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Synthesis of Ba (Zn_{1/3}Ta_{2/3})O₃ by Ball-milling in Ethanol

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Abstract

The attractive dielectric properties of Ba(Zn_{1/3}Ta_{2/3})O₃ (BZT) enable it to be a prime dielectric material applicable in modern communication systems which include cellular phones and satellite communications. BZT was synthesized by Ball-milling in ethanol for (1-10) hrs x 6 and its impacts on the dielectric properties of BZT were studied. The density of the pellets sintered at 1475 °C was close to 70% of the theoretical density. The low frequency (20MHz) dielectric constant (ϵ) was different for pellets with different calcinations time and the dielectric loss ($Tan\delta$) were less than zero.

Keywords: BZT, Ball-milling, Calcinations, Sintering, XRD, dielectric properties.

Introduction

The production of dielectric ceramics and resonators has emerged as one of the fastest growing areas today in electronic ceramic manufacturing due to the worldwide revolution in microwave-based communication technologies [1-3]. In this regard, complex perovskite ceramics have been extensively studied for their applications to dielectric resonators at microwave frequencies. It is well established that complex perovskite ceramics, with the general formula Ba(B'_{1/3}B''_{2/3})O₃ (B' = Mg, Zn; B'' = Ta, Nb), exhibit very good dielectric properties at MHz range as well as GHz [4, 5]. Ba(Zn_{1/3}Ta_{2/3})O₃ (BZT) is one of the most important in this group because of its relatively high dielectric constant ($\epsilon_r > 25$), high quality factor ($Q \times f \approx 80,000-150,000$ GHz) or ultra-low loss tangent ($\tan \delta < 2 \times 10^{-5}$ at 2 GHz) and ability to achieve near-zero temperature coefficient of resonant frequency ($\tau_f \approx 0$) [6, 7]. These very attractive properties allow BZT to be used in type I multilayer capacitors (MLCC) or in high performance resonators, satellite broadcasting, super high Q dielectric resonator in mobile phone base stations, or combiner filter for personal communication system applications [8, 9].

Preparation of dielectric materials with optimal properties for wireless applications requires special thermal treatments due to the difficult control of the cationic ordering [10, 11]. The processing of BZT is, however, complex and materials loss as well as the development of Zn/Ta site ordering can occur during sintering and annealing affecting both the X-ray intensities and the microwave dielectric properties. The formation of complex oxide materials into dense ceramic resonators with optimized dielectric properties requires careful and demanding processing. BZT has excellent materials properties when processed correctly but is difficult to optimize on a commercial scale. This is a significant problem due to the cost and scarcity of Ta. The atomic-scale structure of BZT depends sensitively on the processing conditions since they control the extent to which the octahedral B sites of the parent simple perovskite are occupied in an ordered manner by the Zn and Ta cations [12]. BZT belongs to a class of compounds often referred to as 1/3:2/3 *i.e.* 1:2 complex perovskites [13, 14]. The processing and the thermal conditions are very crucial to achieve the maximum 1:2 ordering. It is known that the microwave dielectric properties of Ba(Zn_{1/3}Ta_{2/3})O₃ (BZT) ceramics are greatly affected by their structure [15]. The crystal structural ordering together with the ceramic microstructure have been found to influence the Q factor of BZT strongly [16]. It has been found that Q improvement corresponds with increased Zn and Ta ordered structures in the ceramics [17].

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BZT ceramic requires high temperature to be correctly sintered ($\geq 1450^\circ\text{C}$)^[18] moreover, as high as 1600°C or for long time ($\sim 100\text{h}$)^[19, 20]. Sintering at high temperatures led to the formation of zinc deficient phases such as, $\text{Ba}_8\text{ZnTa}_6\text{O}_{24}$, $\text{Ba}_3\text{Ta}_2\text{O}_8$ (BaTa_2O_6) due to vaporization of zinc.²¹⁻²⁸ The BZT phase formation starts at 800°C and the precursors disappear at around 1000°C . A secondary phase identified as $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ disappears at temperatures higher than 1100°C ^[29]. Finally, a 1200°C dwell temperature have to be fixed to be sure to have the cubic perovskite single phase^[24].

