



## Preparation and Optical Property of Cadmium Molybdate Particles by a Solid-State Microwave Metathetic Route

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(Received: 6 April 2011;

Accepted: 1 March 2012)

AJC-11136

A solid-state metathetic (SSM) route assisted by microwave irradiation was used to synthesize cadmium molybdate ( $\text{CdMoO}_4$ ) particles under environmentally friendly conditions. Well crystallized  $\text{CdMoO}_4$  particles were formed at 600 °C for 3 h, showing a fine and homogeneous morphology with sizes of 0.5-1.0  $\mu\text{m}$ . The synthesized  $\text{CdMoO}_4$  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:** Cadmium molybdate, Solid-state metathetic, Microwave route, Photoluminescence, Raman spectroscopy.

### INTRODUCTION

Cadmium molybdate ( $\text{CdMoO}_4$ ) is one of the metallic molybdate compounds with a Scheelite structure and has a body-center orthorhombic primitive cell. Each site of Cd and Mo is surrounded by eight oxygen (octahedron) and four equivalent oxygen (tetrahedron) sites, respectively. The calculation of the electronic structure shows that the Cd state localizes at the bottom region of the O valence band and Cd state has a significant contribution to the bottom of the conduction band, composed of the Mo state<sup>1</sup>. Cadmium molybdate is interesting material owing to its excellent optical and chemical properties, electronic excitation at VUV synchrotron radiation, pressure-induced phase transformations and <sup>111</sup>Cd and Cd<sup>113</sup> spin-lattice relaxation<sup>2</sup>. As a wide band gap semiconductor of 3.25 eV,  $\text{CdMoO}_4$  is expected to be a photocatalyst under UV radiation<sup>2</sup>. Recently,  $\text{CdMoO}_4$  has attracted increasing attentions because of its wide range of applications, such as photoluminescence, scintillating materials, humidity sensors, photoelectric devices, photonic crystals, light weight filler materials, photocatalysts and chemical reactors<sup>3-7</sup>.

Cadmium molybdate has a Scheelite-type crystal structure<sup>7</sup> with lattice parameters of  $a = b = 5.16 \text{ \AA}$  and  $c = 11.19 \text{ \AA}$ . Recently, there have been various reports on the synthesis of  $\text{CdMoO}_4$  to enhance the applications of  $\text{CdMoO}_4$  prepared by a range of processes, such as a hydrothermal method<sup>8</sup>, a microwave-assisted synthesis<sup>9</sup>, an aqueous solution method<sup>6</sup>, Czochralski method<sup>10</sup>, a microemulsion-mediated route<sup>11</sup> and a solid-state reaction<sup>12</sup>. Generally, conventional solid-state

route requires prolonged calcinations at elevated temperatures for several hours along with intermediate grinding in order to obtain reasonable phase purity. For practical applications of  $\text{CdMoO}_4$  particles, well-defined particle features with homogeneous particle size distribution and morphology of the  $\text{SrMoO}_4$  particles are required. 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. The solid-state metathetic synthesis of the  $\text{CdMoO}_4$  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<sup>13,14</sup>.

In the present study,  $\text{CdMoO}_4$  particles were synthesized using a solid-state metathetic method with microwave irradiation. The characteristics of the solid-state metathetic reaction of  $\text{CdMoO}_4$  particles are discussed in detail based on the exothermic reaction accompanying the formation of NaCl. The obtained  $\text{CdMoO}_4$  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.

### EXPERIMENTAL

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  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  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  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 and heat-treated 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  $\text{cm}^{-1}$ . The microstructure and surface morphology of the  $\text{CdMoO}_4$  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  $\text{CdMoO}_4$  particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h. All XRD peaks could be assigned to an orthorhombic phase  $\text{CdMoO}_4$  with a scheelite-type structure, which is in good agreement with the crystallographic data of  $\text{CdMoO}_4$  (JCPDS: 07-0209). This means that the orthorhombic phase  $\text{CdMoO}_4$  can be prepared using this solid-state metathetic reaction assisted by microwave irradiation. The formation of  $\text{CdMoO}_4$  crystalline phases requires heat treatment at 600 °C for 3 h. The  $\text{CdMoO}_4$  formed had a scheelite-type crystal structure with lattice parameters of  $a = b = 5.16 \text{ \AA}$  and  $c = 11.19 \text{ \AA}$ . The structure is composed of eight symmetry elements and a body-centered orthorhombic primitive cell, in which each Mo and Cd site is surrounded by four O and eight O sites, respectively. The strong and narrow peaks in the XRD patterns show that the material is well crystallized. This suggests that solid-state metathetic synthesis is suitable for the

