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A Solvothermal Process to Synthesize Barium Metastannate Nanoparticles Assisted by Microwave Irradiation

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Barium metatstannate ($BaSnO_3$) nanoparticles were synthesized successfully using a facile microwave solvothermal route followed by further heat-treatment. Well-crystallized $BaSnO_3$ nanoparticles were formed after heat-treatment at 800 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 60-80 nm. The synthesized $BaSnO_3$ nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy.

Key Words: Barium metatstannate, Microwave irradiation, Solvothermal process, Nanoparticles.

INTRODUCTION

Cubic perovskite type of metal metastannates ($MSnO_3$) 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[1,2]. Barium metatstannate ($BaSnO_3$), belonging to the family of the perovskite, is of particular interest from both fundamental and material technology point of view due to its unusual dielectric and semiconducing properties. These materials found to be interesting for a number of applications in industry such as a glass enamel to improve alkali resistance, a component of dielectric ceramics, a multifunctional signal sensor to detect temperature, humidity and gas, as a negative electrode active material for long life energy storage application and in the fabrication of ceramic boundary-layer capacitors, *etc.*[3-5].

The detailed studies of metal metastannates on different aspects of the manufacturing method have been developed 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] and a self-heat-sustained method[16,17]. The advantages of microwave synthesis are to bring a very 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].

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. The microwave radiation is supplied to the ethylene glycol, so that the components dissolving in the ethylene glycol are capable of coupling with radiation. When the large amount of microwave radiation is applied into the ethylene glycol under the high sealed pressure, the charged particles are vibrated in electric field interdependently. Therefore, it is possible to achieve rapid and uniform heating of microwave dielectric materials. 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 the present study, the barium metatstannate ($BaSnO_3$) nanoparticles were synthesized using a facile solvothermal route assisted by the microwave irradiation. The characteristics of the synthesized $BaSnO_3$ nanoparticles are discussed in detail

based on the microwave solvothermal reaction in ethylene glycol under the high sealed pressure. The synthesized $BaSnO_3$ 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 $BaSnO_3$ nanoparticles by the microwave solvothermal process. $BaCl_2{\cdot}2H_2O$, $Na_2SnO_3{\cdot}3H_2O$ and ethylene glycol of analytic reagent grade were used to prepare the $BaSnO_3$ compound. Each of 0.01 mol $BaCl_2{\cdot}2H_2O$ and 0.01 mol $Na_2SnO_3{\cdot}3H_2O$ for $BaSnO_3$ 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 in ultrasonic bath 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 (MS) 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 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.

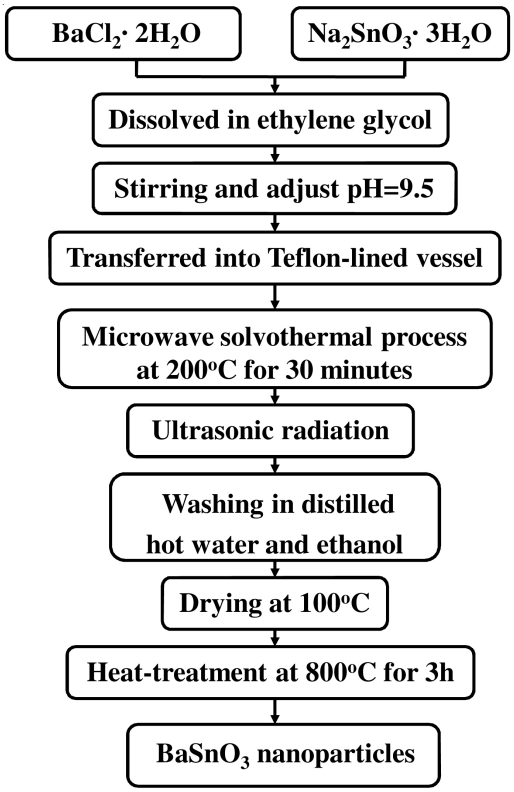

Fig. 1. Flow chart for the synthesis of $BaSnO_3$ nanoparticles by the microwave solvothermal process

The existing phases of the $BaSnO_3$ 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 $BaSnO_3$ particles over the frequency range, 4000 to 400 cm^{-1}. The microstructure, particle morphology and qualitative compositions of the $BaSnO_3$ 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 $BaSnO_3$ nanoparticles synthesized by the microwave solvothermal process after heat-treatment at 800 ºC for 3 h. All XRD peaks could be assigned to a cubic structure of $BaSnO_3$ (space group: Pm3m, JCPDS 15-0780)[9]. It suggests that microwave solvothermal synthesis is suitable for the growth of $BaSnO_3$ crystallites with the strongest major intensity peaks from the (220), (400) and (422) planes with some preferred orientation.

