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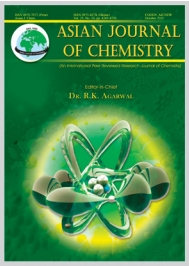

Microwave-Assisted Synthesis of Ag Incorporated $MgWO_4$ Composites by Solid-State Metathetic Approach

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A solid-state metathetic (SSM) route assisted by microwave irradiation was used to synthesize the Ag incorporated $MgWO_4$ composites in 10 min under environmentally friendly conditions. The crystallized Ag incorporated $MgWO_4$ composites were formed at 600 ºC for 3 h, showing a fine and homogeneous morphology with sizes of 0.5-1 μm. The synthesized Ag incorporated $MgWO_4$ composites were characterized by scanning electron microscopy, energy-dispersed X-ray spectroscopy and Fourier transform infrared spectroscopy. The optical properties were investigated by photoluminescence emission and Raman spectroscopy.

Key Words: Ag-$MgWO_4$, Microwave-assisted, Solid-state metathetic, Synthesis, Luminescence, Raman spectroscopy.

INTRODUCTION

Metal tungstates have attracted considerable attention for potential applications in photoluminescence, scintillator, photocatalyst and humidity sensors[1-3]. 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 metal tungstates prepared by a range of processes, such as co-precipitation[4,5], solvothermal method[6-8], spray pyrolysis[9], reverse micelle system[10,11], solution synthesis[12], sol-gel[13], mechano-chemical method[14], molten salt method[15,16], hydrothermal method[17-19], microwave-assisted synthesis[20-24] and solid-state metathetic reaction[25,26]. Wet chemical methods have disadvantages, such as complicated synthetic steps, use of expensive equipment, high synthetic temperatures and long sintering times. On the other hand, solid-state reactions require complex apparatus and techniques, which are becoming gradually unpopular due to the excessive energy consumption.

Compared with the usual methods, 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. 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[23,24]. 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 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.

Silver-incorporated $MgWO_4$ composites are expected to have excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for a wide range of applications, such as sensors, photocatalysts, luminescence, antibacterial matrices and optical effects in the UV and visible region. However, the study of microwave-assisted synthesis of Ag incorporated $MgWO_4$ composites by solid-state metathetic (SSM) reaction has not been published previously. Therefore, the precise nature of the optical properties and microwave metathetic synthesis of Ag incorporated $MgWO_4$ composites is required for a wide range of applications. In this study, Ag incorporated $MgWO_4$ composites were synthesized using a solid-state metathetic (SSM) method with microwave irradiation. The characteristics of the solid-state metathetic reaction of Ag incorporated $MgWO_4$ composites are discussed in detail based on the formation of a high lattice energy by-product of NaCl. The synthesized Ag incorporated $MgWO_4$ composites were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). The optical properties were examined by photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

$MgCl_2 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ of analytic reagent grade were used to prepare the $MgWO_4$ compound. The preparation of $MgWO_4$ was carried out by reacting well-ground mixtures of $MgCl_2 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ at a molar ratio of 1:1. The sample mixtures were dried at 100 ºC for 12 h and 5 wt % $AgNO_3$ was then added for the composition of Ag incorporated $MgWO_4$. The sample mixtures were 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 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 was performed at 600 ºC for 3 h.

