using this solid-state metathetic reaction assisted by microwave irradiation. The formation of the SrMoO_4 crystalline phases requires heat treatment at 600 °C for 3 h. The SrMoO_4 formed had a Scheelite-type crystal structure with lattice parameters of $a = b = 5.406 \text{ \AA}$ and $c = 11.988^{22}$. It suggests that solid-state metathetic synthesis is suitable for the growth of SrMoO_4 crystallites and the development of the strongest intensity peaks at (112), (200) and (312) planes, which were the major peaks of the SrMoO_4 , with some preferred orientation¹⁴.

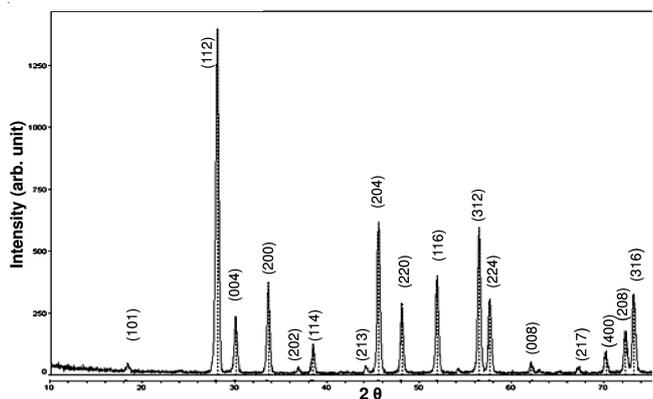


Fig. 1. XRD patterns of the SrMoO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

Fig. 2 shows a SEM image of the SrMoO_4 particles. The SrMoO_4 particles after microwave assisted solid-state metathetic reaction followed heat-treatment had sizes of 1-4 μm . The sample mixtures of SrCl_2 and Na_2MoO_4 were heated to form the SrMoO_4 by microwave-assisted solid-state

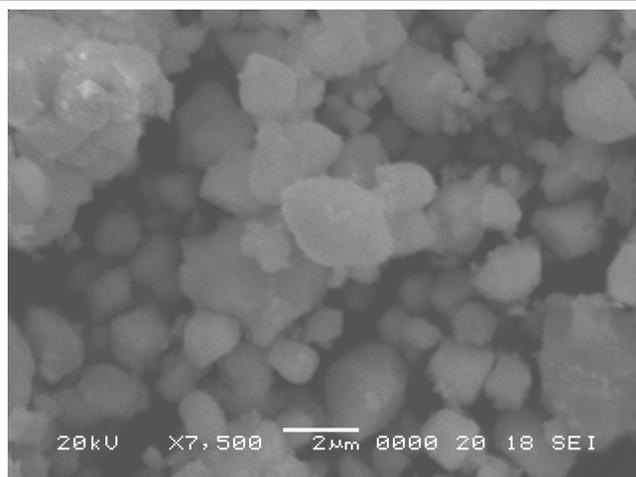


Fig. 2. SEM images of the SrMoO_4 particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

metathetic route. The microwave metathetic synthesis of the SrMoO_4 provided the fine particles with a controlled morphology and the product in a green manner without the generation of solvent waste. Solid-state metathetic reactions, such as $\text{SrCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{SrMoO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, where the driving force is exothermic reaction with a thermodynamically stability accompanying the formation of NaCl with a high lattice energy²³⁻²⁵. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products. The solid-state metathetic reactions provide convenient route for the synthesis of the SrMoO_4 particles which were obtained in the form of loosely connected submicron 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 SrMoO_4 particles synthesized by solid-state metathetic reactions have control over the morphology of the final particles and can be used for such technological applications.

Fig. 3 shows FTIR spectrum of the obtained SrMoO_4 particles at the wavenumber range, 4000-480 cm^{-1} . The stretching vibration was detected as a strong Mo-O stretch in the $[\text{MoO}_4]^{2-}$ tetrahedrons at 800 cm^{-1} . The $[\text{MoO}_4]^{2-}$ 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 an anti-symmetric stretching vibration¹³. All modes are Raman active, but $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ are IR active.