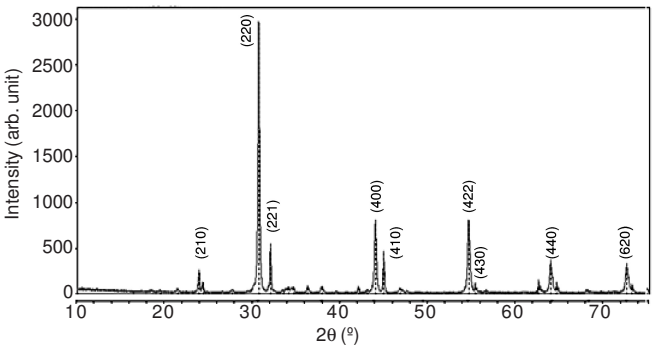

Fig. 2. XRD patterns of the $BaSnO_3$ nanoparticles synthesized by the microwave solvothermal process

Fig. 3 shows FT-IR spectra of the $BaSnO_3$ nanoparticles synthesized by the microwave solvothermal process in the wavenumber range, 4000-480 cm^{-1}. The very strong absorbable peak at 629 cm^{-1} reveals typical characteristics of a strong Sn-O stretching mode. The strong Sn-O stretching modes are contributed to the uniform regular SnO_6 octahedra of the metal stannates[12]. The bands at 856 and 1050 cm^{-1} are due to the presence of carbonates. The band at 1450 cm^{-1} is assumed that the samples prepared contain a small amount of surface-adsorbed water and alcohol[9].

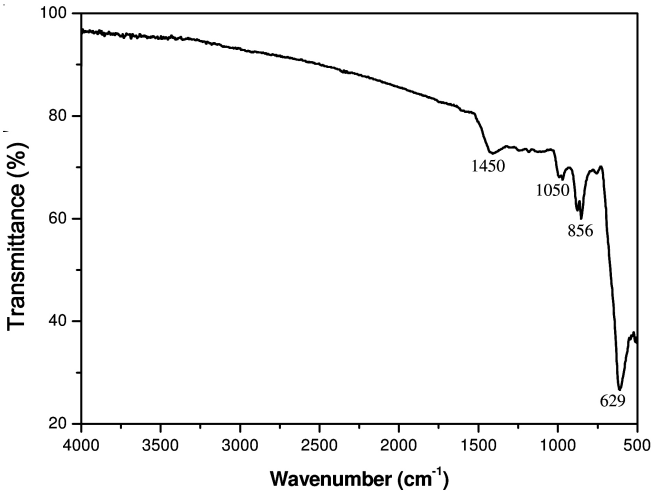

Fig. 3. FT-IR spectrum of the $BaSnO_3$ nanoparticles synthesized by the microwave solvothermal process

Fig. 4 shows a SEM image (a) and a TEM image (b) of the $BaSnO_3$ nanoparticles synthesized by the cyclic microwave solvothermal process. The SEM image of $BaSnO_3$ in Fig. 4(a) shows a well-defined and homogeneous morphology, while the TEM image of $BaSnO_3$ in Fig. 4(b) shows the particle sizes of 60-80 nm. The solvothermal synthesis proceeds the reactions between $BaCl_2 \cdot 2H_2O$ 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 stannates occurs in accordance with the reaction:

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

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 route for the synthesis of $BaSnO_3$ nanoparticles, which were obtained in the form of loosely connected nano-sized particles at considerably lower temperatures with a high pressure than those usually employed for their synthesis. The well-defined $BaSnO_3$ 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.

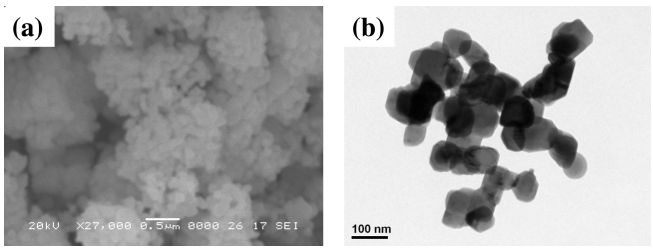

Fig. 4. A SEM image (a) and a TEM image (b) of the barium metatstannate nanoparticles synthesized by the microwave solvothermal process

Conclusion

Barium metatstannate nanoparticles were synthesized successfully by the microwave solvothermal processes between $BaCl_2 \cdot 2H_2O$ and $Na_2SnO_3 \cdot 3H_2O$ 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 stannates. Well-crystallized $BaSnO_3$ nanoparticles were formed after heat-treatment at 800 ºC for 3 h showing showing a fine and homogeneous morphology with particle sizes of 60-80 nm. The very strong absorbable peak at 629 cm^{-1} was typical characteristics of a strong Sn-O stretching mode.

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