The microstructure and surface morphology of the synthesized Ag incorporated $MgWO_4$ composites were observed by SEM (JSM-35CF, JEOL) and energy-dispersive X-ray spectroscopy (EDS). FTIR (Model IR 550, Magna, Nicolet Company) was used to examine the thermal-decomposition behaviour of the metathetic reaction and heat-treated Ag incorporated $MgWO_4$ composites over the frequency range, 400 to 4000 cm^{-1}. The photoluminescence spectra were recorded using a Hitachi 850 Spectrophotometer (Japan) 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 excitation source, the power was kept at 0.5 mW on sample.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of the Ag incorporated $MgWO_4$ composites after microwave metathetic reation and heat-treatment at 600 ºC for 3 h. The sample mixtures were synthesized by microwave-assisted solid-state metathetic reaction, treated with ultrasonic radiation, washed many times and heat-treated at 600 ºC for 3 h. The microwave metathetic synthesis resulted in the homogeneous morphology with sizes of 0.5-1 μm. The spherical small particles of silver were well immobilized in the $MgWO_4$ matrix. The Ag incorporated $MgWO_4$ composites were well synthesized in a green manner without the generation of solvent waste, because the microwave radiation provided the energy required 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 solid state metathesis reaction, such as $MgCl_2 + Na_2WO_4 \rightarrow MgWO_4 + 2NaCl$, involves the exchange of atomic/ionic species, where the driving force is the formation of a thermodynamically stable alkali or alkaline earth halide with high lattice energy[23,24]. The enthalpy change favours the metathesis reaction and is the driving force accompanying the formation of NaCl[25,26]. 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 the Ag incorporated $MgWO_4$ composites, which were obtained in the form of loosely connected micron sized particles at considerably lower temperatures than those usually employed for their synthesis. For the Ag incorporated $MgWO_4$ composites 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 Ag incorporated $MgWO_4$ composites 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 shows EDS patterns (a), qualitative compositions (b), a SEM image (c) and qualitative results (d) of the synthesized Ag incorporated $MgWO_4$ composites. The EDS patterns and qualitative compositions in Fig. 2a and b) could be assigned to the Ag incorporated $MgWO_4$ composites. This means that the Ag incorporated $MgWO_4$ composites can be successfully synthesized using this solid-state metathetic reaction assisted by microwave irradiation. The crystals of $MgWO_4$ were primarily co-mixed with Ag particles. The qualitative results of the morphology in Fig. 2c and d, were composed of Ag and $MgWO_4$.

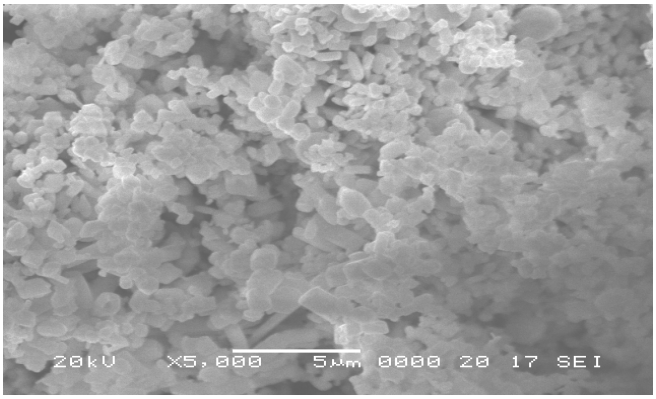
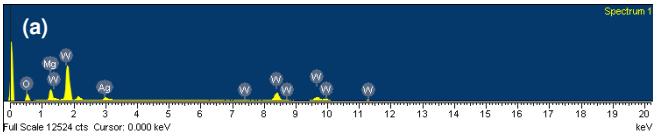


Fig. 1. A SEM image of the Ag incorporated $MgWO_4$ composites after microwave metathetic reaction and heat-treatment at 600 ºC for 3 h



Spectrum	In stats.	O	Mg	Ag	W	Total
Spectrum 1	Yes	24.61	7.27	7.99	60.13	100.00
Spectrum 2	Yes	22.96	7.59	4.64	64.80	100.00
Spectrum 3	Yes	20.65	7.39	4.93	67.03	100.00
Spectrum 4	Yes	21.08	6.69	5.17	67.06	100.00
Mean		22.33	7.23	5.68	64.76	100.00
Std. deviation		1.82	0.39	1.55	3.26	
Max.		24.61	7.59	7.99	67.06	
Min.		20.65	6.69	4.64	60.13	

(b)

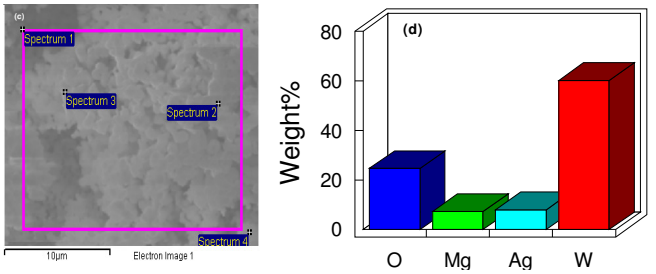


Fig. 2. EDS patterns (a), qualitative compositions (b), a SEM image (c) and qualitative results (d) of the synthesized Ag incorporated $MgWO_4$ composites

Fig. 3 shows FTIR spectra of the Ag incorporated $MgWO_4$ composites at the wavenumber range of 4000-480 cm^{-1}. The bending and stretching vibrations of Mg-O (532, 473 cm^{-1}), W-O (710-633 cm^{-1}) and Mg-O-W bond (877-834 cm^{-1}) could be identified to the synthesized $MgWO_4$. The stretching vibration was detected as a strong W-O stretch in the $[WO_4]^{2-}$ tetrahedrons at 710-633 cm^{-1}. The $[WO_4]^{2-}$ is constituted by four internal modes ($\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$ specified as an antisymmetric stretching vibration[22]. All modes are Raman active, but $\nu_3(F_2)$ and $\nu_4(F_2)$ are IR active.

