

8Y-Stabilized Cubic Zirconia Addition Effect on Barium Titanate

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Abstract: The addition effect of 8Y- stabilized cubic zirconia (8YSZ) on Barium Titanate ($BaTiO_3$) with molar ratios of $x = 0.025, 0.05, 0.1$ was studied using the mixed solid oxides method. The preparation was completed by high temperature solid state reaction at a sintering temperature of 1300°C , 1350°C and 1370°C . X- ray diffraction (XRD) measurements confirmed the presence of single-phase perovskite like structure for the sintered samples. The microstructure observations by scanning electron microscopy (SEM) revealed the sensitivity of the grain growth with the heating schedul of sintering. The electrical conductivity of the different samples had been elucidated by ac measurements as a function of temperature. The dielectric results show high increase of the dielectric constant with some decrease of the curie temperature.

Keywords: Barium Titanate Zirconate; Dielectric properties; Lead free ceramic Capacitor; Positive temperature coefficient thermistors; Piezoelectric Transducers

1. Introduction

Perovskite type mixed oxides such as: $PbTiO_3$, $Pb(Zr,Ti)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$...etc had been found to be extensively useful because of their excellent ferroelectric properties. However, in order to minimize the use of toxic lead, several other materials had been investigated⁽¹⁾. Barium Titanate (BT) Perovskite structure is a common ferroelectric material with a high dielectric constant, lead free, environmental friendly material, widely utilized to manufacture electronic components such as: multilayer capacitor, positive temperature coefficient thermistors; piezoelectric transducers, and variety of electro-optic devices^(2,3). The high dielectric constant of barium titanate makes it an especially desirable material is the fact that its electrical properties can be controlled within a wide range by means of mixed crystal formation and doping. Electrolytic capacitors are the first to be considered when large blocks of capacitance are needed in electrical circuits. Other capacitors offer such a large capacitance per unit volume at a low cost. Electrolytic capacitors are deservedly popular in bypass, blocking and power supply filter applications and for motor starting purpose⁽²⁾.

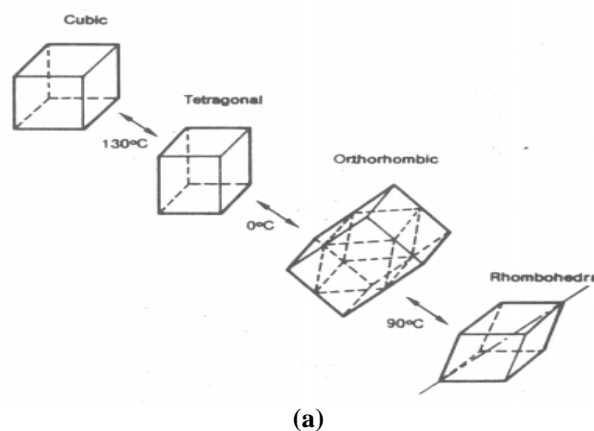
Barium titanate powder is usually mixed with various types of additives in order to obtain better performances and a good control over grain size and electrical characteristics of ceramics. It has been found that the dielectric properties of polycrystalline barium titanate depend to a great extent on the grain growth during sintering and on additive type and concentration. Additives which change the microstructure can also modify the dielectric properties of barium titanate ceramics

Barium Titanate ($BaTiO_3$) is known to have a large electrochemical coupling factor. The substitution of Ti^{4+} (atomic weight of 47.9, ionic radius of 0.0745nm) with Zr^{4+} (atomic weight of 91.2, ionic radius of 0.086nm) exhibit several interesting dielectric behavior of $BaTiO_3$ ceramics. At Zr content less than 10 mole%, this Barium Zirconate Titanate (BZT) ceramics show normal

ferroelectric behavior and dielectric anomalies corresponding to cubic to tetragonal (T_c), tetragonal to orthorhombic (T_2), and orthorhombic to rhombohedral (T_3) phase transition⁽⁴⁾.

Barium Zirconate Titanate (BZT) ceramics are attractive candidates for dynamic random access memories and tunable microwave devices, as a storage capacitor for the next DRAM generation, and the dielectric material for the Multi Layer Ceramic Capacitor (MLCC)⁽⁴⁻⁶⁾.

