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Solid-state metathetic synthesis of MWO_4 (M=Zn, Co) particles assisted by microwave irradiation

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Abstract Metathetic route for the MWO_4 (M=Zn, Co) particles is a simple method of synthesis and a viable alternative method in a short time. MWO_4 (M=Zn, Co) particles were synthesized using solid-state metathetic (SSM) method with microwave irradiation. The MWO_4 (M=Zn, Co) particles were formed completely at 600°C for 3 h. The crystallization process, thermal decomposition and morphology of the MWO_4(M= Zn, Co) particles were evaluated. The characteristics of the SSM reaction and the formation of a high lattice energy by-product NaCl were discussed.

Key words Solid-state metathetic (SSM) synthesis, $ZnWO_4$, $CoWO_4$, Microwave irradiation

1. 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) favor the formation of a wolframite-type monoclinic structure. The main difference between the above two structures is that every W atom is surrounded by four O atoms in a scheelite-type structure, whereas six O atoms surround every W atom in MWO_4 tungstate crystallizing in the wolframite-type structure. 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], co-precipitation [9], molten salt [10], combustion [11], mechano-chemical [12] sol-gel [13], hydrothermal reaction [14-16], citrate combustion [17], solvothermal [18], and metathetic approach [19-21].

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.

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 SSM 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.

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2. Experimental

$ZnCl_2$, $CoCl_2 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ 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 $ZnCl_2$, $CoCl_2 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ at a molar ratio of 1 : 1. The sample mixtures were dried at 100°C 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°C in an oven. Heat-treatment of the samples was performed at 600°C for 3 h.

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 behavior of the metathetic reaction and heat-treated powders over frequency range, 400 to 4000 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).

3. Results and Discussion

Fig. 1 shows XRD patterns of the $ZnWO_4$ particles heat-treated at 600°C 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. 2 shows XRD patterns of the $CoWO_4$ particles heat-treated at 600°C 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°C 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 ade-

