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Microwave-Assisted Metathetic Synthesis of MWO_4 (M = Zn, Co) Particles†

C.S. Lim

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

Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

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Solid-state metathetic approach assisted microwave energy has been successfully applied to the synthesis of wolframite-type monoclinic MWO_4 (M = Zn, Co) particles. Well crystalline phases of MWO_4 (M = Zn, Co) particles were synthesized where the characteristics of solid-state metathetic reaction and the formation of high lattice energy by-product NaCl drives the reaction toward completion. Single phases of $ZnWO_4$ and $CoWO_4$ particles were formed completely at 600 ºC for 3 h.

Key Words: Solid-state metathetic, Synthesis, $ZnWO_4$, $CoWO_4$, Microwave irradiation.

INTRODUCTION

Metal tungstates 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. The main difference between the above two structures is that every tungeston atom is surrounded by four O atoms in a scheelite-type structure, whereas six O atoms surround every tungeston atom in MWO_4 tungstate crystallizing in the wolframite-type structure. Metal tungestates (MWO_4) (M = Zn, Co) are a technologically important material with a monoclinic wolframite-type[1]. The presence of two non-equivalent oxygen atoms is responsible for three pairs of M-O and W-O bonds with different lengths. Therefore, both M (M = Zn, Co) and W atoms are surrounded by six oxygen atoms, forming distorted octahedral coordination.

In recent years, $ZnWO_4$ and $CoWO_4$ have attracted considerable attention for potential applications as a scintillator, microwave devices, luminescent material and photocatalyst[2-7]. The physical, chemical and photochemical properties of MWO_4 (M = Zn, Co) are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of MWO_4 (M = Zn, Co). MWO_4 (M = Zn, Co) are prepared by a range of processes, such as solid-state reactions[8], a co-precipitation method[9], from a molten salt[10], by combustion[11], a mechano-chemical method[12], a sol-gel method[13], from a hydrothermal reaction[14-16], by citrate combustion[17], solvothermal method[18] and metathetic approach[19-21].

Microwave irradiation[17-21], as a heating method, has a number of applications in chemistry and ceramic processing. Compared with the usual method, microwave synthesis has the advantages of a very short reaction time, small particle size, narrow particle size distribution and high purity method for preparing polycrystalline samples. Among these methods, the 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 long diffusion paths, impurities and agglomeration, which result in products with improved homogeneity.

Wet chemical methods have disadvantages, such as complicated synthetic steps, use of expensive equipment, high synthetic temperature and long sintering times. On the other hand, the solid-state reaction requires complex apparatus and techniques, which are becoming gradually unpopular due to excessive energy consumption. However, solid-state synthesis of materials by the metathetic route is a simple method of synthesis, cost-effective, high yield and easy scale up and is emerging as a viable alternative approach for synthesizing high-quality novel inorganic materials in a short time. The solid state metathetic approach assisted by microwave irradiation has been applied successfully to the synthesis of metal tungstate of wolframite-type MWO_4 (M = Zn, Mn, Ni) and scheelite-type MWO_4 (M = Ca, Sr, Ba)[19]. MWO_4 (M = Zn, Co) particles are expected to have excellent characteristics for a wide range of applications, such as sensors, photocatalysts, luminescence and optical effects in the UV and visible region.

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In this study, MWO_4 (M = Zn, Co) particles were synthesized using a solid-state metathetic (SSM) method with microwave irradiation. The characteristics of the solid-state metathetic reaction and the formation of a high lattice energy by-product NaCl were discussed. The MWO_4 (M = Zn, Co) particles were synthesized from mixed metathetic precursors at moderate temperatures. The crystallization process, thermal decomposition and morphology of the MWO_4 (M = Zn, Co) particles were evaluated.

EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of MWO_4 (M = Zn, Co) particles from the solid-state metathetic method using microwave irradiation. $ZnCl_2$, $CoCl_2·6H_2O$ and $Na_2WO_4·2H_2O$ were used to prepare the metal tungstate compound. The preparation of MWO_4 (M = Zn, Co) particles was carried out by reacting a well-ground mixture of $ZnCl_2$, $CoCl_2·6H_2O$ and $Na_2WO_4·2H_2O$ at a molar ratio of 1:1. The sample mixtures were dried at 100 ºC for 12 h and the samples were placed into crucibles and exposed to domestic microwave (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 10 min. 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 ºC in an oven. Heat-treatment of the samples was performed at 600 ºC for 3 h.

