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

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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 $Ta(NO_3)_5$

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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

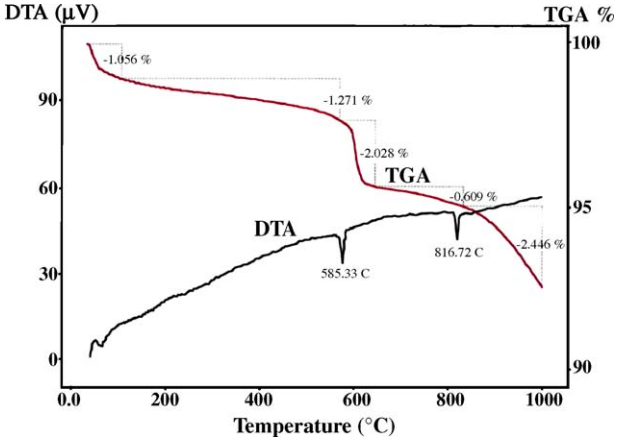

Fig. 1. TGA/DTA pattern of the precursor synthesized through chloride route.

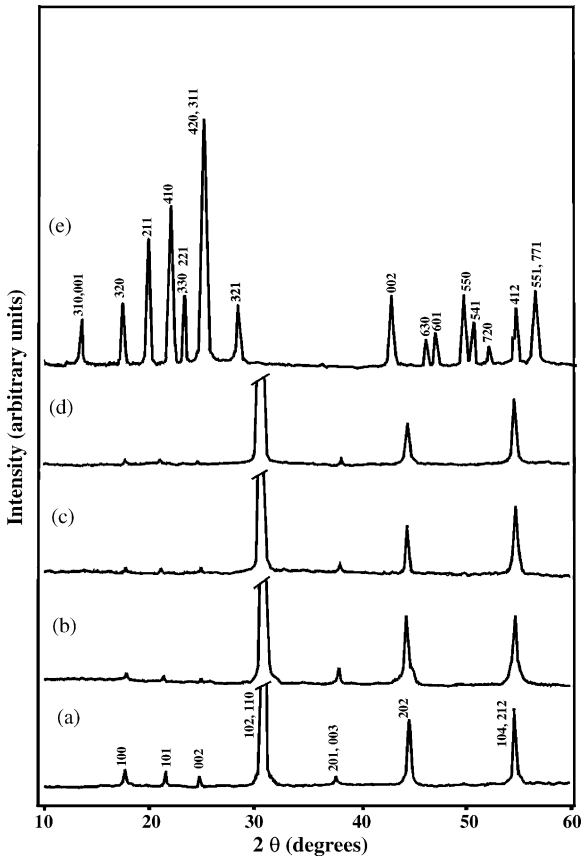

Fig. 2. XRD patterns of BZT synthesized by chloride and nitrate route. (a) BZT synthesized by conventional solid-state ceramics route. (b) Citrate polymer precursor gel (chloride route) heated at 900 °C/4 h. (c) Citrate polymer precursor gel (chloride route) heated at 1000 °C/4 h. (d) Citrate polymer precursor gel (nitrate route) heated at 900 °C/4 h. (e) Sintered pellets of BZT nanopowders (chloride route) sintered at 1450 °C/4 h in air showing complete transformation to $BaTa_2O_6$.

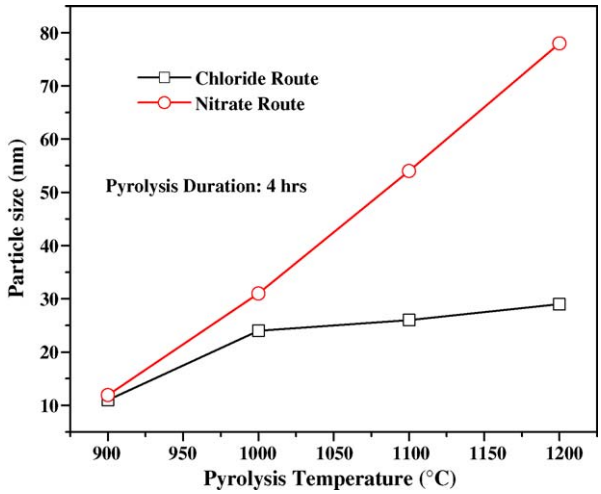

Fig. 3. Effect of heating temperature on the particle size of BZT synthesized by citrate gel decomposition method: nitrate route and chloride route.