Powder X-ray diffraction (XRD) methods are utilized to investigate the variation of the ordering of the B-site cations with the firing conditions (annealing temperature and time)^[30-32].

This paper discusses initial processing parameters such as calcinations time, ball milling time, the effect of solvents used during ball milling in the synthesis of BZT and explore how the processing conditions influence the parameters that influence the properties of $\text{BaZn}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (BZT). The sinterability, crystalline structure, phase composition, and dielectric properties have been analyzed.

Experimental Procedure

BZT samples were prepared by solid-state reaction. The starting materials were BaCO_3 (99+ %, Sigma Aldrich, USA), ZnO (99+ %, Sigma Aldrich, USA), and Ta_2O_5 (99%, Sigma Aldrich, USA). The starting materials were dried at 500°C for 10-12 hrs in Muffle furnace. Samples were prepared by weighing the stoichiometric quantities of the constituents and processing conditions applied for samples were varied. The six samples of the batches C were ball-milled in ethanol (absolute) with zirconia balls for different

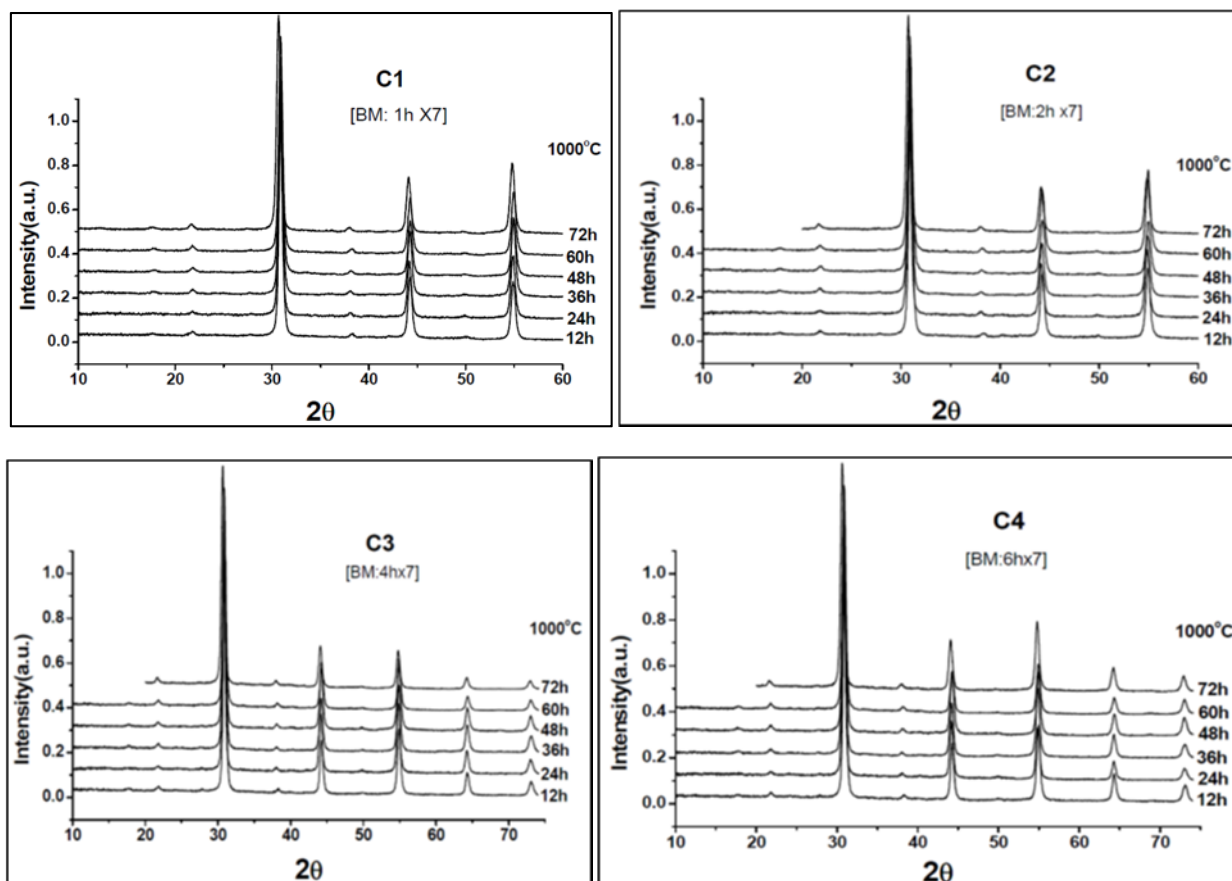
durations (1-10 hrs) x 6 times. All the samples were dried over a heating plate and then subjected to calcinations at 1000°C for 12 hrs. The processes of ball-milling for 1-10 hours (Table 1) followed by calcinations at 1000°C for 12h were repeated for six times in sequence.