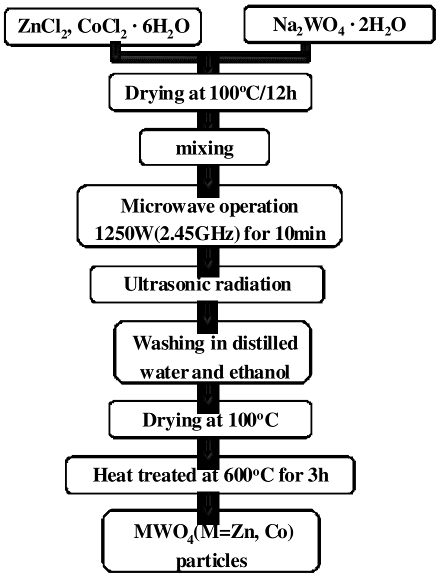


Fig. 1. Flow chart for the synthesis of MWO_4 (M = Zn, Co) particles from the SSM method using microwave irradiation

The existing phase in the powders after heat-treatment was examined by powder X-ray diffraction (XRD, CuK_α, 40 kV, 30 mA, Rigaku, Japan) at a scan rate of 3 °/min. Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used to examine the thermal decomposition behaviour of the metathetic reaction and heat-treated powders over frequency range, 4000-400 cm^{-1}. The FT-IR spectra were measured in KBr pellets. The microstructure and surface morphology of the nanocrystalline powders were observed by scanning electron microscopy (SEM, JSM-35CF, JEOL) and energy-dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the $ZnWO_4$ particles heat-treated at 600 ºC for 3 h. The XRD patterns are indexed on basis of the crystallographic data of the structure of $ZnWO_4$ (JCPDS code 15-0774). The major peak intensities were higher and confirmed that the phases were wolframite $ZnWO_4$. Fig. 3 shows XRD patterns of the $CoWO_4$ particles heat-treated at 600 ºC for 3 h. The XRD patterns are indexed on basis of the crystallographic data of the structure of $CoWO_4$ (JCPDS code 15-0867). The major peak intensities were higher and confirmed that the phases were wolframite $CoWO_4$. The formations of $ZnWO_4$ and $CoWO_4$ crystalline phases were needed to heat at 600 ºC for 3 h. The tungstates follow a wolframite monoclinic crystal structure. Their lattice parameters as follows: a = 4.692 Å, b = 5.721 Å, c = 4.928 Å and β = 90.6° for $ZnWO_4$ and a = 4.670 Å, b = 5.687 Å, c = 4.951 Å and β = 90.0° for $CoWO_4$. It indicates that the solid-state metathetic synthesis is adequate for the growth of $ZnWO_4$ and $CoWO_4$ crystallites.