The ferroelectric nature of barium titanate related to its tetragonal crystal structure results in high dielectric constants. Above the so-called Curie temperature, the change in crystal structure from tetragonal to cubic (for pure barium titanate at 130°C), the dielectric constant drops down strongly. Figure (1) represents the Phase transition of barium titanate, and the cubic perovskite structure of barium Titanate from the (a) origin on titanium, (b) origin on barium ion.



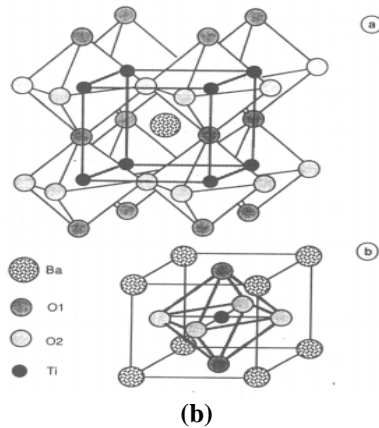


Figure 1: Phase transition of barium titanate, cubic perovskite structure of barium titanate, (a) Origin on titanium, (b) Origin on barium ion, ref. (7)

Studies on the effect of Zirconium addition to barium titanate show that the zirconium addition shifted the curie point and depressed the dielectric peak. Addition of zirconia particles into barium titanate can form a core-shell structure, which can exhibit temperature-stable dielectric behavior.

The aim of this work is to study the addition effect of 8Y-stabilized cubic zirconia on the barium titanate as a traditional important powder, and investigate the resulted dielectric constant with the different temperatures.

2. Experimental Work

Calculated amounts of molar weights of pure commercial BaTiO₃ (from Alfa Aesar, Karlsruhe, Germany) and 8Y-

SZ (Tosoh, Japan) were mixed to prepare the different samples of the composition: Ba (Zr_x Ti_{1-x} Y_{0.08x}) O_{3-δ}, where x= 0.025, 0.05, 0.1, and δ = 0.08x/2, by the conventional solid state reaction technique. The powders were mixed in alcohol and then dried at 100°C for 24h, before pressing using a uniaxial pressing (Hydraulic press – Perkin Elmer) to form pellets of 1cm diameter and 2mm thick. The pressed pellets were then sintered at different sintering temperatures. The phases of the resulting products were analyzed with X-ray diffraction (XRD), (3A Shimadzu – Japan).

For the electrical measurements, the different samples were painted with Pt. paint on the two sides of the pellets, to make the two electrodes, and then heated to 900°C for 1h. For some samples I used a carbon conductive sheet instead of the Pt past to expire the difference between them. The electrical measurements were done using RCL meter [Philips, PM6304] in air at temperatures ranging from room temperature to 180°C. The microstructures of the different samples were observed by the Scanning Electron Microscope (SEM), [JEOL - Japan, JSM 5400].

3. Results and Discussion

1. XRD Analysis

Figure 2 illustrates the XRD pattern for the BZT ceramics sintered at 1350°C for 2h. The sintered density of the sample was 5.6 g/cm³, i.e. about 93% of the theoretical density. The XRD pattern shows a single phase tetragonal perovskite structure, in agreement with F.Moura, et.al.⁽⁴⁾.