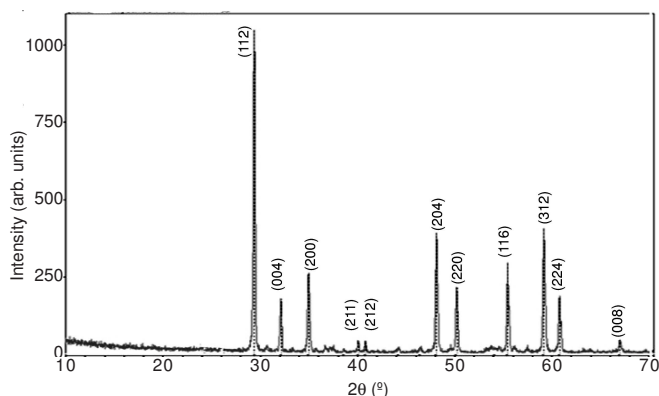


Fig. 1. XRD patterns of the  $\text{CdMoO}_4$  particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

growth of  $\text{CdMoO}_4$  crystallites and development of the strongest intensity peaks at (112), (200) and (312) planes, which were the major peaks of the  $\text{CdMoO}_4$ , with some preferred orientations.

Fig. 2 shows a SEM image of the  $\text{CdMoO}_4$  particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h. The SEM image shows a fine and homogeneous morphology with particle sizes of 0.5-1.0  $\mu\text{m}$ . The sample mixtures of  $\text{CdCl}_2$  and  $\text{Na}_2\text{MoO}_4$  were heated by microwave-assisted solid-state metathetic route. The cyclic microwave-assisted solid-state metathetic synthesis provided fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste. The solid-state metathetic reactions, such as  $\text{CdCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{CdMoO}_4 + 2\text{NaCl}$ , involve the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of  $\text{NaCl}$  with high lattice energy<sup>13-16</sup>. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products. The solid-state metathesis reactions provide convenient route for the synthesis of metal molybdates, 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  $\text{CdMoO}_4$  particles synthesized by solid-state metathetic reactions have control over the morphology of the final particles and can be used for such technological applications.

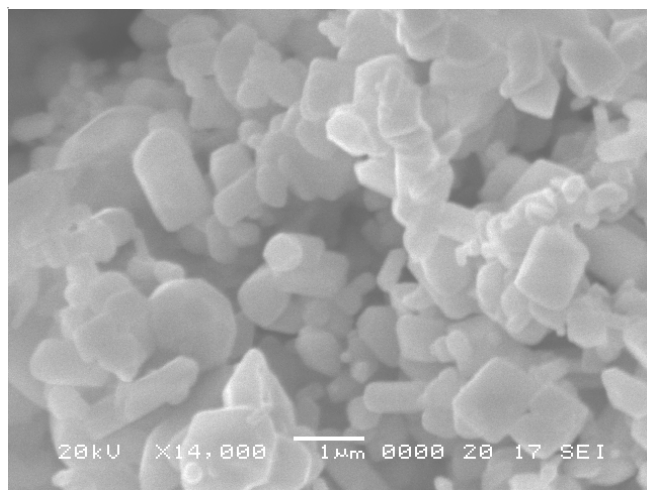


Fig. 2. SEM images of the  $\text{CdMoO}_4$  particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

Fig. 3 shows FTIR spectrum of the obtained  $\text{CdMoO}_4$  particles at the wavenumber range, 4000-480  $\text{cm}^{-1}$ . The stretching vibration was detected as a strong Mo-O stretch in the  $[\text{MoO}_4]^{2-}$  tetrahedrons at 895-743  $\text{cm}^{-1}$  and additional weak peaks of the Mo-O bending mode around 500  $\text{cm}^{-1}$ . This is one of the internal modes specified as an antisymmetric stretching vibration. This result is in agreement with that reported in the literature<sup>9</sup>.