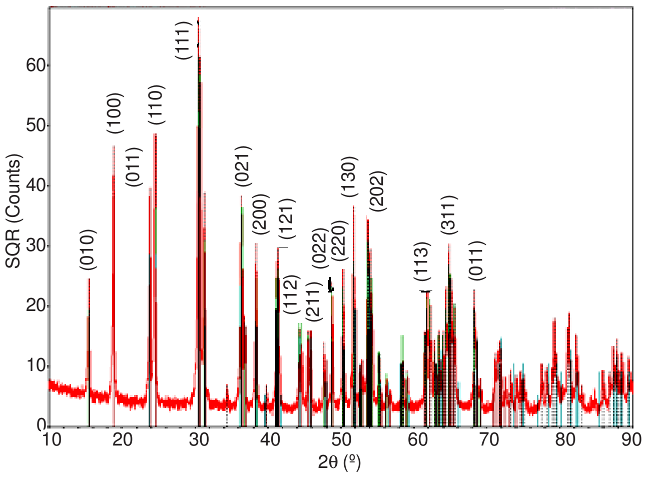


Fig. 2. XRD patterns of the $ZnWO_4$ particles heat-treated at 600 ºC for 3 h

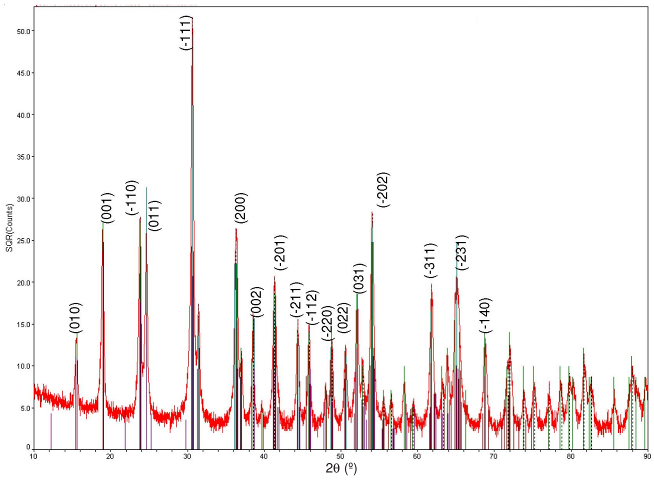


Fig. 3. XRD patterns of the $CoWO_4$ particles heat-treated at 600 ºC for 3 h

Fig. 4 shows FT-IR spectra of the $ZnWO_4$ particles after (a) microwave metathetic reaction ($ZnWO_4$-m) and (b) heat-treated at 600 ºC for 3 h ($ZnWO_4$-m 600). The absorption bands at 532 cm^{-1} can be assigned to symmetric and asymmetric

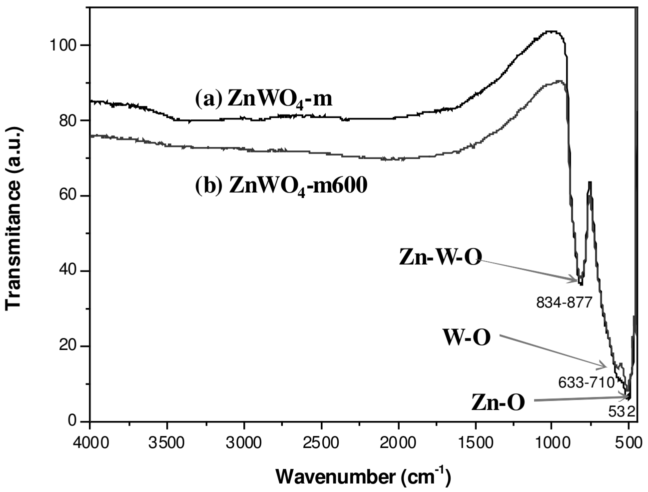


Fig. 4. FT-IR spectra of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600 ºC for 3 h

deformation mode of Zn-O in ZnO_6 octahedra. The absorption bands with their maxima at 633 and 710 cm^{-1} can be due to the stretching modes of W-O in WO_6 octahedra. The bands at 834 and 877 cm^{-1} were due to symmetrical vibrations of bridge oxygen atoms of the Zn-O-W groups. These vibrations could be identified to the synthesized $ZnWO_4$.

Fig. 5 shows FT-IR spectra of the $CoWO_4$ particles after (a) microwave metathetic reaction ($CoWO_4$-m) and (b) heat-treated at 600 ºC for 3 h ($CoWO_4$-m 600). The absorption bands at 532 cm^{-1} can be assigned to symmetric and asymmetric deformation mode of Co-O in CoO_6 octahedra. The absorption bands with their maxima at 633 and 710 cm^{-1} can be due to the stretching modes of W-O in WO_6 octahedra. The bands at 834 and 877 cm^{-1} were due to symmetrical vibrations of bridge oxygen atoms of the Co-O-W groups. These vibrations could be identified to the synthesized $CoWO_4$. The band at 1630 cm^{-1} [Fig. 5(a)] in $CoWO_4$-m are assigned to the HOH bending vibrations. It is assumed that the samples prepared contain a significant amount of surface-adsorbed water and alcohol. Obviously, the bands at 1630 cm^{-1} disappeared after heat-treated at 600 ºC for 3 h in Fig.5(b) $CoWO_4$-m600.