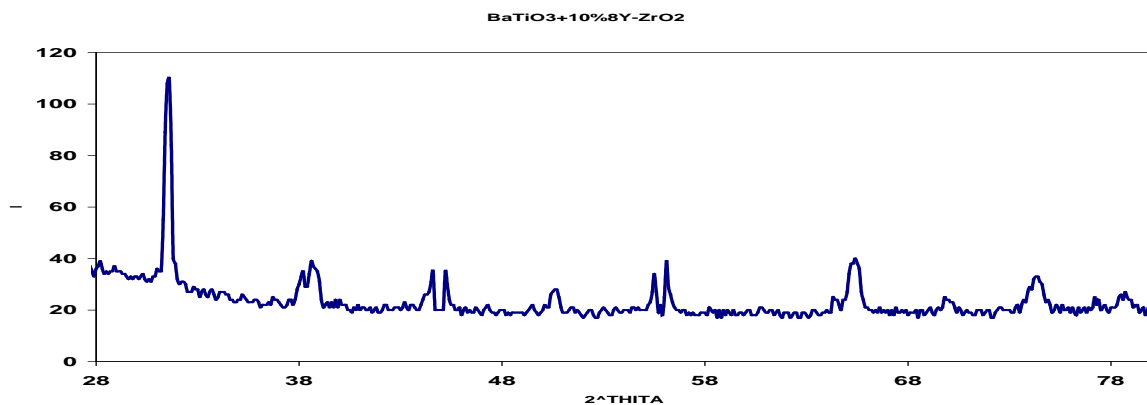


Figure 2: XRD pattern of the barium titanate with 10 mol. % 8YSZ

2. Electrical

Figure (3) (a &b) give the relative permittivity and the dielectric losses respectively for zirconium barium Titanates, (BaTi_{0.9}Zr_{0.1}Y_{0.008} O_{3-δ}) sintered at 1300°C, 1350°C and 1370°C. The highest relative permittivity detected for these samples are at the temperature ≤100°C, and the values are about 20000 for the samples sintered at 1300°C and 1370°C, and increased to about 20000 for the sample sintered at 1350°C. The dielectric losses ranged from 0.1 and 0.15 for the sample sintered at 1300°C, and

ranged from 0.2 and 0.25 for the sample sintered at 1370°C. It ranged from 0.3 to 0.4 for the sample sintered at 1350°C at temperatures ≤ 100°C, and decreased to about 0.2 at temperatures ≥ 105°C.

Figure (4) (a &b) give the relative permittivity and the dielectric losses of zirconium barium Titanates, (BaTi_{0.95}Zr_{0.05}Y_{0.004} O_{3-δ}) sintered at 1350°C with no holding time at this temperature, but holding time at 1100°C. The highest relative permittivity detected for this sample is at 130°C, (Curie temperature), and the values are

about 3000 and 4000, but these values increased to about 20000 to 30000 after resintering at 1350°C with holding time at this temperature for 2hrs. The dielectric losses is around 0.15, but these losses increased clearly when a carbon conductive sheet was used as an electrodes instead of the platinum paste to values from 0.2 to 0.8.

Figure (5) gives the relative permittivity and the dielectric losses of zirconium barium Titanates, ($BaTi_{0.975}Zr_{0.025}Y_{0.002}O_{3-\delta}$) sintered at 1350°C with no holding time at this temperature, but holding time at 1100°C. The highest relative permittivity detected for this sample is at temperature 130°C, (Curie temperature), and the values are about 4500 with the platinum electrodes, and about 5000 to 6000 with the carbon conductive sheet as electrodes. The dielectric losses were generally low for this sample, ranging from 0.02 to 0.04.

All the measurements show clear increase in the relative permittivity with respect to the pure barium titanate which had been measured in a previous study⁽⁸⁾ which gave a highest relative permittivity about 10000.

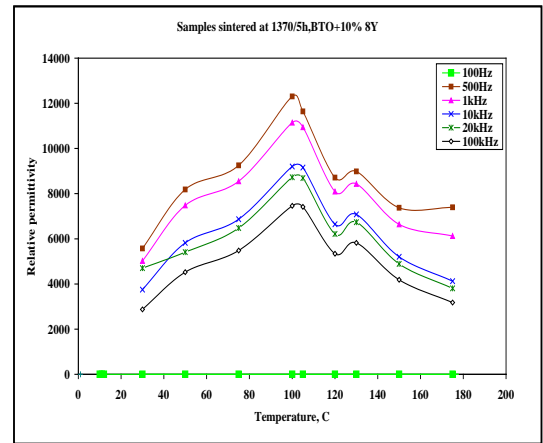


Figure (3-a): Relative permittivity of $BaTi_{0.9}Zr_{0.1}Y_{0.008}O_3$ sintered at 1300°C 1350°C and 1370°C.

