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Preparation of phase pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ nanopowders for microwave dielectric resonator applications

Manoj Raama Varma*, S. Biju, M.T. Sebastian

Regional Research Laboratory, CSIR, Trivandrum 695019, India

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Abstract

Nanosized phase pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) was prepared by decomposition of a citrate polymer precursor and subsequent pyrolysis. The powders were pyrolysed at different elevated temperatures and the effect of temperature on particle size was investigated. The sinterability of BZT ceramics made from nanopowders was very poor. Sintering at high temperatures led to formation of barium tantalite ($BaTa_2O_6$) due to vaporization of zinc. The samples were sintered by muffling with calcined BZT powder. Microwave dielectric properties of sintered dielectric resonators prepared from nanopowders of BZT are discussed.

Keyword: Grain size; Dielectric properties; Perovskites; Dielectric resonators

1. Introduction

$Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) is a well-known ceramic material having a high dielectric constant ($\varepsilon_r \sim 29$), low temperature coefficient of resonant frequency ($\tau_f \sim 4$ ppm/°C), and high quality factor ($Q \times f \sim 80{,}000$–$150{,}000$ GHz).[1,2] BZT has a complex perovskite structure and belongs to the family of materials $A(B'_{1/3}B''_{2/3})O_3$ [A = Ba; B′ = Mg, Zn; B″ = Ta, Nb] used in microwave communication systems. There have been many attempts to explain the material's excellent microwave dielectric properties and to further improve its properties.[3–5] In all these reports, BZT was synthesized by solid-state ceramic route. Disadvantage of the solid-state synthesis route is the high calcination and sintering temperatures as well as the relatively high particle size. Moreover, the particles are strongly agglomerated which may affect the properties of the final product.[6,7] To overcome these difficulties and to synthesize nanocrystalline fine particles at relatively lower temperatures, wet chemical methods are being employed.[8–10] Among the chemical methods, sol–gel synthesis is the easiest and is known to yield nanocrystalline powders. However, this method has some limitations like the usage of expensive alkoxides. Several authors have attempted to synthesize $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) by sol–gel method.[11–15] They reported the synthesis of phase pure, low temperature of formation (as low as 600 °C), and well sinterable (~1500–1600 °C) BMT powders. These BMT powders on sintering achieve more than 95% of theoretical density. Other materials like $Ba_2Ti_9O_{20}$,[16] (Zr,Sn)TiO_4,[17] etc. have also been successfully prepared by the sol–gel method. Other chemical techniques include homogeneous precipitation synthesis,[18] co-precipitation,[19] inverse micro-emulsion,[20] hydrothermal synthesis,[21] etc. It was reported that the synthesis based on decomposition of a polymer gel is an excellent method for the formation of metallic ion complex in the form of nanoparticles.[22–24] This process was originally used to obtain highly dispersed mixed oxides or oxide solid solutions. The process was later applied for the preparation of high-temperature superconducting oxides.[23–25] In the present paper we report the synthesis of BZT by the decomposition of a citrate precursor gel.

2. Experimental

In the present investigation BZT was synthesized by decomposition of a citrate precursor gel. Two modified versions of the method namely nitrate route and chloride route were attempted for the synthesis.

2.1. Nitrate route

In the nitrate route, $TaCl_5$ was first hydrolyzed to $Ta(OH)_5$, which was reacted with concentrated HNO_3 to get $Ta(NO_3)_5$

* Corresponding author.
E-mail address: mailadils@yahoo.com (M.R. Varma).

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in solution. $Ba(NO_3)_2$ and $Zn(NO_3)_2$ were dissolved in deionized water and heated to 80 °C under constant stirring. To this solution, $Ta(NO_3)_5$ and predetermined amount of $C_6H_8O_7$ dissolved in deionized water were added. The solution was stirred at 90 °C for 2 h and slowly concentrated at 120 °C in an oven. The solution was further concentrated by fast heating with vigorous stirring to form a gel, which was further decomposed at about 300 °C to get a black precursor mass.

The reactions involved in the processes are

$$TaCl_5 + 5H_2O \xrightarrow{H^+} Ta(OH)_5 + 5HCl$$

$$Ta(OH)_5 + 5HNO_3 \rightarrow Ta(NO_3)_5 + 5H_2O$$

$$2Ta(NO_3)_5 + Zn(NO_3)_2 + 3Ba(NO_3)_2 \xrightarrow[300°C]{C_6H_8O_7/HNO_3} Ba_3ZnTa_2O_9 \text{ (BZT precursor)}$$