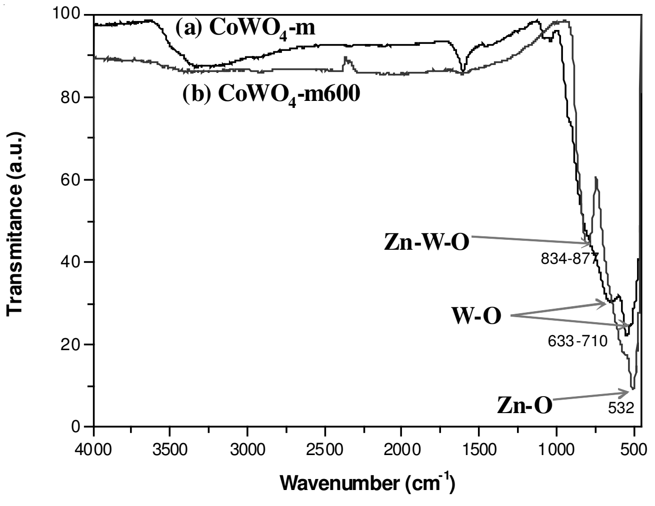


Fig. 5. FT-IR spectra of the $CoWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600 ºC for 3 h

Fig. 6 shows SEM images of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600 ºC for 3 h and the $CoWO_4$ particles after (c) microwave metathetic reaction and (d) heat-treated at 600 ºC for 3 h. Fig. 6(a) shows a SEM image of the $ZnWO_4$ synthesized by a SSM reaction showing relatively exaggerated growth including rectangular elongated NaCl in the distributed $ZnWO_4$ powders, which was co-produced with high lattice energy. Parhi *et al.*[19] reported the microwave metathetic synthesis of various metal tungstates and showed that microwave radiation provided the energy required to overcome the energy barrier that precludes a spontaneous reaction and helped heat the bulk of the material uniformly, resulting in fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste.

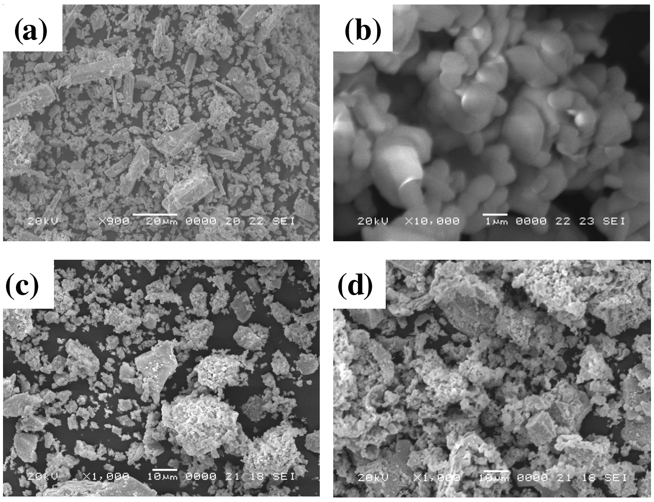


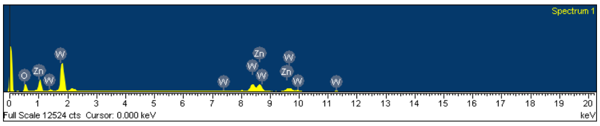
Fig. 6. SEM images of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600 ºC for 3 h and the $CoWO_4$ particles after (c) microwave metathetic reaction and (d) heat-treated at 600 ºC for 3 h

Solid state metathesis reactions, such as $ACl_2 + Na_2WO_4 \rightarrow AWO_4 + 2NaCl$, involves the exchange of atomic/ionic species, where the driving force is the formation of thermodynamically stable alkali or alkaline earth halides with high lattice energy. The thermodynamic basis for such metathetic reactions has been reported. Parhi *et al.*[19] calculated the enthalpy (ΔH) and free energy change (ΔG) associated with the formation of tungstates and reported ΔH = -36.17 KJ/mol for $ZnWO_4$ showing that both the enthalpy change favours the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products, usually raising the alkali halide near or above its normal boiling point and have been recognized to be approximately adiabatic in nature.