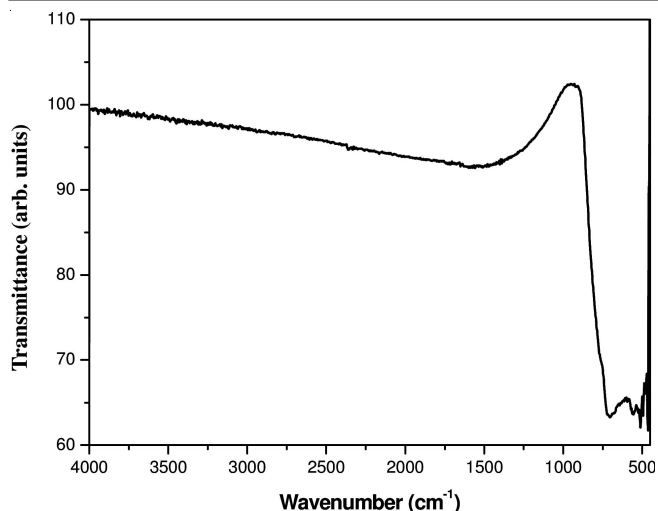


Fig. 3. FT-IR spectra of the CdMoO<sub>4</sub> particles after solid-state metathetic reaction followed by heat-treatment at 600 °C for 3 h

Fig. 4 presents a room-temperature photoluminescence emission spectrum of the CdMoO<sub>4</sub> particles by microwave metathetic synthesis followed heat-treatment at 600 °C for 3 h. With excitation at 250 nm, CdMoO<sub>4</sub> particles exhibit major photoluminescence emissions in the blue wavelength range of 380-400 nm. The neighbored shoulder is located at 430 nm and the sloped shoulders are at 490, 520, 530 and 540 nm. The spectrum shows rugged peaks, which are in agreement with that reported spectra of the BaWO<sub>4</sub><sup>17</sup> and BaMoO<sub>4</sub><sup>18</sup> particles. It is generally assumed that the measured emission spectrum of metal molybdates are mainly attributed to the charge-transfer transitions within the [MoO<sub>4</sub>]<sup>2-</sup> complex<sup>19,20</sup>. The emission spectrum of five narrow shoulders at approximately 430-540 nm is considered to form by defect structures. Such peaks, namely the ‘spread-eagle’ shape of the blue emission can be explained by the influence of the Jahn-Teller effect<sup>21,22</sup> on the degenerated excited state of [MoO<sub>4</sub>]<sup>2-</sup> tetrahedron. Generally, the presence of Gaussian components indicates that the electronic levels corresponding to relaxed excited state of an emission centre belong to a degenerate excited state influenced by some perturbation, *e.g.* local low symmetry crystal field<sup>23,24</sup>.

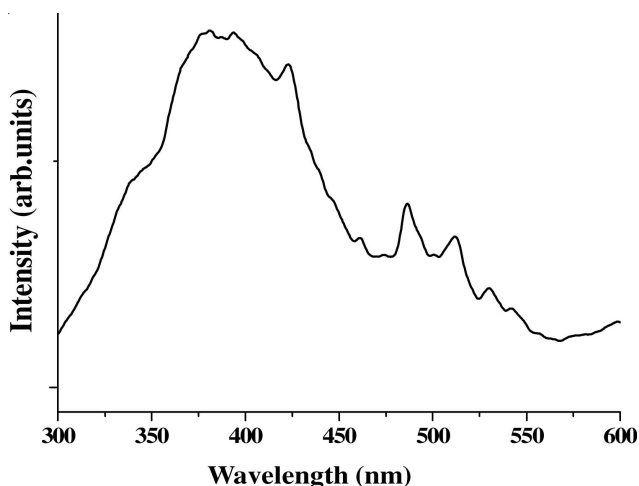


Fig. 4. Photoluminescence emission spectra of the CdMoO<sub>4</sub> particles excited at 250 nm at room temperature