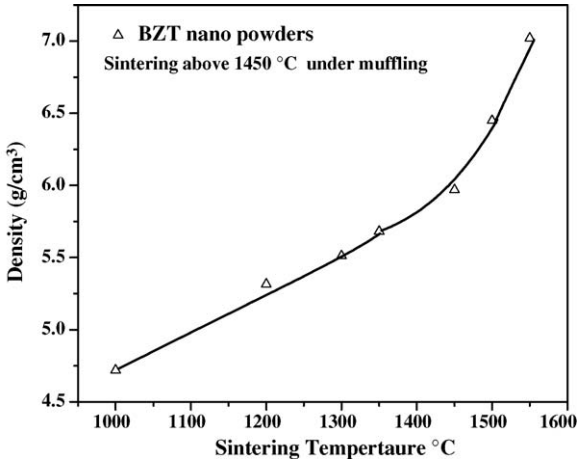

Fig. 4. Effect of sintering temperature on the density of BZT synthesized by citrate gel decomposition method (chloride route). The pellets were muffled with calcined BZT powder for sintering above 1450 °C.

Table 1
Effect of dopant addition on particle size of chemically derived $Ba(Zn_{1/3}Ta_{2/3})O_3$

Method of synthesis	Dopant added (2 wt.%)	Particle size (nanometers)
Chloride method (pyrolysis at 900 °C/4 h)	Nil	11.0
	TiO_2	16.3
	ZrO_2	28.2
Nitrate method (pyrolysis at 900 °C/4 h)	Nil	11.5
	TiO_2	23.9
	ZrO_2	31.3

1450 °C/4 h are shown in Fig. 2e. Sintering at temperatures above 1450 °C, in air completely transform BZT to $BaTa_2O_6$. This was due to the volatile nature of the Zn atoms, which can escape easily due to the high surface area of the nanoparticles. The high surface area and small particle size of the nanoparticles lead to the depletion of zinc. The BZT pellets made from nanopowders were then sintered by muffling in BZT powder synthesized through the solid-state method. However, the sin-

Table 2
Microwave dielectric properties of BZT synthesized by modified citrate gel route as compared with that prepared by solid-state route

Material	Density and sintering conditions	$Q \times f$ (GHz) before and after annealing	ε_r	τ_f (ppm/°C)
BZT chloride precursor route	91% density (Ga doped 1550 °C /6 h)	44,000 71,000 (annealed 5 h)	25.2	1.6
BZT nitrate precursor route	89% density (Ga doped 1550 °C/6 h)	44,000 65,500 (annealed 5 h)	25.0	2.1
BZT (solid-state route)[30]	96% density (undoped 1650 °C/2 h)	65,000 85,000 (annealed 20 h)	28.9	1.6

Table 3
Microwave dielectric properties of BZT synthesized by chloride route and sintered by addition of dopants (2 wt.%)

Dopant	% Densification	$Q \times f$ (GHz) before annealing	$Q \times f$ (GHz) after annealing	ε_r	τ_f (ppm/°C)
WO_3	86	7,000	9,000	22.5	4.7
TiO_2	87	12,000	15,000	23.1	3.8
Cr_2O_3	87	24,000	26,000	23.4	4.2
ZrO_2	88	40,000	48,500	24.5	2.7
Ga_2O_3	91	44,000	71,000	25.2	1.6
CeO_2	86	22,000	29,000	23.9	2.7
Bi_2O_3	86	13,000	17,000	23.8	4.2

