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A novel wet-chemical process to synthesise $Ba(Mg_{1/3}Ta_{2/3})O_3$ nanopowders

Lihua Xu[a,b], Fang Lian[a], Juan Yang[b], J.M.F. Ferreira[b,*]

[a]*Department of Inorganic Material, University of Science and Technology Beijing, Beijing 100083, PR China*
[b]*Department of Ceramic and Glass Engineering, University of Aveiro, Aveiro 3810-193, Portugal*

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Abstract

The present work proposes an easily operated and low cost wet-chemical process for the synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) nanopowders. Tantalum pentaoxide, Ta_2O_5, was selected as the starting material, instead of the currently used $TaCl_5$. The process involves the melting of the precursor Ta_2O_5 in the presence of sodium hydroxide followed by dissolution of the cooled glassy phase and washing several times with distilled water to remove the Na^+ ions. A key step is the obtaining of a high quality $Ta_2O_5{\cdot}nH_2O$ colloid by controlling the concentration of Ta ion during dissolution and washing processes. The fine BMT powders were then fabricated by mixing the colloidal $Ta_2O_5{\cdot}nH_2O$ with barium acetate and magnesium acetate, according to the required molar proportions, followed by gelation and heat treatment. Nano BMT powders with an average particle size of 70 nm could be prepared at temperatures as low as 800 °C. In addition, the as prepared nanopowders revealed good sintering ability at low temperatures and the sintered nanoceramics exhibited excellent microwave dielectric properties.

Keywords: $Ba(Mg_{1/3}Ta_{2/3})O_3$ nanopowder; $Ta_2O_5{\cdot}nH_2O$ colloid; Wet-chemical process; Microwave dielectric properties

1. Introduction

Great attention has recently been attracted to $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramics with the complex perovskite structure because of the extremely high quality factor value ($Q = 15{,}000$ at $f = 10$ GHz). These materials have been regarded as a new family of dielectric ceramics and promising candidates for applications as dielectric resonators (DRs) or microwave components of the X-band or millimeter-wave communication systems, satellite transmission systems and other defence and military affairs [1–4]. The preparation technology of BMT powders has been mainly based on the solid phase reaction method, which is usually regarded as the most popular process. However, the required temperatures to promote diffusion among various oxides are usually high and the as synthesised BMT powders [or BZT, $Ba(Zn_{1/3}Ta_{2/3})O_3$ powders], are relatively coarse and strongly agglomerated. These powder characteristics are detrimental for the properties of the final products [5–7].

Wet-chemical processes have been widely recognised as an efficient approach to prepare nano-crystalline fine particles at low temperatures [1,8–9]. Sol-gel processing is probably one of the easiest approaches to obtain good-quality powders, films or multilayers, or even bulk materials. However, this method has some limitations in preparing BMT powders. As a matter of fact, one of the currently used precursors, $Ta(OC_2H_5)_5$, is usually obtained from the expensive starting $TaCl_5$ by a refluxing process, which lasts for more than 48 h under a protecting atmosphere [1,10]. Furthermore, $TaCl_5$ is difficult to prepare experimentally due to its extremely unstable physical and chemical characteristics [11]. Therefore, BMT powders are difficult to be economically and efficiently synthesised by the sol-gel process.

On the other hand, Ta_2O_5 being a low cost and abundant natural resource would be regarded as an interesting starting material if a way to reduce the size of particles to the nanometric scale could be envisaged. The present paper reports on a simple wet-chemical process to prepare BMT nanopowders from Ta_2O_5. The method involves the preparation of a colloidal $Ta_2O_5{\cdot}nH_2O$ by dissolving the glassy phase resulting from the molten reaction of Ta_2O_5 with alkali, followed

* Corresponding author. Fax: +351-234-425-300.
E-mail address: jmf@cv.ua.pt (J.M.F. Ferreira).

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by neutralisation/precipitation, filtration and washing (with distilled water) processes, as intermediate steps. The final BMT nanopowders could be obtained after mixing the as prepared colloidal $Ta_2O_5{\cdot}nH_2O$ with Mg-acetate and Ba-acetate, followed by homogeneous precipitation and heat treatment. The evolutions of the microstructure and of the crystalline phases formed along the heat treatments have been investigated. The microwave dielectric properties are also additionally reported.