The particle size of the sample powder after calcinations was measured using Dynamic Light Scattering (DLS, Zetasizer, Malvern instrument). The samples were characterized by using Bragg-Brentano (Cu-K α radiation, D8 Bruker) X-ray diffractometer and their dielectric measurements were done using C50, Alpha-A Novocontrol Broadband high performance frequency analyser.

Table 1: Ball-milling and Calcinations (BMC) details table

Samples		BMC	
		BM	Calcinations
C1 (Ethanol)	D1 (Acetone)	1h x 6	1000 °C/ (12h x 6)
C2	D2	2h x 6	
C3	D3	4h x 6	
C4	D4	6h x 6	
C5	D5	8h x 6	
C6	D6	10h x 6	

Powder X-ray of the samples (Fig.1 & 2) shows the 1:2 ordering peaks appearing at $\sim 17.5 2\theta$, after 24 hours of calcinations. Similar ordering peaks also appear for 2 hours ball milling time. However, increasing the ball-milling time (4 hours and 6 hours) shows the appearance of (100) peak even at 12 hours of calcinations. When the ball-milling time is further increased (8 hours and 10 hours) the ordering peak starts appearing only after 24 hours as can be seen from figures 12 & 13 similar to 1 and 2 hours ball milling time.



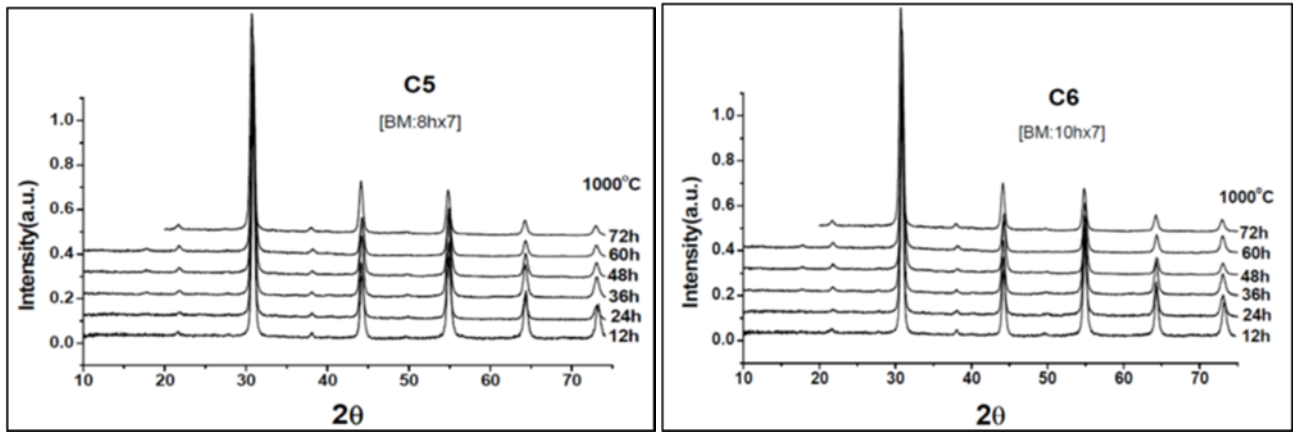


Fig 1: Powder XRD patterns of the six samples:

- C1: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 1 hour.
- C2: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 2 hour.
- C3: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 4 hour.
- C4: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 6 hour.
- C5: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 8 hour.
- C6: Calcined at 1000 °C for 12 hours with intermittent ball-milling (BM) for 10 hour.

The particle size (dnm) measurements of the calcined powders are shown in the table 2. The distribution of

particle size generally increased with increase in ball-milling. The particle size is almost in the same range.

Table 2: Particle size and density of Batch-C pellets sintered at 1475 °C.

Samples	Particle size (dnm)	Density (g/cm ³)	Density (%)
C1	342-531.2	5.6066	71
C2	342-458.7	5.8561	74
C3	295.3-396.1	5.4584	69
C4	295.3-531.2	5.4403	69
C5	295.3-531.2	5.4403	69
C6	295.3-615.1	5.5683	70

The calcined powder were compacted into pellets and the pellets were fired at 1300 °C for 12 hours to check the ordering and all the samples showed 1:2 ordered single phase. The powders were then compacted into pellets and

sintered at 1475 °C for 10 hours. Figure 2 shows the powder X-ray diffraction pattern on the surface of the sintered pellet.

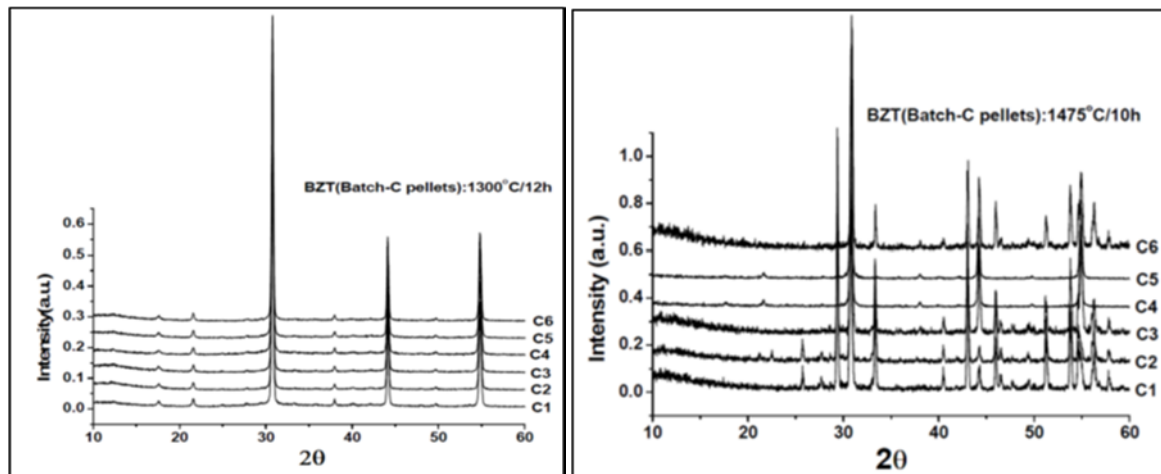


Fig 2: XRD patterns of the C1-C6: pellets sintered at 1300 °C for 12 hours and at 1475 °C for 10 hours.