2.2. Chloride route

In chloride route, $TaCl_5$ was dissolved in concentrated HCl. This was added to a solution of predetermined amounts of $Ba(NO_3)_2$, $Zn(NO_3)_2$, and $C_6H_8O_7$ in distilled water. The solutions were mixed, stirred at 90 °C for 2 h and concentrated by heating with vigorous stirring forming a gel which was further decomposed at about 300 °C to get a black precursor mass. The reactions involved in the processes are

$$TaCl_5 + 5HCl \rightarrow Ta^{5+} + 10Cl^- + 5H^+$$

$$2TaCl_5 + ZnCl_2 + 3BaCl_2 \xrightarrow[300°C]{C_6H_8O_7/HNO_3} Ba_3ZnTa_2O_9 \text{ (BZT precursor)}$$

TGA and DTA patterns of the precursors were recorded for both chloride and nitrate routes up to 1000 °C which showed a major weight loss and a phase transformation occurring at about 585 °C. Hence the lowest pyrolysis temperature of the precursor was fixed at 600 °C. The precursor was pyrolysed at different temperatures from 600 °C onwards and phase formation was confirmed using XRD technique. The size of the particles were determined using Debye Scherrer equation.[26] After pyrolysis these powders were ground well for about 1 h in an agate mortar and 3 wt.% of polyvinyl alcohol was added to it as a binder. It was then dried in a hot air oven and ground to fine powder. This powder was pelletized at a pressure of about 150 MPa and sintered at different temperatures to get the final dielectric resonators of size about 13 mm in diameter and about 6.5 mm in height. The microwave dielectric properties of the sintered samples were measured using Agilent 8753 ET Network Analyzer in the frequency range 3–6 GHz. Dielectric constant was determined by Hakki and Coleman method[27,28] using $TE_{01\delta}$ mode and quality factor was determined using cavity method.[29] Thermal variation of resonant frequency was studied in the temperature range 25–80 °C keeping the sample in the end shorted position and temperature coefficient of resonant frequency was determined.

3. Results and discussion

TGA and DTA patterns of the precursors (chloride route) were recorded up to 1000 °C and are shown in Fig. 1. TGA data in Fig. 1 showed a weight loss of 2.028% at about 600 °C whereas DTA showed a phase transformation at 585 °C. However, X-ray diffraction study of pyrolysed samples at 600 °C did not indicate the formation of BZT. A second phase formation was found at 816 °C in the DTA curve. Hence on heating at 850 °C onwards, BZT could be easily obtained from chemically derived precursor. The XRD patterns for the nitrate route and chloride route synthesized BZT powders are shown in Fig. 2. The formation temperature of BZT was 1200 °C for powders prepared by solid-state method. For comparison purpose XRD pattern of BZT synthesized by conventional solid-state route is also shown in Fig. 2. The phase purity of the BZT synthesized by nitrate and chloride routes is comparable with those prepared by solid-state method. As the pyrolysis temperature is increased to 1000 °C, the BZT retains its phase purity. Chemically synthesized BZT nanopowders were pyrolysed at different temperatures such as 900, 1000, 1100, and 1200 °C for 4 h and the variation of particle size was studied. The variation of particle size of BZT powders obtained by both chloride and nitrate routes with temperature is shown in Fig. 3. The particle size increases with heating temperature and the rate of increase is more for powders prepared by nitrate route. Dopants like TiO_2 and ZrO_2 were added to the precursor powders to improve the phase stability and the doped powders were pyrolysed at 900 °C for 4 h. Effect of dopant addition on particle size of nanopowders is shown Table 1. The addition of ZrO_2 allows the formation of larger particles as compared to TiO_2 addition when heated to 900 °C for 4 h.

Pellets made from the powder synthesized by chloride route was subjected to sintering at different temperatures. Fig. 4 shows the effect of sintering temperature on the density of sintered pellets. It is evident from the figure that the densification of nanopowders was poor when sintered at temperatures below 1450 °C. Reasons for the poor densification of nanopowders of BZT were further investigated. XRD pattern of the BZT nanopowders after calcination at 1200 °C/4 h and sintered at

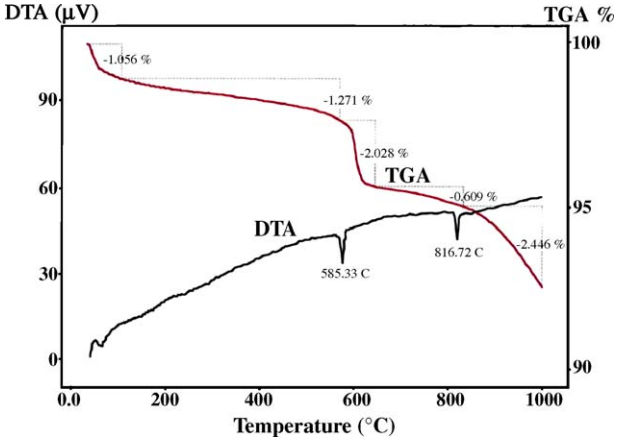

Fig. 1. TGA/DTA pattern of the precursor synthesized through chloride route.