Fig. 4 presents a photoluminescence emission spectrum of the SrMoO_4 particles by microwave metathetic synthesis and heat-treatment at 600 °C for 3 h. The emission spectrum of metal molybdates is due mainly to charge-transfer transitions within the $[\text{MoO}_4]^{2-}$ complex^{27,28}. With excitation at 250 nm, SrMoO_4 particles exhibit a strong photoluminescence emission in the blue wavelength range of 470-480 nm.

Fig. 5 shows a Raman spectrum of the SrMoO_4 particles excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the sample. The vibration modes in the Raman spectrum of molybdates are classified into two groups, internal and external^{29,30}. The internal vibrations are related to the $[\text{MoO}_4]^{2-}$ molecular group with a stationary mass center. The

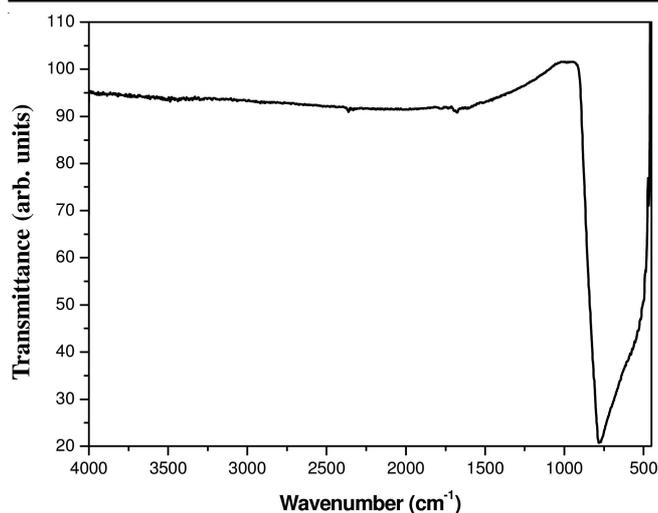


Fig. 3. FT-IR spectra of the obtained SrMoO₄ particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

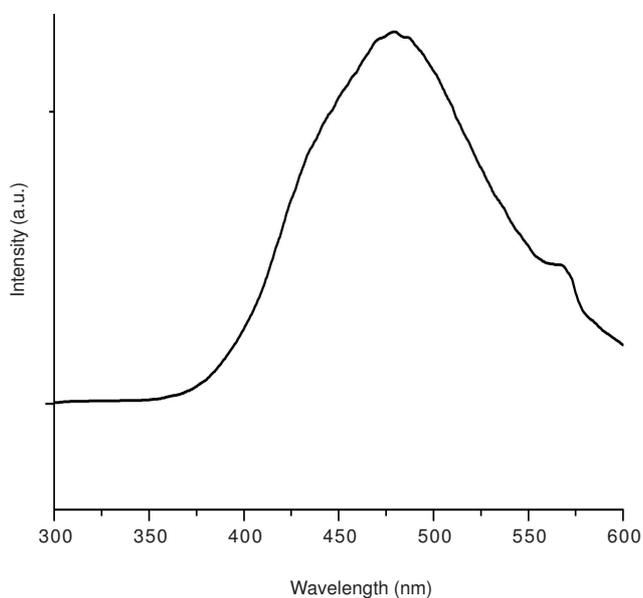


Fig. 4. Photoluminescence emission spectra of the SrMoO₄ particles excited at 250 nm at room temperature

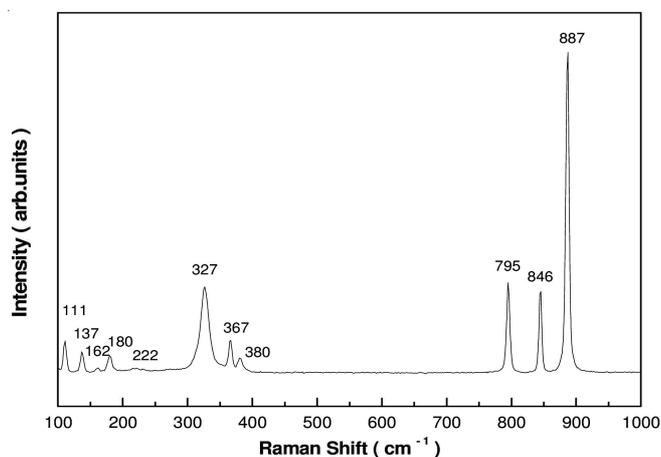


Fig. 5. Raman spectra of the SrMoO₄ particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