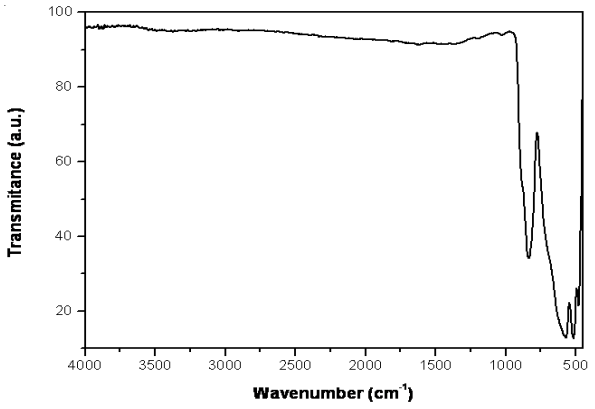


Fig. 3. FT-IR spectra of the Ag incorporated $MgWO_4$ composites

Fig. 4 presents room-temperature photoluminescence emission spectra of the Ag incorporated $MgWO_4$ composites by microwave metathetic synthesis and heat-treatment at 600 ºC for 3 h. It is generally assumed that the measured emission spectra of metal tungstates are mainly attributed to the charge-transfer transitions within the $[WO_4]^{2-}$ complex[27,28]. With excitation at 250 nm, the spectra show rugged peaks, which are composed of three kinds of groups. The first major peaks are located at the green wavelength of 480 nm, the left sloped shoulders at 425, 450 and 470 and the right sloped shoulders at 520, 530 and 540 nm. The emission spectra of 6 narrow neighbored sloped shoulders, namely the spread-eagle-shape are considered to form by defects structure[29]. 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[30]. Such emission peaks can be explained by the influence of the Jahn-Teller effect[31,32] on the degenerated excited state of $[WO_4]^{2-}$ tetrahedron.

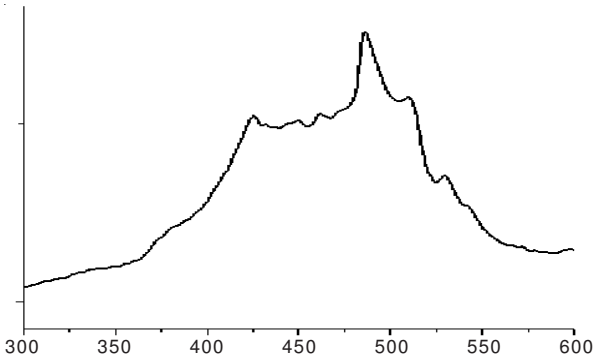


Fig. 4. Photoluminescence emission spectra of the Ag incorporated $MgWO_4$ composites exited at 250 nm at room temperature

Fig. 5 shows a schematic diagram of the crystal-field of the Jahn-Teller splitting effect and hybridization of the $[WO_4]^{2-}$ complex on the spread-eagle-shapes. The ground state of the system corresponds to the filling of all one-electron states below the band gap, resulting in a many-electron state of $^1A_1$ symmetry. The lowest exited states involve one hole in the t_1 (primarily O 2pπ) states and one electron in the e (primarily W4d) states, corresponding to the many electron states, $^1T_1$, $^3T_1$, $^1A_2$ and $^3A_2$. Of these states, only the $^1A_1 \rightarrow {}^1T_2$ transition is a dipole-allowed transition. However, it is the lower $^3T_1$ or $^3T_2$ states that account for the intrinsic luminescence by a spin-forbidden transition to the ground $^1A_1$ state in optically detected electron paramagnetic resonance experiments on metal tungstates[32]. Both $^1A_1 \rightarrow {}^1T_1$, $^1T_2$ and $^1A_1 \rightarrow {}^3T_1$, $^3T_2$ transitions, causing at room temperature a radiating transition from the triple levels $^3T_1$, $^3T_2 \rightarrow {}^1A_1$ at the lowest transition energy, were detected in the luminescent spectra[33]. The directions of the principal axes of the fine structure and tensors support the idea that the effect results from the combined action of the Jahn-Teller instability and the crystal field. The preliminary interpretation of the spectroscopic properties has been carried out on the basis of local atomic and electronic structure of tungsten ions in $MgWO_4$ crystals of scheelite and wolframite types[34].