Fig. 5 shows a Raman spectrum of the CdMoO<sub>4</sub> particles excited by 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 spectra of molybdates are classified into two groups, internal and external<sup>25,26</sup>. The internal modes are related to the [MoO<sub>4</sub>]<sup>2-</sup> molecular group with a stationary mass center. The external (rotation and translation) modes or lattice phonons are associated to the motion of the Cd<sup>2+</sup> cation and rigid molecular units. In the free space, [MoO<sub>4</sub>]<sup>2-</sup> tetrahedrons show T<sub>d</sub>-symmetry. Among them, seven modes are internal stretching vibrations of ν<sub>1</sub>(A<sub>g</sub>), ν<sub>3</sub>(B<sub>g</sub>) and ν<sub>3</sub>(E<sub>g</sub>) and bending of ν<sub>2</sub>(A<sub>g</sub>), ν<sub>2</sub>(B<sub>g</sub>), ν<sub>4</sub>(B<sub>g</sub>) and ν<sub>4</sub>(E<sub>g</sub>). The six remaining are external modes, three rotations, two translations and an unidentified mode. When [MoO<sub>4</sub>]<sup>2-</sup> ions are present in a scheelite-type structure, its point symmetry reduces to S<sub>4</sub>. Therefore, all degenerative vibrations are split due to the crystal field effect. For a tetragonal scheelite primitive cell with a k = 0 wave vector<sup>9,21</sup>, there are 26 different vibrations (Γ = 3A<sub>g</sub> + 5A<sub>u</sub> + 5B<sub>g</sub> + 3B<sub>u</sub> + 5E<sub>g</sub> + 5E<sub>u</sub>), as determined by group-theory calculations. Among them, the 3A<sub>g</sub>, 5B<sub>g</sub> and 5E<sub>g</sub> vibrations are Raman-active. Only 4A<sub>u</sub> and 4E<sub>u</sub> of the 5A<sub>u</sub> and 5E<sub>u</sub> vibrations are active in the IR frequencies and the remaining (1A<sub>u</sub> and 1E<sub>u</sub>) are acoustic vibrations. The 3B<sub>u</sub> vibration is a silent mode. The Raman modes for the CdMoO<sub>4</sub> particles in Fig. 5 were detected as ν<sub>1</sub>(A<sub>g</sub>), ν<sub>3</sub>(B<sub>g</sub>), ν<sub>3</sub>(E<sub>g</sub>), ν<sub>4</sub>(E<sub>g</sub>, B<sub>g</sub>) and ν<sub>2</sub>(A<sub>g</sub>, B<sub>g</sub>) vibrations at 865, 824, 760, 397 and 307 cm<sup>-1</sup>, respectively. The rotation and translation modes of [MoO<sub>4</sub>]<sup>2-</sup> were localized at 191, 154 and 133 cm<sup>-1</sup>. The well-resolved sharp peaks for the CdMoO<sub>4</sub> particles indicate that the synthesized particles are highly crystallized.

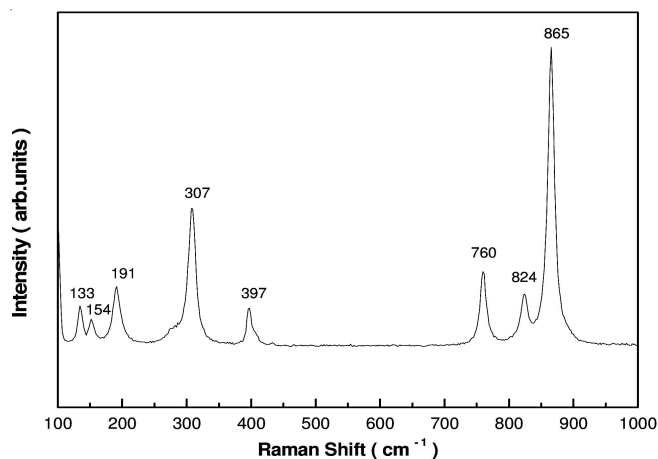


Fig. 5. Raman spectra of the CdMoO<sub>4</sub> particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

