Synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ Nanopowders by Glycothermal Process

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Abstract : Phase pure barium magnesium tantalate $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) nanopowders were synthesized at temperature as low as 220℃ through glycothermal reaction by using $Ba(OH)_2{\cdot}8H_2O$, $Mg(NO_3){\cdot}6H_2O$, and $TaCl_5$ as precursors and 1,4-butandiol as solvent. XRD, SEM, and TGA data support that glycothermal processing method provides a simple low temperature route for producing fine grained BMT nanopowders without alkaline mineralizers. BMT nanopowders synthesized at 220℃ showed more homogenous with rounded morphologies.

Key Words : $Ba(Mg_{1/3}Ta_{2/3})O_3$, Glycothermal, Nanopowder, 1,4-Butanediol, Microwave dielectric

1. Introduction

The demand for microwave dielectric resonators is rapidly rising as communication systems depend on more and more on microwave technology. As for a suitable dielectric materials of the general formula $Ba(B_{1/3}B'_{2/3})O_3$ where B=Zn or Mg and B'=Nb or Ta, have increased enormously because of their remarkable microwave dielectric properties, high dielectric constant and small temperature coefficient of resonant frequency, especially the highest dielectric loss ever known for a perovskite material. Therefore, these materials are commonly used in microwave devices such as dielectric resonators, filters, voltage-controlled oscillators, and antennas.

Recently, use of organic media for inorganic synthesis has attracted much attention. To our knowledge, no studies on the glycothermal synthesis of crystalline $Ba(Mg_{1/3}Ta_{2/3})O_3$ powders have been reported.

The objective of the current work was to prepare uniform $Ba(Mg_{1/3}Ta_{2/3})O_3$ particles by the glycothermal method. A wet chemical reaction route for the synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ was developed by using 1,4-butanediol solution. Thus, the formation of phase-pure $Ba(Mg_{1/3}Ta_{2/3})O_3$ nanoparticles via glycothermal treatments is described.

2. Experimental

Barium hydroxide octahydrate, $Ba(OH)_2{\cdot}8H_2O$ (99%, JUNSEI Chemical. Co., EP.) was used as raw material. Magnesium nitrate, $Mg(NO_3)_2{\cdot}6H_2O$ (99%, YAKURI Chemical. Co., EP) and tantalum pentachloride, $TaCl_5$ (99.8%, KISAN KINZOKU Chemicals) was used as a source of magnesium and tantalum, respectively. Magnesium and tantalum were added in the form of a coprecipitated $Mg_xTa_{(1-x)}$ gel (x=1/3).

Stoichiometric amounts of magnesium nitrate and tantalum chloride were dissolved in 70mL 2-propanol to obtain a stable solution because $TaCl_5$ is hydrolysed readely by reacting with water from air. Subsequent hydrolysis of this solution at room temperature by 1M NH_4OH solution produced a coprecipitated $Mg_xTa_{(1-x)}$ (MT) gel. The MT gel was separated and washed with CO_2-free water and ethyl alcohol by two times of centrifugation for 4min at 5000rpm in a centrifuge (Model J2-21 M, Beckman Instruments, USA). Redispersion of gel sediment was performed with Maxi Mix II (Thermolyne, USA). Excess ethyl alcohol was decanted after final washing and wet precursors was redisperced in 1,4-butandiol solution (99% Aldrich Chemical). $Ba(OH)_2{\cdot}8H_2O$ was then added into 1,4-butandiol. Total solvent volume was 70mL. In all runs, a Ba/(Mg+Ta) molarity ratio of 1.5 were employed. The glysothermal treatments were carried out at temperatures from 90 to 220℃. The resulting suspension was placed in a 100mL stainless-steel Teflon-lined autoclave (Parr Instruments, USA). The reaction time at the desired temperature was 24h. The powders were washed with pH adjusted (pH~10) CO_2-free deionized water to remove the unreacted Ba in solution, and also prevent incongruent dissolution of the barium ions from the BMT powder surface. The recovered BMT nanopowders were dried at 50℃ in a desiccator for 24h.

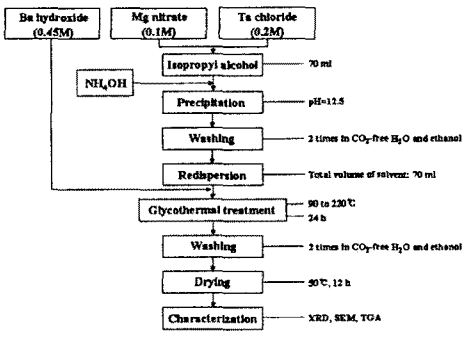

Fig. 1. Schematic representation of processing steps for the preparation of $Ba(Mg_{1/3}Ta_{2/3})O_3$ nanoparticles via glycothermal process.

