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A Facile Solvothermal Process to Synthesize $MSnO_3$ (M = Sr, Mg) Nanoparticles Assisted by Microwave Irradiation

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$MSnO_3$ (M = Sr, Mg) nanoparticles were synthesized successfully using a facile microwave solvothermal route followed by further heat-treatment. Well-crystallized $SrSnO_3$ and $MgSnO_3$ nanoparticles were formed after heat-treatment at 800 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 20-40 nm for $SrSnO_3$ and 50-200 nm for $MgSnO_3$. The synthesized $SrSnO_3$ and $MgSnO_3$ nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy.

Key Words: $SrSnO_3$, $MgSnO_3$, Nanoparticles, Microwave irradiation, Solvothermal process.

INTRODUCTION

Metal metastannates, with structures closely realated to the perovskite one, are of particular interest due to their unusual dielectric and semiconducting properties, leading to various applications such as thermally stable capacitors, ceramic dielectric bodies, gas and humidity sensors and battery electrode materials[1,2]. Cubic perovskite type of metal stannates ($MSnO_3$) have attracted considerable attention for potential applications. It has been observed that a partial substitution of cations at M/Sn sites results in substantial modification in their physical properties so as to make them suitable for a wide variety of industrial applications[3-5]. Metal metastannates have attracted considerable attention for potential applications in ceramic dielectric bodies, gas and humidity sensors, thermally stable capacitors and battery electrode materials[1-5].

Several processes have been developed over the past decade to enhance the applications of metal metastannates prepared by a range of processes, such as a solid-state reaction[6], a co-precipitation method[7], sol-gel[8], a combustion method[9], a precursor route[10,11], a microwave synthesis[12], a polymerized complex method[13], a molten salt synthesis[14], a pulsed laser deposition[15], a self-heat-sustained method[16,17]. The advantages of microwave synthesis are to bring a short reaction time, a small particle size and a narrow particle size distribution. Microwave energy 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 to the material through molecular interactions with an electromagnetic field[18]. Hydrothermal process is an efficient low temperature method that allows the formation of particles with high degree of crystallinity and easy dispersion in an aqueous medium. The use of microwave energy in hydrothermal system promotes the development of a rapid heating to the required temperature with rapid rates of crystallization[19,20].

The microwave solvothermal process is adjusted to heat the metal stannates uniformly resulting in fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste. Recently, microwave solvothermal processes have been reported the use of a facile and fast method in preparing nanocrystalline particles of metal tungstates with unique and enhanced properties[21,22]. When the solvent is ethylene glycol, the reactions proceed in a sealed pressure autoclave at temperatures above boiling point of the ethylene glycol. Microwave solvothermal process using a solvent of ethylene glycol is a facile process that provides a high-qualified yield with cost-effective method in short time periods.

In this study, $SrSnO_3$ and $MgSnO_3$ nanoparticles were synthesized using a facile solvothermal route assisted by the microwave irradiation. The characteristics of the synthesized $SrSnO_3$ and $MgSnO_3$ nanoparticles are discussed in detail based on the microwave solvothermal reaction in ethylene glycol under the high sealed pressure. The synthesized $SrSnO_3$ and $MgSnO_3$ nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy.

EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of $SrSnO_3$ and $MgSnO_3$ nanoparticles by the microwave solvothermal process. $SrCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $Na_2SnO_3 \cdot 3H_2O$ and ethylene glycol of analytical reagent grade (Aldrich) were used to prepare the of $SrSnO_3$ compound. Each of 0.01 mol $SrCl_2 \cdot 6H_2O$ and 0.01 mol $Na_2SnO_3 \cdot 3H_2O$ for $SrSnO_3$ was dissolved in 30 mL ethylene glycol. In the same way, each of 0.01 mol $MgCl_2 \cdot 6H_2O$ and 0.01 mol $Na_2SnO_3 \cdot 3H_2O$ for $MgSnO_3$ was dissolved in 30 mL ethylene glycol. The solutions were mixed and adjusted at a pH 9.5 using NaOH. The aqueous solution was stirred at room temperature. In the sequence, the mixture was transferred into a Teflon-lined digestion vessel of 120 mL capacity. The Teflon vessel was placed into a microwave solvothermal autoclave (2.45 GHz, maximum power of 800 W). The microwave solvothermal conditions were kept at 200 ºC for 0.5 h. After microwave solvothermal process, the microwave autoclave was cooled at room temperature. The resulting solutions were treated with ultrasonic radiation and washed many times with distilled hot water. The white precipitates were corrected and dried at 100 ºC in a dry oven. The final products were heat-treated at 800 ºC for 3 h.