The samples were washed with distilled water and ethanol to dissolve the NaCl. Fig. 6(b) shows a SEM image of the $ZnWO_4$ heat-treated at 600 ºC for 3 h after removing the NaCl. Zinc tungstate crystallizes in the wolframite crystal structure. The presence of sodium chloride confirmed that the reaction had proceeded in a solid-state metathesis manner. Fig. 6(c) and (d) show the $CoWO_4$ particles after microwave metathetic reaction and heat-treated at 600 ºC for 3 h. The particles at 600 ºC in Fig. 6(d) show well crystallized monoclinic-like crystals of $CoWO_4$.

Fig. 7 shows EDS patterns (a), quantitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized $ZnWO_4$ particles. The $ZnWO_4$ particles are well defined in EDS patterns, quantitative compositions and quantitative result in Fig. 7. For tungstate materials to be used for practical applications, versatile characteristics are required for the particle size distribution and morphology of the particles. The well-defined particle features of the $ZnWO_4$ synthesized by SSM reactions have control over the morphology of the final particles and can be used for such technological applications. Fig. 8 shows EDS patterns (a), quantitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized $CoWO_4$ particles. The $CoWO_4$ particles are also well defined in EDS patterns, quantitative compositions and quantitative result in Fig. 8. Owing to the enthalpy change by the driving force for the metathetic formation of NaCl. The SSM reactions affect not only the morphology of the MWO_4 (M = Zn, Co) particles, but also the formation of crystalline. Therefore, a variation of metathetic reactions of $MCl_2 + Na_2WO_4 \rightarrow MWO_4 + 2NaCl$ is required to control the well-defined particle features of the MWO_4 (M = Zn, Co) particles.

(a)



(b)

Spectrum	In stats.	O	Zn	W	Total
Spectrum 1	Yes	17.69	31.74	50.57	100.00
Mean		17.69	31.74	50.57	100.00
Std. deviation		0.00	0.00	0.00	
Max.		17.69	31.74	50.57	
Min.		17.69	31.74	50.57	

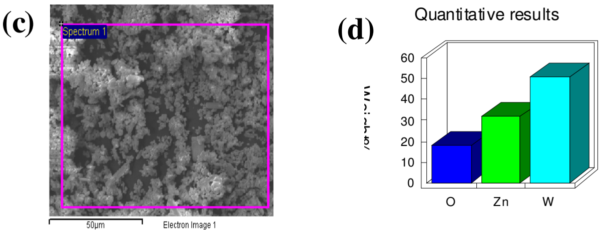
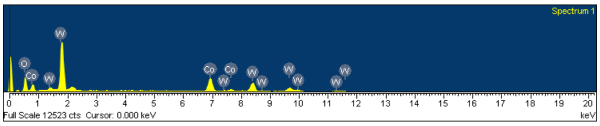


Fig. 7. EDS patterns (a), quantitative compositions (b), a SEM image and quantitative results of the synthesized $ZnWO_4$ particles

(a)



(b)

Spectrum	In stats.	O	Co	W	Total
Spectrum1	Yes	22.11	22.55	55.34	100.00
Mean		22.11	22.55	55.34	100.00
Std.deviation		0.00	0.00	0.00	
Max.		22.11	22.55	55.34	
Min.		22.11	22.55	55.34	

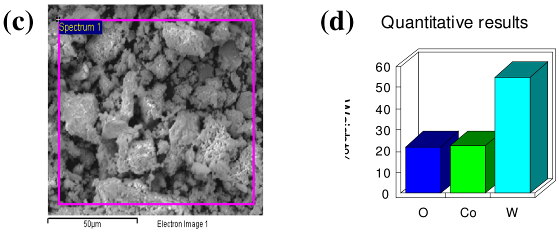


Fig. 8. EDS patterns (a), quantitative compositions (b), a SEM image and quantitative results of the synthesized $CoWO_4$ particles

Conclusion

MWO_4 (M = Zn, Co) particles were synthesized using solid-state metathetic method with microwave irradiation. The MWO_4 (M = Zn, Co) particles were completed entirely at 600 ºC. Well crystalline phases of MWO_4 (M = Zn, Co) particles were synthesized where the characteristics of SSM reaction and the formation of high lattice energy by-product NaCl drives the reaction toward completion. Solid-state metatheticreactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products. The metathetic route for the MWO_4 (M = Zn, Co) particles is a simple method of synthesis, cost-effective, high yield and easy scale up and is emerging as a viable alternative approach for synthesizing high-quality novel inorganic materials in a short time.

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