Phase composition and crystal structure were analyzed using X-ray diffraction (XRD, CuK_α, Rigaku, Japan) over the 2θ range from 10° to 100° at a scan rate of 2°/min. The morphology of the synthesized particles was observed using field-emission scanning electron microscopy (FESEM, Hitachi

S-4200, Japan). Thermo gravimetric analysis (TGA) were carried out to understand the decomposition and synthesis process and to optimize the calcination temperature. TGA (TG-DTA 2000, MAC Science, Japan) was performed with heating rate of at 2℃/min up to 1200℃.

3. Result and Discussion

In order to investigate effect of the reaction temperature on the phase and morphology of glycothermal derived BMT nanoparticles, precursors were treated at different temperatures with molarity ratio of Ba:(Mg+Ta) to 1.5:1 for 24h. Fig. 2 shows XRD patterns of $Ba(Mg_{1/3}Ta_{2/3})O_3$ powder synthesized in glycothermal condition at different reaction temperatures. It is relatively straightforward to produce BMT nanopowder with the desired perovskite phase. XRD results indicate that the products were amorphous at 90℃ and BMT phase started to form at 120℃. Thus, the transition temperature of the amorphous precursors to crystalline solid in glycothermal condition was around of 120℃.

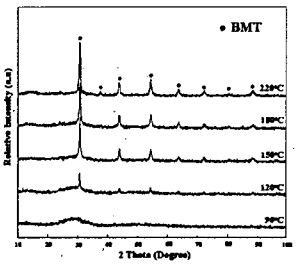

Fig. 2. XRD patterns of $Ba(Mg_{1/3}Ta_{2/3})O_3$ powder synthesized in glycothermal condition at various reaction temperatures (24h, pH=12.5, Ba:Mg:Ta molarity ratio of 0.45:0.1:0.2).

FESEM micrographs of BMT nanoparticles synthesized at different temperatures are given in Fig. 3. The size and shape of BMT nanoparticles was also strongly dependent on reaction temperatures. The morphology of BMT nanoparticles gradually changed from a raspberry-like shape to round and approximately equiaxed shape with some irregularities when reaction temperature was changed from 120℃ to 220℃.

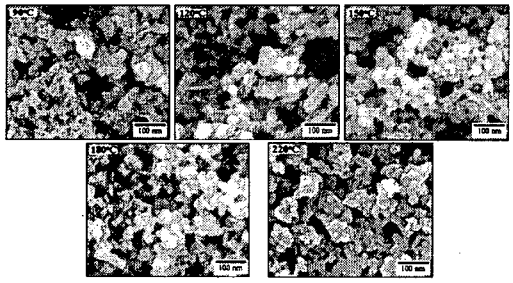

Fig. 3. FESEM micrographs of BMT Nanopowders Prepared by Glycothermal Method at Various Reaction Temperatures (24h, pH=12.5, Ba:Mg:Ta molarity ratio of 0.45:0.1:0.2).

Fig. 4 shows TGA of BMT nanoparticles synthesized at different reaction temperatures. The total weight losses synthesized at 90, 120, 150, 180, and 220℃ for 24h were, respectively, 19.2, 12.8, 11.5, 10.7, and 9.3wt%. The total weight loss between 100 and 800℃ is less than 12.8wt% for the powder synthesized at 120℃ and decreases significantly with increasing synthesis temperatures, becoming less than 9.3wt% at 220℃.

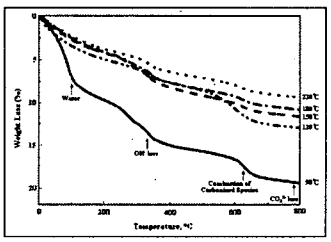

Fig. 4. Thermogravimetric analysis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ powder synthesized in different reaction temperatures (24h, pH=12.5, Ba:Mg:Ta molarity ratio of 0.45:0.1:0.2).

4. Conclusions

In this work, a new glycothermal process has been developed for synthesizing phase-pure $Ba(Mg_{1/3}Ta_{2/3})O_3$ nanopowders using 1,4-butandiol as the reaction medium in glycothermal environment. Well crystallized phase pure perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ was successfully produced at as low as 220℃. The average particle size of the as-prepared powder was 50nm.

References

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