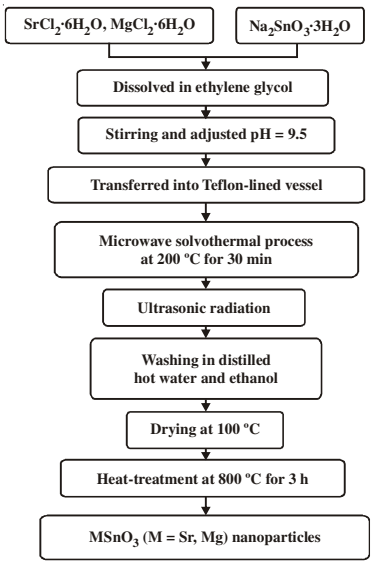

Fig. 1. Flow chart for the synthesis of $MSnO_3$ (M = Sr, Mg) nanoparticles by the microwave solvothermal process

The existing phases of the $SrSnO_3$ and $MgSnO_3$ particles after the microwave solvothermal process were identified by powder XRD (CuK_α, Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the absorption behaviour of the synthesized $SrSnO_3$ and $MgSnO_3$ particles over the frequency range, 400 to 4000 cm^{-1}. The microstructure, particle morphology and qualitative compositions of the $SrSnO_3$ and $MgSnO_3$ particles were observed by SEM (JSM-5600, JEOL, Japan) and TEM (JEM 2000-FX, 250 kV, Japan).

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the $SrSnO_3$ nanoparticles synthesized by the microwave solvothermal process after heat-treatment at 800 ºC for 3 h. All XRD peaks could be assigned to an orthorhombic structure of $SrSnO_3$ (JCPDS: 09-0086)[12]. These suggest that microwave solvothermal synthesis is suitable for the growth of $SrSnO_3$ crystallites with the strongest major intensity peaks from the (210), (220) and (400) planes with some preferred orientation, respectively. Fig. 3 shows XRD patterns of the $MgSnO_3$ nanoparticles. All XRD peaks could be assigned to an orthorhombic structure of $MgSnO_3$ (JCPDS: 30-0798)7. These suggest that microwave solvothermal synthesis is suitable for the growth of $MgSnO_3$ crystallites with the strongest major intensity peaks from the (104), (110) and (024) planes with some preferred orientation, respectively.