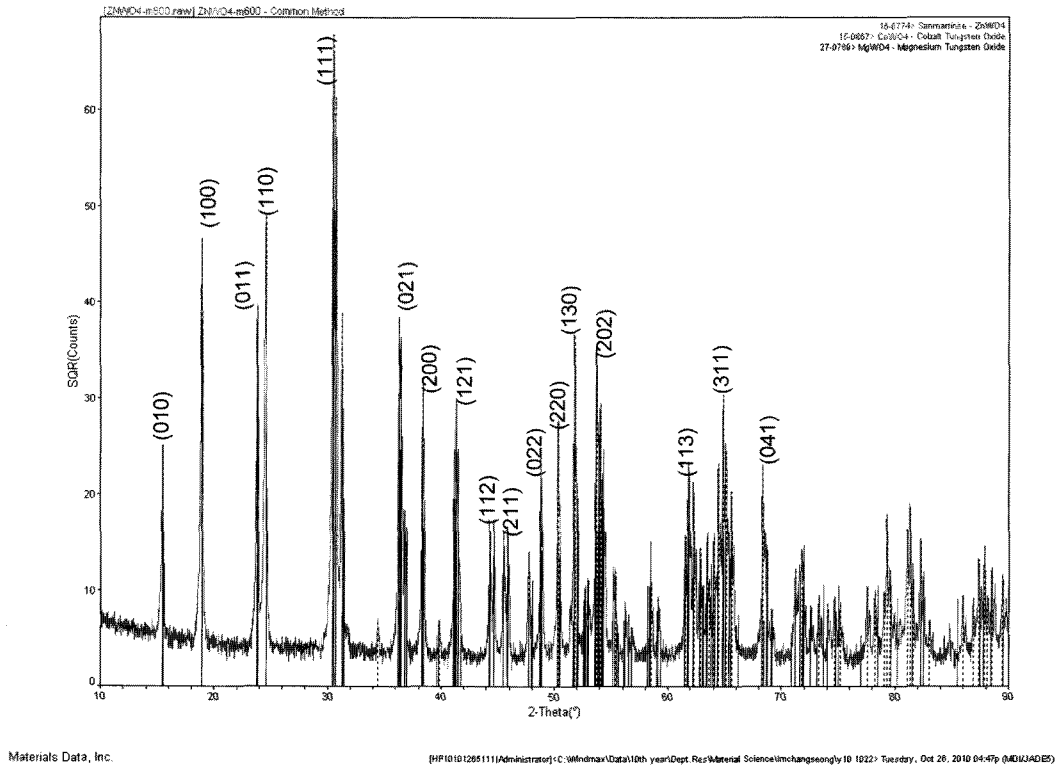

Fig. 1. XRD patterns of the $ZnWO_4$ particles heat-treated at 600°C for 3 h.

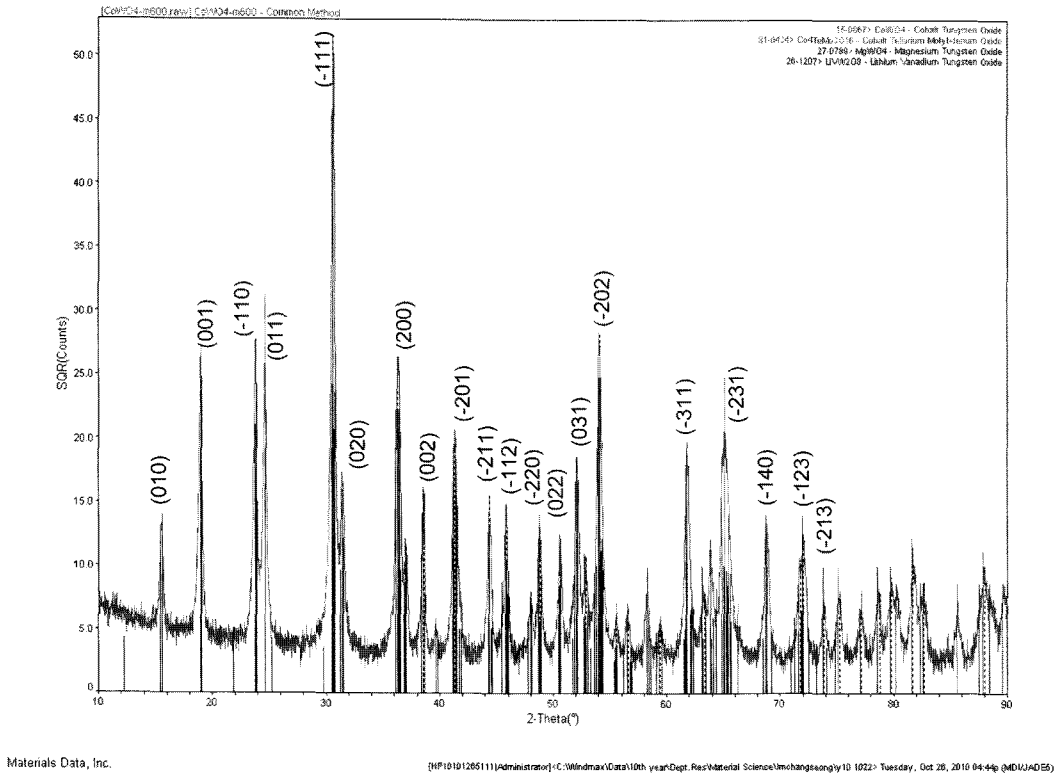

Fig. 2. XRD patterns of the $CoWO_4$ particles heat-treated at 600°C for 3 h.