2. Experimental procedure

Ta_2O_5 is an almost water insoluble substance, except when it has been previously molten in alkali metallic bisulphates and carbonates or caustic alkalis [5]. Caustic soda was thus selected as a molten agent for Ta_2O_5. The resulting glassy phase was then dissolved into distilled water and the excess alkali was neutralised with 0.1 M CH_3COOH, adjusting the pH value to 7. A precipitate formed, which was then vacuum filtered. Colloidal $Ta_2O_5{\cdot}nH_2O$ nanoparticles could be obtained by redispersing and washing the filtrate for at least 5 times to remove the remaining sodium ions. Portions of the as obtained colloidal $Ta_2O_5{\cdot}nH_2O$ nanoparticles were dried and heat-treated to determine the content in Ta_2O_5. Subsequently, the colloidal $Ta_2O_5.nH_2O$ nanoparticles were finally redispersed and mixed with barium acetate, $Ba(CH_3COO)_2$, and magnesium acetate hydrate, $Mg(CH_3COO)_2{\cdot}4H_2O$, in the appropriate molar ratio (Ba^{2+}:Mg^{2+}:Ta^{5+} = 3:1:2). Well-dispersed mixtures could be obtained as the acidity of the dispersing media was adjusted to pH = 6.4 by adding ammonia. Heat treating the mixture in a water bath at 80 °C under vigorous stirring led to a gradual evaporation of water and finally to gelation. The as prepared gel was dried for 6 h at 110 °C and then calcined at different temperatures (600–1000 °C) to obtain the final BMT powders. The microstructural characteristics and crystalline phase analysis of the as prepared powders were investigated by TEM and XRD, respectively, and compared with those derived from a powder of the same composition but fabricated by solid state reaction. Finally, cylindrical ($\phi = 20\times5$ mm) ceramic bodies were shaped by uniaxial pressing the BMT powders at 25 MPa and sintering at 1400 °C for 1 h. Microwave characteristics were determined by the dielectric resonator method within the frequency range of 0.1–4.5 GHz [12].

3. Results and discussion

The obtaining of a high quality $Ta_2O_5{\cdot}nH_2O$ colloid revealed to be a prerequisite for the synthesis of nano BMT powders. It was found that the concentration of Ta^{5+} in the solution during both the dissolution and washing processes would play an important role in the formation of colloidal $Ta_2O_5{\cdot}nH_2O$ particles. Achieving the above target required a proper concentration of 0.25 M Ta^{5+}, as shown in Table 1. When the concentration of Ta^{5+} in the washing solution was less than 0.1 M the size of colloidal particles was too small, and the amount of water was relatively too high to enable gelation after adding the Mg and Ba acetates. Once concentration of Ta^{5+} was more than 0.4 M, agglomeration of colloidal particles inevitably occurred due to the higher frequency of collisions between attracting particles (rapid rate of colloidal coagulation). Such situations would cause some disadvantages in the subsequent processing steps for the synthesis of ultrafine and uniform powders. Therefore, it is important to start from a suitable Ta^{5+} concentration.

Fig. 1 shows the evolution of phase transformation during calcination. It can be seen from the XRD patterns that at low heat-treatment temperatures (600–700 °C), two crystalline phases have been formed, namely, a predominant phase $Ba(Mg_{1/3}Ta_{2/3})O_3$ and a subsidiary $BaTa_2O_6$ phase.

With the heat-treatment temperature increasing to >800 °C, the subsidiary $BaTa_2O_6$ phase disappeared and the single phase $Ba(Mg_{1/3}Ta_{2/3})O_3$ was formed. Therefore, it can be deduced that $BaTa_2O_6$ transformed into BMT cubic perovskite type near 800 °C. With the temperature increasing, the crystal plane (100) appears,

Table 1
Effect of molar concentration of Ta^{5+} on the colloidal characteristics of $Ta_2O_5{\cdot}nH_2O$

Concentration of Ta^{5+} (M)	0.1	0.25	0.4
Colloidal characteristics	No colloids	White colloid	Precipitation

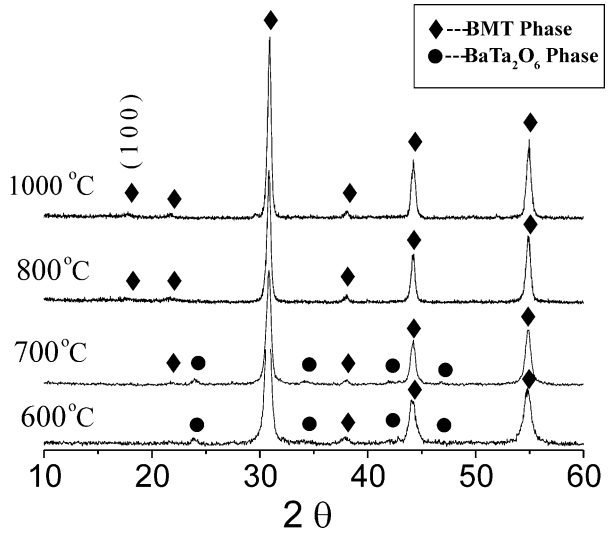

Fig. 1. XRD patterns of BMT powders after heat-treatment at different temperatures.