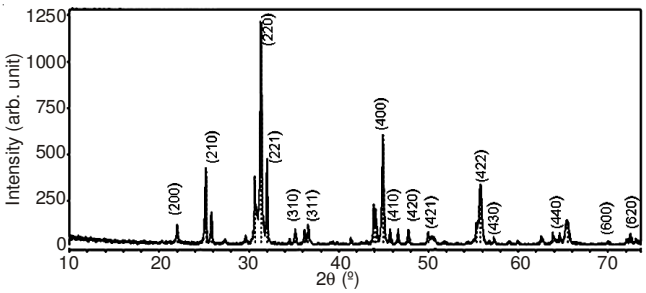

Fig. 2. XRD patterns of the $SrSnO_3$ nanoparticles

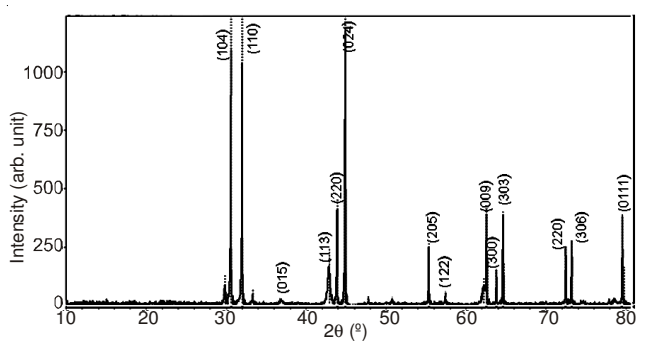

Fig. 3. XRD patterns of the $MgSnO_3$ nanoparticles

Fig. 4 shows FT-IR spectra of the $SrSnO_3$ and $MgSnO_3$ nanoparticles in the wavenumber range, 4000-480 cm^{-1}. The very strong absorbable peak at 629 cm^{-1} in Fig. 4(a) reveals typical characteristics of a strong Sr-O stretching mode. The strong Sn-O stretching modes are contributed to the uniform regular SrO_6 octahedra of the metal stannates[12]. The bands at 856 and 1050 cm^{-1} are due to the presence of carbonates. The bands at 2350, 1640 and 1450 cm^{-1} are assumed that the samples prepared contain a small amount of surface-adsorbed water and alcohol[9]. The very strong absorbable peak at 629 cm^{-1} in Fig. 4(b) reveals typical characteristics of a strong Mg-O stretching mode. The strong Mg-O stretching modes are contributed to the uniform regular MgO_6 octahedra of the metal stannates[12]. The bands at 856 cm^{-1} due to the presence of carbonates.

Fig. 5 shows a SEM image (a) and a TEM image (b) of the $SrSnO_3$ nanoparticles. The SEM image of $SrSnO_3$ in Fig. 5(a) shows a well-defined and homogeneous morphology, while the TEM image of $SrSnO_3$ in Fig. 5(b) shows the particle sizes of 20-40 nm. Fig. 6 shows a SEM image (a) and a TEM image (b) of the $MgSnO_3$ nanoparticles. The SEM image of $MgSnO_3$ in Fig. 6(a) shows a well-defined and homogeneous morphology,