external vibrations or lattice phonons are associated with the motion of the Sr²⁺ cation and rigid molecular units. In the free space, [MoO₄]²⁻ tetrahedrons show T_d-symmetry. In this case, the vibrations of the [MoO₄]²⁻ ions are constituted by four internal modes [$\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$], one free rotation mode [$\nu_{fr}(F_1)$] and one transition mode (F_2). When [MoO₄]²⁻ ions are present in a Scheelite-type structure, its point symmetry reduces to S₄. Therefore, all degenerative vibrations are split due to the crystal field effect. For a tetragonal Scheelite primitive cell with a $k = 0$ wave vector^{13,28}, there are 26 different vibrations ($\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$), as determined by group-theory calculations. Among them, the 3A_g, 5B_g and 5E_g vibrations are Raman-active. Only 4A_u and 4E_u of the 5A_u and 5E_u vibrations are active in the IR frequencies and the remaining (1A_u and 1E_u) are acoustic vibrations. The 3B_u vibration is a silent mode. The Raman modes for the SrMoO₄ particles 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 887, 846, 795, 380, 367 and 327 cm⁻¹, respectively. The well-resolved sharp peaks for the SrMoO₄ particles indicate that the synthesized particles are highly crystallized. A free rotation mode was detected at 180 cm⁻¹ and the external modes were localized at 162, 137 and 111 cm⁻¹. The internal vibration mode frequencies exhibited dependence on lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group [MoO₄]²⁻. The type of cations (Ca²⁺, Sr²⁺, Ba²⁺) can influence on the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect³⁰. It was found that the splitting of totally symmetric ν_1 valence vibration of [MoO₄]²⁻ tetrahedrons grows in the series Ba→Sr→Ca scheelites. The essential dependence of the bandwidth of $\nu_1(A_g)$ Raman mode on the peculiarities of crystal lattice and the type of Me²⁺ cation in the series of MMoO₄ (M = Ca, Sr, Ba, Pb) crystals with Scheelite structure. The combination of a heavy metal cation and large interionic distance in the lattice results in low probability of up-conversion and phonon splitting relaxation process in MMoO₄ crystals.

Conclusion

Strontium molybdate (SrMoO₄) particles were synthesized using a solid-state metathetic method assisted by microwave irradiation. Well crystallized SrMoO₄ particles were formed at 600 °C for 3 h, showing a spherical and homogeneous morphology with sizes of 0.5-1 μm. The stretching vibration in FTIR was detected as a strong Mo-O stretch in the [MoO₄]²⁻ tetrahedrons at 800 cm⁻¹. With excitation at 250 nm, SrMoO₄ particles exhibit photoluminescence emission in the blue wavelength range of 470-480 nm. The internal Raman mode was detected at 887, 846, 795, 380, 367 and 327 cm⁻¹. The free rotation mode was detected at 180 cm⁻¹ and the external modes were localized at 162, 137 and 111 cm⁻¹. The well-resolved sharp peaks for the SrMoO₄ particles indicate that the synthesized particles are highly crystallized.

ACKNOWLEDGEMENTS

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0026911).

