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Synthesis of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ by Agate grinding in Acetone

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Abstract

The perovskite $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT)- currently applied in mobile telecommunications base stations, was prepared by solid-state reaction using acetone for Agate grinding. The powders were then calcined at 1000 °C for various durations. The density of (20MHz) dielectric constant (ϵ) was different for pellets with different calcinations time and the dielectric loss ($\text{Tan}\delta$) were less than zero.

Keywords: Perovskites, Tantalates; Agate grinding, XRD, Dielectric properties.

Introduction

Modern communication systems which include cellular phones and satellite communications have moved to the microwave (MW) frequency region, where advanced dielectric ceramics are frequently used in resonators and filters. 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]. It is well established that complex perovskite ceramics, with the general formula $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ ($\text{B}'=\text{Mg, Zn; B}''=\text{Ta, Nb}$), exhibit very good dielectric properties at MHz range as well as GHz. ^{4,5} $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (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].

BZT belongs to a class of compounds often referred to as 1/3:2/3 *i.e.* 1:2 complex perovskites [8, 9]. The structure of this phase is based on the simple cubic perovskite lattice in which corner shared, BO_6 octahedra describe a cuboctahedral A-site interstice [10]. BZT can form disordered-type structure with a cubic space group of $\text{Pm}\bar{3}\text{m}$ and ordered-type structure with a trigonal space group of $\text{P}\bar{3}\text{m1}$ depending on the processing and the temperature conditions [11]. The processing and the thermal conditions are very crucial to achieve the maximum 1:2 ordering. Dense ceramics (density ≈ 7.76 g/cm³) has been obtained in the ordered perovskite with the relatively larger grain (1.0–1.5 μm). Whereas the disordered perovskite has the lower density (density ≈ 5.0 g/cm³) with the smaller grain size (0.4–0.6 μm). Thus these two factors strongly relate each other in the BZT system.

Preparation of dielectric materials with optimal properties for wireless applications requires special thermal treatments due to the difficult control of the cationic ordering [12, 13]. 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. 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 [14]. 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 [15]. Finally, a 1200 °C dwell temperature have to be fixed to be sure to have the cubic perovskite single phase [16]. 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) [17-20].

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This paper discusses initial processing parameters in the synthesis of BZT such as influence of Agate grinding, the effect of solvents used and calcinations time. 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. A batch of samples (A) was prepared by weighing the stoichiometric quantities of the constituents. The stoichiometrically weighed raw materials were ground in acetone to homogenize using Agate mortar and pestle for half an hour. The powders were then calcined at 1000 °C for various durations as shown in the table 1. 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: Calcinations, Particle size, and density data of batch-A samples.

Sample No.	Calcinations	Particle size*1 (dnm)	Density*2 (g/cm ³)	Density (%)
A1	1000 °C/12h	220.2-295.3	4.8658	62
A2	1000 °C/24h	295.3-458.7	4.9473	63
A3	1000 °C/36h	122.4-531.2	5.0579	64
A4	1000 °C/48h	255-396.1	5.0589	64
A5	1000 °C/60h	255-615.1	5.0980	64
A6	1000 °C/72h	220.2-396.1	5.0487	64
A7	1000 °C/84h	255-458.7	5.4352	69

Particle size*1: After calcinations of batch-A powder at 1000°C for 12-84 hrs.

Density*2: After sintering the batch-A pellets at 1475°C/10h

Result and Discussion

The calcinations for all the samples were done, to ensure that they all form a single phase, which was monitored using powder X-ray diffraction pattern. Figure 1 shows the powder X-ray pattern of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ powder synthesized by hand ground with acetone in an agate –mortar and pestle. Seven different samples were prepared in each case the starting materials were ground with acetone before calcinations, the calcination was done at 1000 °C for 12 hours. After every twelve hours the powders were hand ground again with acetone before loading it in the furnace for the next cycle of 1000 °C for 12 hours. This was done to monitor exactly initial time of calcinations required and the corresponding dielectric properties. As shown in the Figure 1 all the patterns show single disordered cubic phase corresponding to $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$, there is no secondary phase and no appreciable evidence for 1:2 ordering at this temperature, in spite of longer calcinations time (e.g. 84 hours), with intermittent grinding).

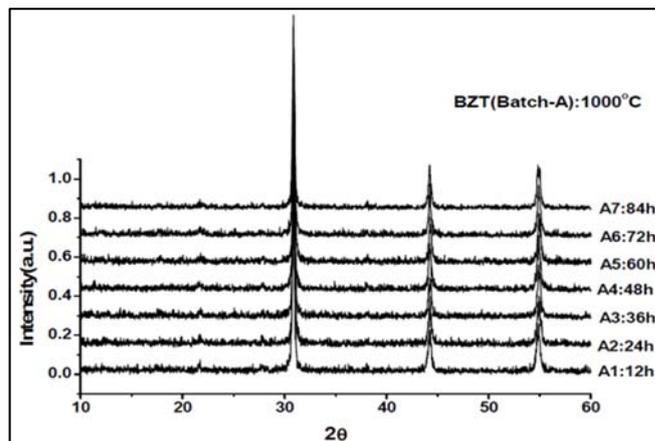


Fig 1: Powder XRD pattern of batch –A: Calcined samples at 1000°C for different duration (12-84 hours).

The particle size distribution of the calcined powders was measured, as the time of calcinations increased (Table 1) the particle distribution slightly increased with particle size. The calcined powders were compacted into pellets and the pellets were sintered in air at 1475 °C for 10 hours. Fig. 2 shows the powder X-ray diffraction pattern on the surface of the sintered pellet. 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 $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}_8\text{ZnTa}_6\text{O}_{24}$ patterns.