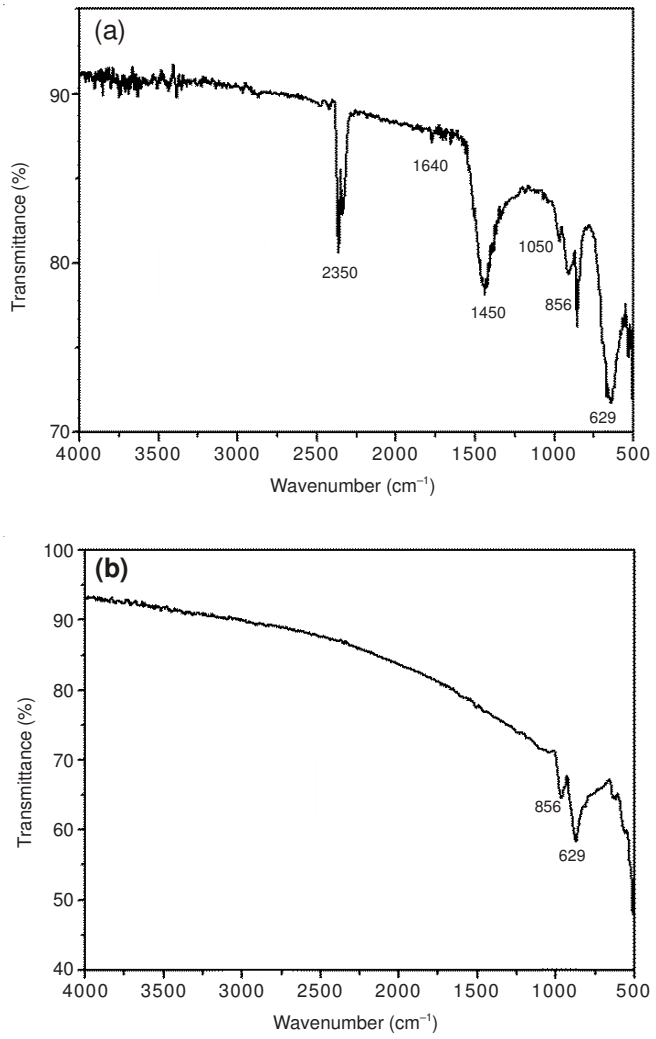

Fig. 4. FT-IR spectra of the (a) $SrSnO_3$ and (b) $MgSnO_3$ nanoparticles

while the TEM image of $MgSnO_3$ in Fig. 6(b) shows the particle sizes of 50-200 nm. The solvothermal synthesis proceeds the reactions between $MCl_2 \cdot 6H_2O$ and $Na_2SnO_3 \cdot 3H_2O$ in a hot ethylene glycol solution as a polar solvent above a boiling point of 197 ºC. The microwave solvothermal process of metal metastannates occurs in accordance with the reaction:

$$MCl_2 \cdot xH_2O + Na_2SnO_3 \longrightarrow MSnO_3 + 2NaCl + xH_2O$$

When the microwave radiation is supplied to the ethylene glycol under a sealed pressure above boiling point, the components dissolving in the ethylene glycol are charged and vibrated in electric field interdependently. The microwave solvothermal process is adjusted to heat the metal stannates 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 microwave-assisted solvothermal reaction involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction in ethylene glycol accompanying the formation of NaCl with a high lattice energy. The microwave exothermic reaction occurs so rapidly that the temperature and the pressure of the ethylene glycol increases so quickly that the reaction products are essentially heated up. The microwave-assisted solvothermal reactions provide a facile and fast route for the synthesis of $SrSnO_3$ and $MgSnO_3$ nanoparticles at consi-derably lower temperatures with a high pressure than those usually employed for their synthesis. The well-defined nanoparticles features synthesized by the microwave-assisted solvothermal process have a control over the morphology of the fine particles and can be used for technological applications.

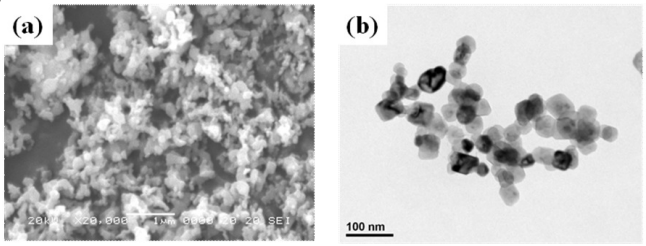

Fig. 5. A SEM image (a) and a TEM image (b) of the $SrSnO_3$ nanoparticles

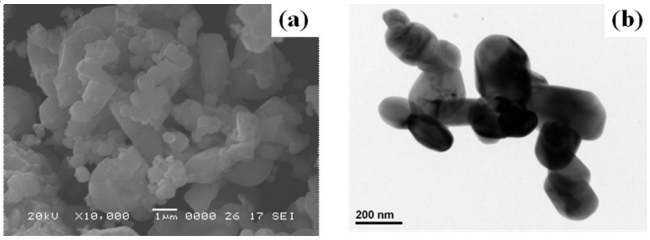

Fig. 6. A SEM image (a) and a TEM image (b) of the $SrSnO_3$ nanoparticles

Conclusion

$SrSnO_3$ and $MgSnO_3$ nanoparticles were synthesized successfully by the microwave solvothermal processes between $SrCl_2 \cdot 6H_2O$ and $Na_2SnO_3 \cdot 3H_2O$ for $SrSnO_3$ and $MgCl_2 \cdot 6H_2O$ $Na_2SnO_3 \cdot 3H_2O$ for $MgSnO_3$ in a hot ethylene glycol solution as a polar solvent. The microwave solvothermal reactions occured so rapidly that the exothermic reaction was essentially used to heat up the metal metastannates. Well-crystallized $SrSnO_3$ and $MgSnO_3$ and nanoparticles were formed after heat-treatment at 800 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 20-40 nm for $SrSnO_3$ and with particle sizes of 50-200 nm for $MgSnO_3$. The very strong absorbable peak at 629 cm^{-1} was typical characteristics of a strong Sr-O and Mg-O stretching modes.

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