REFERENCES

- R. Sundaram and K.S. Nagaraja, *Sens. Actuators B*, **101**, 353 (2004).
- L. Zhen, W.S. Wang, C.Y. Xu, W.Z. Shao, M.M. Ye and Z.L. Chen, *Scripta Mater.*, **58**, 461 (2008).
- R.N. Singh, J.P. Singh and A. Singh, *Int. J. Hyd. Ener.*, **33**, 4260 (2008).
- X. Zhao, T.L.Y. Cheung, Y. Xi, K.C. Chung, D.H.L. Ng and J. Yu, *J. Mater. Sci.*, **42**, 6716 (2007).
- T. Thongtem, S. Kungwankunakorn, B. Kuntalue, A. Phuruangrat and S. Thongtem, *J. Alloys Compd.*, **506**, 475 (2010).
- P. Yu, J. Bi, D.J. Gao, Q. Xiao, L.P. Chen, X.L. Jin and Z.N. Yang, *J. Electroceram.*, **21**, 184 (2008).
- P. Yu, J. Bi, D.Q. Xiao, L.P. Chen, X.L. Jin and Z.N. Yang, *J. Electroceram.*, **16**, 473 (2006).
- Y. Sun, J. Ma, J. Fang, C. Gao and Z. Liu, *Ceramics Inter.*, **37**, 683 (2011).
- J.W. Yoon, J.H. Ryu and K.B. Shim, *Mater. Sci. Eng. B*, **127**, 154 (2006).
- X. Wu, J. Du, H. Li, M. Zhang, B. Xi, H. Fan, Y. Zhu and Y. Qian, *J. Solid State Chem.*, **180**, 3288 (2007).
- G. Zhang, S. Yu, Y. Yang, W. Jiang, S. Zhang and B. Huang, *J. Crystal Growth*, **312**, 1866 (2010).
- K. Eda, Y. Kato, Y. Ohshiro, T. Sugitani and M.S. Whittingham, *J. Solid State Chem.*, **183**, 1334 (2010).
- J.T. Kloprogge, M.L. Weier, L.V. Duong and R.L. Frost, *Mater. Chem. Phys.*, **88**, 438 (2004).
- J.C. Sczancoski, L.S. Cavalcante, M.R. Joya, J.A. Varela, P.S. Pizani and E. Longo, *Chem. Eng. J.*, **140**, 632 (2008).
- L.S. Cavalcante, J.C. Sczancoski, R.L. Tranquilin, J.A. Varela, E. Longo and M.O. Orlandi, *Particuology*, **7**, 353 (2009).
- J.H. Ryu, J.W. Yoon, C.S. Lim, W.C. Oh and K.B. Shim, *J. Alloys Compd.*, **390**, 245 (2005).
- J.H. Ryu, B.G. Choi, S.H. Kim, J.W. Yoon, C.S. Lim and K.B. Shim, *Mater. Res. Bull.*, **40**, 1468 (2005).
- J.H. Ryu, S.M. Koo, J.W. Yoon, C.S. Lim and K.B. Shim, *Mater. Lett.*, **60**, 1702 (2006).
- J.H. Ryu, B.G. Choi, S.H. Kim, J.W. Yoon, C.S. Lim and K.B. Shim, *J. Mater. Sci.*, **40**, 4979 (2005).
- J.H. Ryu, B.G. Choi, J.W. Yoon, K.B. Shim, K. Machi and K. Hamada, *J. Lum.*, **67**, 124 (2007).
- T. Thongtem and A. Phuruangrat, *J. Nanopart. Res.*, **12**, 2287 (2010).
- T. Thongtem, A. Phuruangrat and S. Thongtem, *Mater. Lett.*, **62**, 454 (2008).
- S. Das, A.K. Mukhopadhyay, S. Datta and D. Basu, *Bull. Mater. Sci.*, **32**, 1 (2009).
- K.P.F. Siqueira, R.L. Moreira, M. Valadares and A. Dias, *J. Mater. Sci.*, **45**, 6083 (2010).
- P. Parhi, S.S. Sing, A.R. Ray and A. Ramanan, *Bull. Mater. Sci.*, **29**, 115 (2006).
- V. Thangadurai, C. Knittlmayer and W. Weppner, *Mater. Sci. Eng. B*, **106**, 228 (2004).
- D.A. Spassky, S.N. Ivanov, V.N. Kolobanov, V.V. Mikhailin, V.N. Zemskov, B.I. Zadneprovski and L.I. Potkin, *Radiat. Measur.*, **38**, 607 (2004).
- G.Y. Hong, B.S. Jeon, Y.K. Yoo and J.S. Yoo, *J. Electrochem. Soc.*, **148**, H161 (2001).
- T.T. Basiev, A.A. Sobol, Y.K. Voronko and P.G. Zverev, *Opt. Mater.*, **15**, 205 (2000).
- T.T. Basiev, A.A. Sobol, P.G. Zverev, L.I. Ivleva, V.V. Osiko and R.C. Powell, *Opt. Mater.*, **11**, 307 (1999).