terability was very poor with about 80% of their theoretical density and the samples have very low quality factors of about $Q \sim 1000$. In order to overcome this problem and to improve the density of sintered pellets, 2 wt.% of dopant powders of ZrO_2, TiO_2, Ga_2O_3, Cr_2O_3, WO_3, CeO_2, and Bi_2O_3 were added to BZT nanopowder. These pellets were muffled with BZT powder and sintered at 1550 °C for 6 h in a platinum crucible. This procedure has improved density of sintered samples to about 90% of its theoretical density. Sintered samples were annealed at 1300 °C for different time intervals. Fig. 5 shows the variation of $Q \times f$ with annealing duration for both nano-BZT and solid-state ceramic route. Table 2 compares the dielectric properties of BZT prepared by the chemical methods using the nanopowder with that prepared by solid-state route. Variation of density and $Q \times f$ of sintered BZT with ionic radius of different dopants is shown in Fig. 6. The density and $Q \times f$ increase when the ionic radii of the dopants are close to 0.65 Å. It is found recently[30] that the quality factor of doped BZT reaches a maximum when the ionic radii of the dopants are close to the ionic radius of Ta (0.64 Å) or Zn (0.74 Å). The ε_r and τ_f of the samples sintered by the addition of 2 wt.% of different dopants are given in Table 3. Addition of dopants except Ga_2O_3 did not improve the dielectric properties. The dielectric constant of BZT prepared using nanopowders were relatively low due to their relatively poor densification. However, it may be possible to further improve the quality factor and ε_r by improving the sintered density.

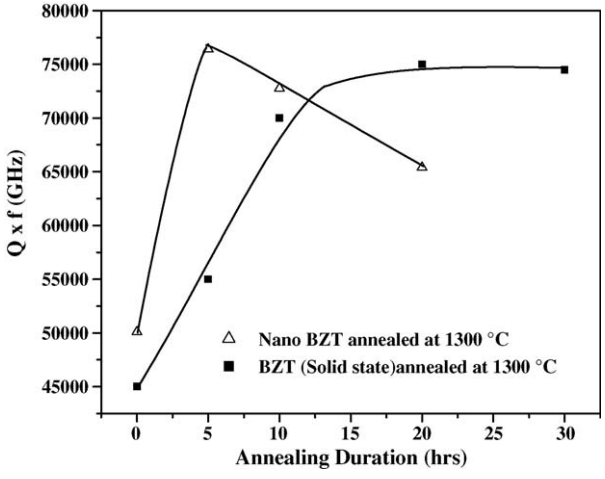

Fig. 5. Variation of $Q \times f$ with annealing duration for both nano-BZT doped with Ga_2O_3 (pellets made from powder obtained through chloride route) and solid-state synthesized BZT.

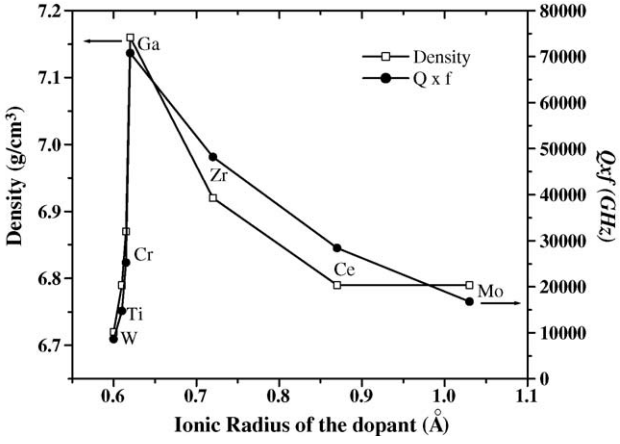

Fig. 6. Variation of density and $Q \times f$ of sintered (pellets made from powder made through chloride route) BZT with ionic radii of the different dopants.

4. Conclusions

Phase pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ nanopowders were synthesized by a modified citrate gel route. Effect of pyrolysis on the particle size of these powders was investigated. The formation temperature of $Ba(Zn_{1/3}Ta_{2/3})O_3$ was found to be 850 °C whereas for solid-state route it was about 1100–1200 °C. Sinterablity of the powder was found to be poor due to the volatile nature of Zn and its depletion. High surface area of the nanoparticles is believed to accelerate the zinc depletion process during sintering resulting in the formation of $BaTa_2O_6$. The sinterability could be improved up to 90% of its theoretical density, by doping with Ga_2O_3 and muffling the sample with BZT powder during sintering. The quality factor of sintered pellets made from nanopowders was found to be lower than those synthesized by solid-state ceramic route. The low ε_r of the ceramics is attributed to the poor sintered density of the samples. The Ga_2O_3 doped samples sintered up to 90% of its theoretical density and showed a $Q \times f$ of 71,000 GHz which indicated that the quality factor may considerably increase by improving the percentage density of the ceramics prepared from nanopowders.

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