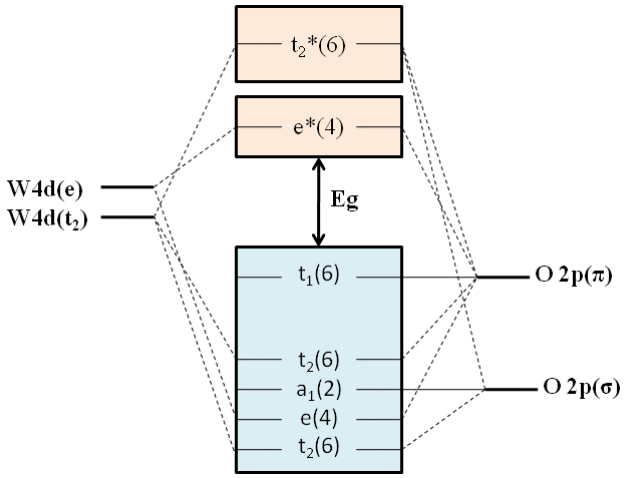


Fig. 5. Schematic diagram of the crystal-field of the Jahn-Teller splitting effect and hybridization of the $[WO_4]^{2-}$ complex on the spread-eagle-shapes

Fig. 6 shows Raman spectra of the Ag incorporated $MgWO_4$ composites excited 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on sample. The vibration modes in the Raman spectra of the Ag incorporated $MgWO_4$ composites are classified into two groups, internal and external[35,36]. The internal vibrations are related to the $[WO_4]^{2-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Sr^{2+} cation and rigid molecular units. The major internal Raman modes for the Ag incorporated $MgWO_4$ composites in Fig. 6 were detected at 920, 815, 712, 552, 422 and 354 cm^{-1}. The well-resolved sharp peaks for the Ag incorporated $MgWO_4$ composites indicate that the synthesized particles are highly crystallized. The free rotation mode was detected at 213 cm^{-1} and the external modes were localized at 187 and 156 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 $[WO_4]^{2-}$.

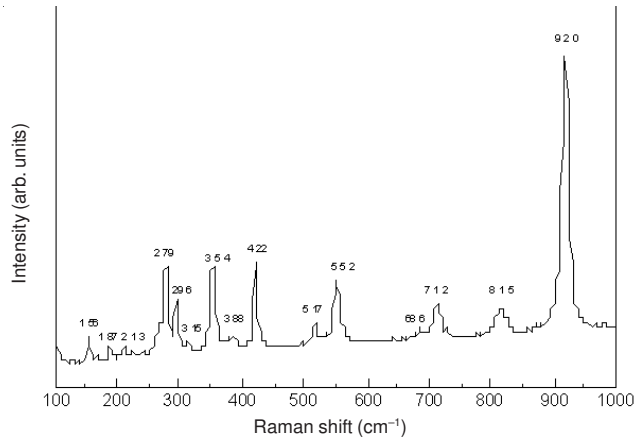


Fig. 6. Raman spectra of the Ag incorporated $MgWO_4$ composites excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on sample

Conclusion

The Ag incorporated $MgWO_4$ composites were successfully synthesized by the solid-state metathetic route with microwave irradiation, showing the well-defined morphology with sizes of 0.5-1 μm. The FTIR spectra of the Ag incorporated $MgWO_4$ were detected as a strong W-O stretch in the $[WO_4]^{2-}$ tetrahedrons at 710-633 cm^{-1}. With excitation at 250 nm, Ag incorporated $MgWO_4$ particles exhibit photoluminescence emission in the green wavelength range of 480 nm. The major internal Raman modes for the Ag incorporated $MgWO_4$ composites were detected at 920, 815, 712, 552, 422 and 354 cm^{-1}. The well-resolved sharp peaks for the Ag incorporated $MgWO_4$ composites indicate that the synthesized particles are highly crystallized. The free rotation mode was detected at 213 cm^{-1} and the external modes were localized at 187 and 156 cm^{-1}.

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