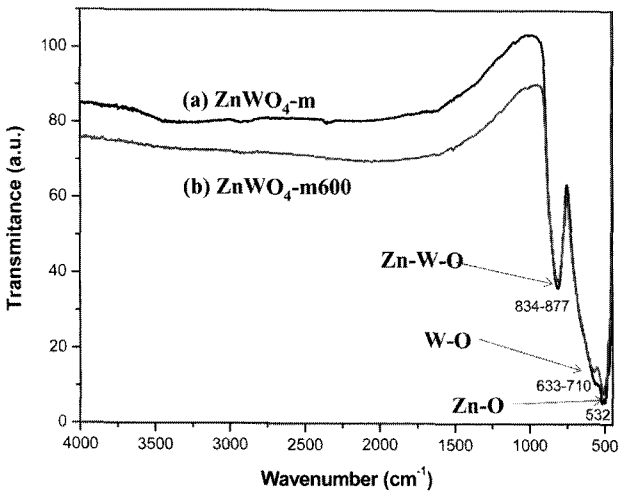

Fig. 3. FT-IR spectra of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600°C for 3 h.

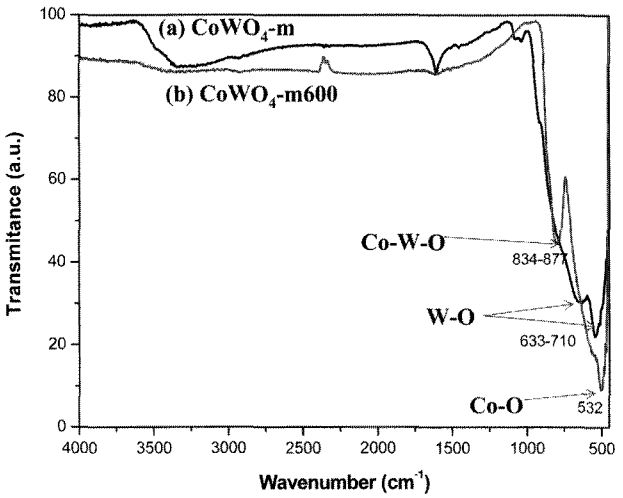

Fig. 4. FT-IR spectra of the $CoWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600°C for 3 h.

quate for the growth of $ZnWO_4$ and $CoWO_4$ crystallites.

Fig. 3 shows FT-IR spectra of the $ZnWO_4$ particles after (a) microwave metathetic reaction ($ZnWO_4$-m) and (b) heat-treated at 600°C for 3 h ($ZnWO_4$-m600). The absorption bands at 532 cm^{-1} can be assigned to symmetric and asymmetric 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. 4 shows FT-IR spectra of the $CoWO_4$ particles after (a) microwave metathetic reaction ($CoWO_4$-m) and (b) heat-treated at 600°C for 3 h ($CoWO_4$-m600). The absorption bands near 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

633~710 cm^{-1} can be due to the stretching modes of W-O in WO_6 octahedra. The bands at 834~877 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 absorption bands of the $CoWO_4$ near 532, 633~710, 834~877 cm^{-1} are similar with the band of $ZnWO_4$ particles, because the symmetrical vibrations of M-O in MnO_6 octahedra, W-O in WO_6 octahedra and M-O-W groups are similar by accompanying the wolframite crystallographic lattice parameters. The band at 1630 cm^{-1} can in Fig. 4(a) $CoWO_4$-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°C for 3 h in Fig. 4(b) $CoWO_4$-m600. In the case of $ZnWO_4$, the reason why the band at ~1630 cm^{-1} in Fig. 4(a) are not assigned is attributed that the amounts of surface-adsorbed water and alcohol were not incorporated during drying process.

Fig. 5 shows SEM images of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600°C for 3 h, and the $CoWO_4$ particles after (c) microwave metathetic reaction and (d) heat-treated at 600°C for 3 h. Fig. 5(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