illustrating further ordering of Mg and Ta atoms in perovskite structure according to the DTA curve [13]. However, it was reported that the formation of the single BMT phase from the conventional process (solid state phase reaction) would require annealing temperatures higher than 1200 °C [11].

Fig. 2a and b compares the TEM photographs of BMT powders prepared by the wet-chemical synthesis process used in the present work, and by the traditional solid state reaction process, respectively. It can be observed that the average particle size was only about 70 nm when using the novel technology, far less than the 1.5 μm obtained through the traditional solid state reaction method. In addition, nanoceramics with high density (93.4%) could be obtained after sintering at 1400 °C for 1 h, compared with the significantly lower sintered density (86.7%) measured for the compacts made of the powder derived from the solid state reaction method. The enhanced sintering ability of the as prepared nano BMT powders enabled us to achieve improved microwave dielectric properties, as shown in Table 2. As detailed elsewhere [2,14–15] the dielectric loss is considered as an important parameter when the ceramics are to be applied as dielectric resonators (DRs) or microwave components. The measured values of microwave dielectric loss of BMT ceramics (Table 2) show that a Q value as high as 20684, and a tanδ as low as 4.83×10^{-5} could be obtained for BMT ceramic at 1.563 GHz. These values compare favourably with the much lower Q value (8811) and the associated higher tanδ (11.35×10^{-5}) measured at the same frequency for the compacts made of the powder derived from the solid state reaction method. In other words, the sintered nanoceramics exhibited excellent microwave dielectric properties, and they could reasonably be regarded as candidate materials for microwave components.

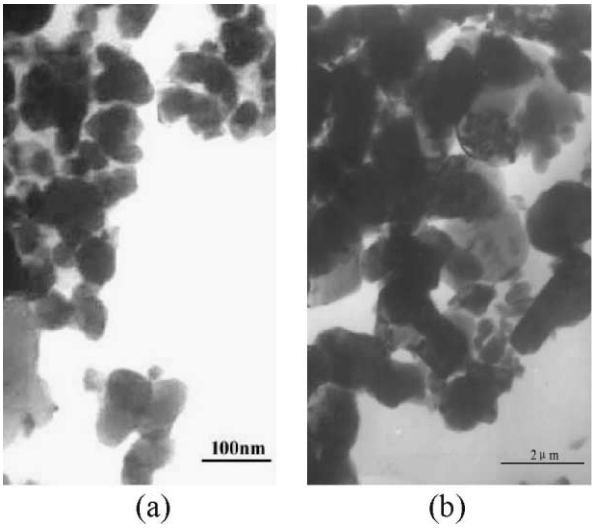

Fig. 2. TEM photographs of BMT powders prepared by two different methods: (a) wet-chemical synthesis process (800 °C for 1 h); (b) solid state reaction process (1200 °C for 1 h).

Table 2
Dielectric microwave properties of BMT ceramics

Frequency (GHz)	Tanδ	Q (= 1/ tanδ)
1.523	5.1613×10^{-5}	19375
1.563	4.8346×10^{-5}	20684

4. Summary

$Ba(Mg_{1/3}Ta_{2/3})O_3$ nanopowders were synthesised by a wet-chemical process in which Ta_2O_5 was used as starting material, molten in the presence of sodium hydroxide, and wet-chemically treated to prepare an intermediate $Ta_2O_5{\cdot}nH_2O$ colloidal suspension. Homogeneous mixing of the colloidal $Ta_2O_5{\cdot}nH_2O$ with barium acetate and magnesium acetate, as well as good gelling behaviour could be obtained at the optimal concentration of 0.25 M Ta^{5+} in the $Ta_2O_5{\cdot}nH_2O$ colloids. Full-formed BMT powders with an average particle size of ~70 nm could be obtained by heat treating the dried powders at 800 °C for 1 h. Ceramics derived from the nano BMT powders could achieve high sintering densities at a relatively low sintering temperature and exhibited a high quality factor at microwave frequency. They can, therefore, be regarded as potential candidates for microwave applications.

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