The X-ray pattern is similar to the pattern reported in the literature, showing the peaks corresponding to zinc deficient phase on the surface of the pellet. All the peaks can be indexed using Ba (Zn_{1/3}Ta_{2/3})O₃ and Ba₈ZnTa₆O₂₄ patterns. The densities of the pellets were around 70 % of the theoretical density. The dielectric properties on the silver

coated pellets were measured as shown in the fig.3. The dielectric constant ε is different for all the samples, even though they all have similar densities. The dielectric loss for the all the samples were well below zero, as expected for the Ba (Zn_{1/3}Ta_{2/3})O₃.

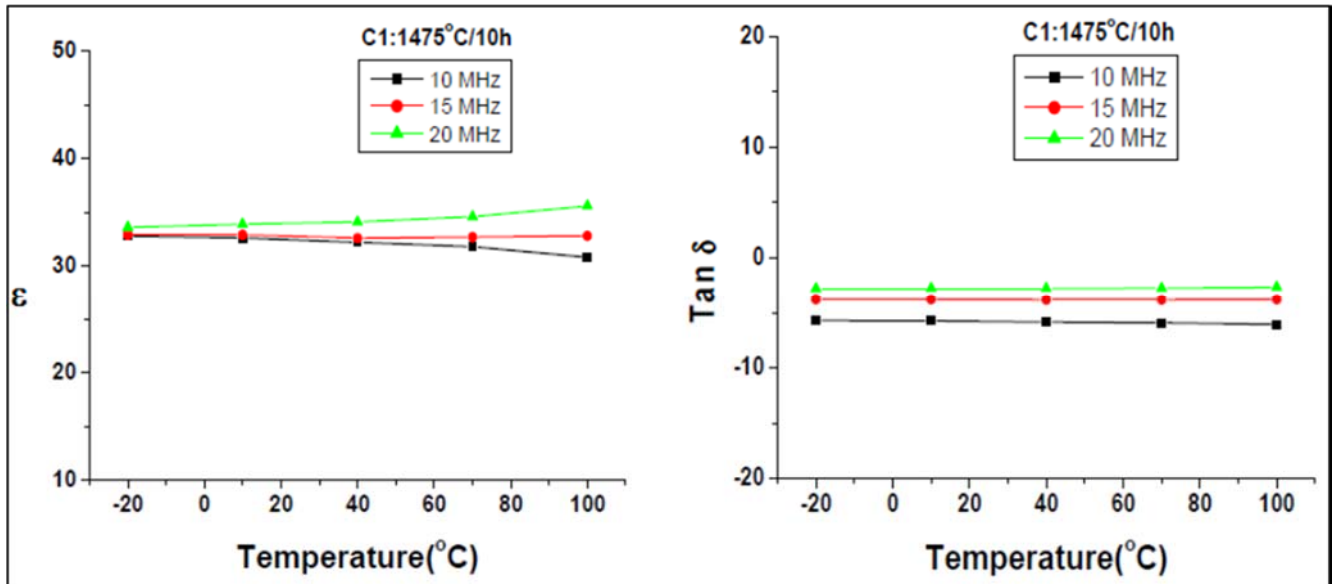


Fig 3: Plots of permittivity (ϵ) and Dielectric loss ($\text{Tan}\delta$) vs. Temperature ($^{\circ}\text{C}$) at 10 MHz, 15 MHz and 20 MHz frequencies for the C1 pellet sintered at 1475 $^{\circ}\text{C}$ for 10 hours.

Table 3: Dielectric data of the samples (C1-C6) obtained experimentally.

Samples	Density (%)	ϵ	$\text{Tan}\delta$
C1	71	32	0
C2	74	37	0
C3	69	37	0
C4	69	30	0
C5	69	30	0
C6	70	40	0

Conclusion

Sintering of the $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ samples at high temperatures led to the formation of secondary phase. The X-ray pattern is similar to the pattern reported in the literature, showing the peaks corresponding to zinc deficient phase on the surface of the pellet. The dielectric constant of the samples shows some variations with the initial processing conditions. However, the dielectric loss value is below zero for almost all the samples synthesized in this study.

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