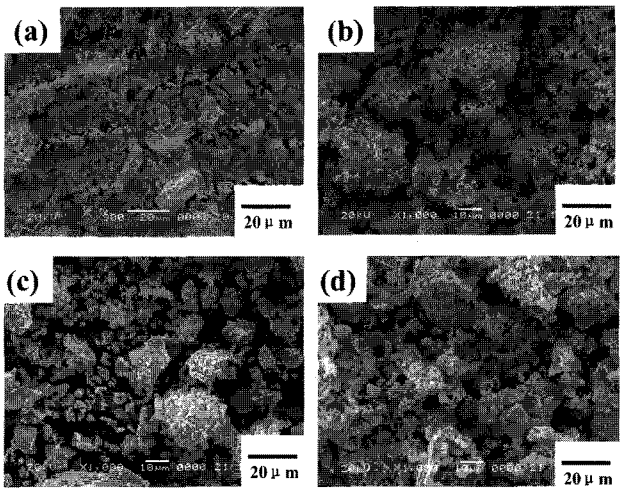

Fig. 5. SEM images of the $ZnWO_4$ particles after (a) microwave metathetic reaction and (b) heat-treated at 600°C for 3 h, and the $CoWO_4$ particles after (c) microwave metathetic reaction and (d) heat-treated at 600°C for 3 h.

the product in a green manner without the generation of solvent waste.

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 $\Delta H = -36.17$ KJ/mol for $ZnWO_4$ showing that both the enthalpy change favors the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. SSM 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 boil-

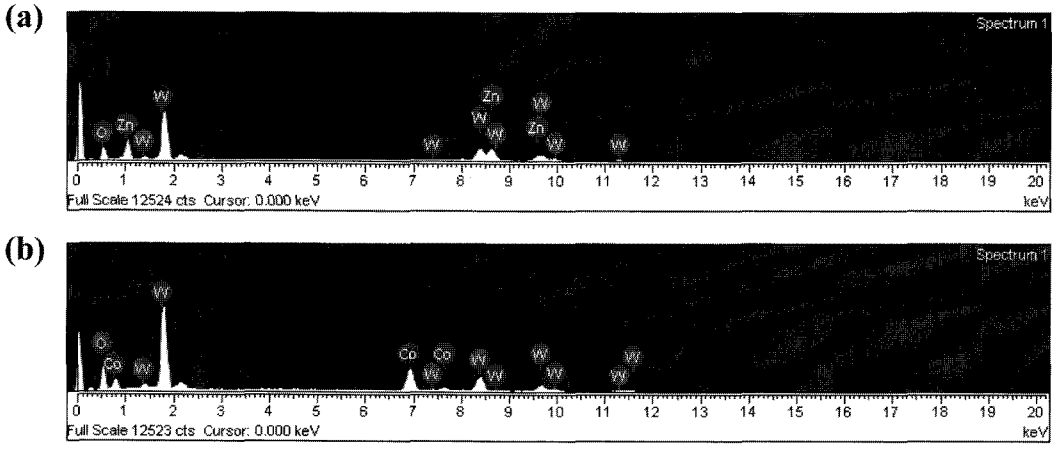

Fig. 6. EDS patterns of the synthesized $ZnWO_4$ particles (a) and of the synthesized $CoWO_4$ particles (b).

ing 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. 5(b) shows a SEM image of the $ZnWO_4$ heat-treated at 600°C 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. 5(c) and (d) show the $CoWO_4$ particles after microwave metathetic reaction and heat-treated at 600°C for 3 h. The particles at 600°C in Fig. 5(d) show well crystallized monoclinic-like crystals of $CoWO_4$.

Fig. 6 shows EDS patterns of the synthesized $ZnWO_4$ particles (a) and of the synthesized $CoWO_4$ particles (b). The $ZnWO_4$ and $CoWO_4$ particles are well defined in qualitative compositions of the synthesized $ZnWO_4$ and $CoWO_4$ particles in Table 1 and Table 2. 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 $ZnWO_4$ and $CoWO_4$ synthesized by SSM reactions have control over the morphology of the final particles, and can be used for such technological applications. 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.

Table 1
Qualitative compositions of the synthesized $ZnWO_4$ particles

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	

Table 2
Qualitative compositions of the synthesized $CoWO_4$ particles

Spectrum	In stats.	O	Co	W	Total
Spectrum 1	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	

4. Conclusions

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°C. 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. SSM reactions 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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