## Conclusion

Cadmium molybdate (CdMoO<sub>4</sub>) particles were well crystallized by a solid-state metathetic method with microwave irradiation, showing a fine and homogeneous morphology with sizes of 0.5-1.0 μm. The stretching vibration of FTIR was detected as a strong Mo-O stretch in the [MoO<sub>4</sub>]<sup>2-</sup> tetrahedrons at 895-743 cm<sup>-1</sup> and additional weak peaks of the Mo-O bending mode around 500 cm<sup>-1</sup>. With excitation at 250 nm, CdMoO<sub>4</sub> particles exhibit photoluminescence emission in the blue wavelength range of 380-400 nm. The neighbored shoulder at 430

nm and the sloped shoulders at 490, 520, 530 and 540 nm could be interpreted by the existence of defect structures. The internal Raman mode for the CdMoO<sub>4</sub> particles was detected at 865, 824, 760, 397 and 307 cm<sup>-1</sup>, respectively. The rotation and transition modes of [MoO<sub>4</sub>]<sup>2-</sup> were localized at 191, 154 and 133 cm<sup>-1</sup>. The well-resolved sharp peaks for the CdMoO<sub>4</sub> 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

- H. Liu and L. Tan, *Ionics*, **16**, 57 (2010).
- W.S. Wang, L. Zhen, C.Y. Xu and W.Z. Shao, *Cryst. Growth Des.*, **9**, 1558 (2009).
- X. Jiang, J. Ma, B. Liu, Y. Ren, J. Liu, X. Zhu and J. Tao, *J. Am. Ceram. Soc.*, **90**, 977 (2007).
- A. Phuruangrat, T. Thongtem and S. Thongtem, *J. Phys. Chem. Solids*, **70**, 955 (2009).
- X. Wu, J. Du, H. Li, M. Zhang, B. Xi, H. Fan, Y. Zhu and Y. Qian, *J. Solid State Chem.*, **180**, 3288 (2007).
- L. Zhen, W.S. Wang, C.Y. Xu, W.Z. Shao, M.M. Ye and Z.L. Chen, *Scripta Mater.*, **58**, 461 (2008).
- R. Sundaram and K.S. Nagaraja, *Sens. Actuators B*, **101**, 353 (2004).
- M. Daturi, L. Savary, G. Costentin and J.-C. Lavalley, *Catal. Today*, **61**, 231 (2000).
- A. Phuruangrat, N. Ekthammathat, T. Thongtem and S. Thongtem, *J. Phys. Chem. Sol.*, **72**, 176 (2011).
- A. Kotlov, L. Joenson, H. Kras, V. Mikhailik, V. Nagirnyi, G. Svensson and B.I. Zadneprovski, *Radiat. Measur.*, **42**, 767 (2007).
- Q. Gong, G. Li, X. Qian, H. Cao, W. Du and X. Ma, *J. Colloid. Interf. Sci.*, **304**, 408 (2006).
- E. Tomaszewicz, S.M. Kacmarek and H. Fuk, *Mater. Chem. Phys.*, **122**, 595 (2010).
- 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, T.N. Karthik and V. Manivannan, *J. Alloys Compd.*, **465**, 380 (2008).
- V. Thangadurai, C. Knittlmayer and W. Weppner, *Mater. Sci. Eng. B*, **106**, 228 (2004).
- G. Zhang, R. Jia and Q. Wu, *Mater. Sci. Eng. B*, **128**, 254 (2006).
- J.H. Ryu, B.G. Choi, S.H. Kim, J.W. Yoon, C.S. Lim and K.B. Shim, *J. Mater. Sci. Lett.*, **40**, 4979 (2005).
- 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).
- J.V. Tol and J.H. Van der Waals, *Mol. Phys.*, **88**, 803 (1996).
- Y. Toyozawa, M. Inoue, *J. Phys. Soc. Jpn.*, **21**, 1663 (1966).
- K. Polak, M. Nikl, K. Nitsch, M. Kobayashi, M. Ishii, Y. Usuki and O. Jarolimek, *J. Lumun.*, **72-74**, 781 (1997).
- A. Kuzmin and J. Purans, *Radiat. Measur.*, **33**, 583 (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).