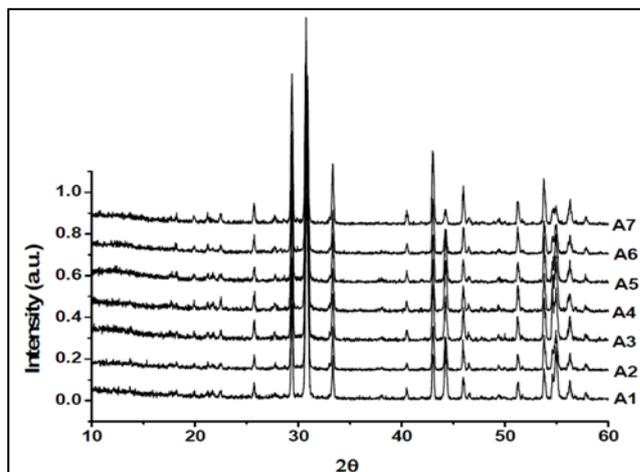


Fig 2: Powder XRD patterns of BZT pellets (A1-A7) sintered at 1475°C for 10 hours.

The densities of the pellets were around to 65% of the theoretical density. The dielectric properties on the silver coated pellets were measured (Fig. 3). The dielectric constant ϵ is different for all the samples, even though they all have similar densities. This is very interesting fact that the particle size and calcinations time have a real impact on the dielectric constant. The dielectric loss for all the samples are well below zero, as expected for the $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$.

Dielectric measurements (Plots)

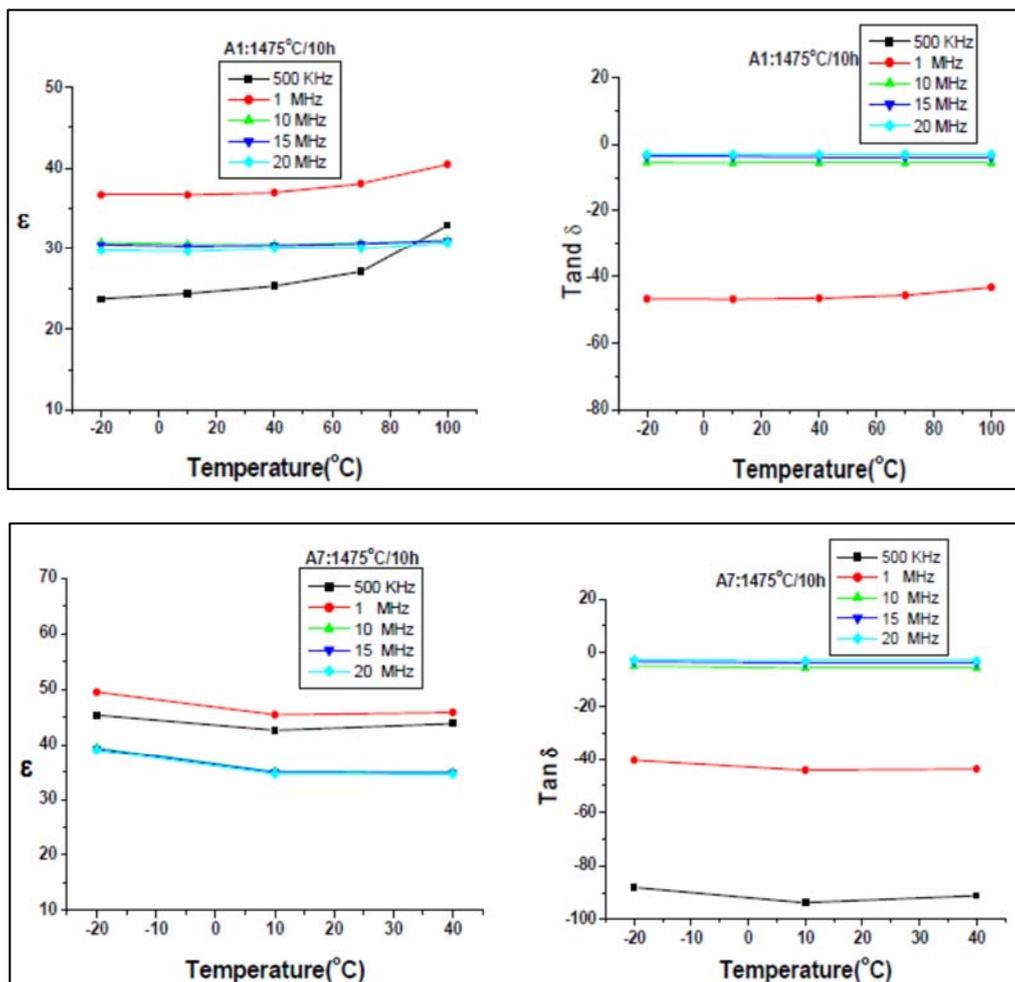


Fig 3: Plots of permittivity (ϵ) and Dielectric loss ($\text{Tan}\delta$) vs. Temperature ($^{\circ}\text{C}$) at 500 KHz, 1 MHz, 10 MHz, 15 MHz and 20 MHz frequencies for the A1 & A7 pellets sintered at 1475 $^{\circ}\text{C}$ for 10 hours.

Conclusion

The calcinations time does make a real difference in the dielectric properties. 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 dielectric constant of the samples shows some variations with the processing conditions. However, the dielectric loss value is below zero for almost all the samples synthesized in this study.

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