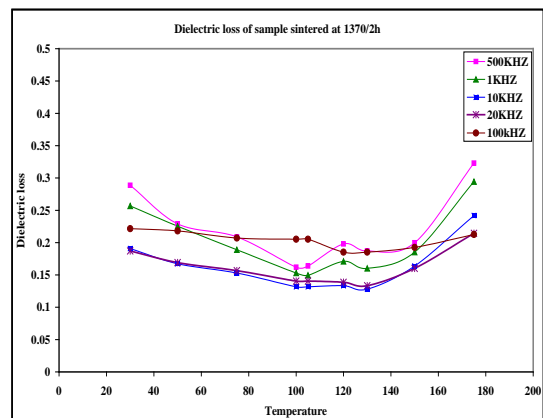
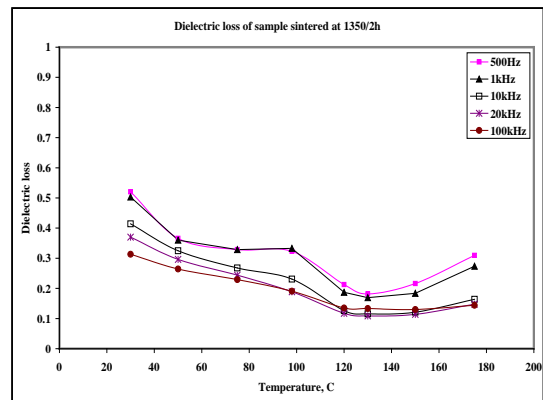
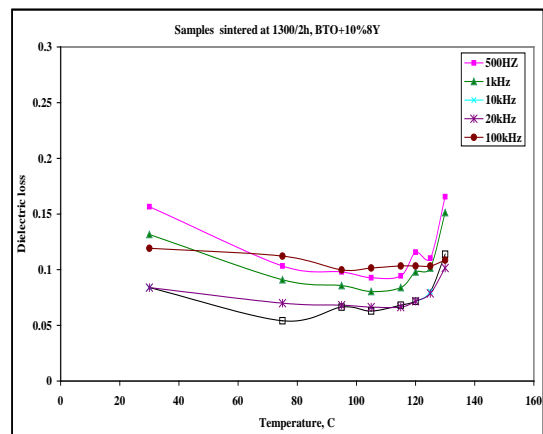
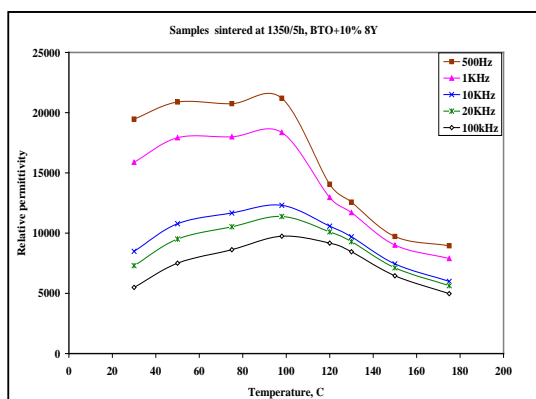
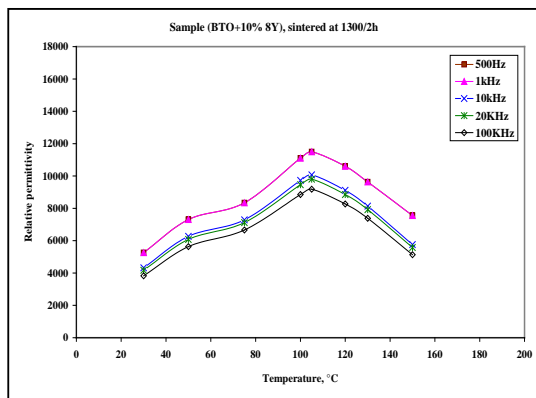


Figure (3-b): Dielectric losses of $BaTi_{0.9}Zr_{0.1}Y_{0.008}O_3$ sintered at 1300°C, 1350°C and 1370°C.

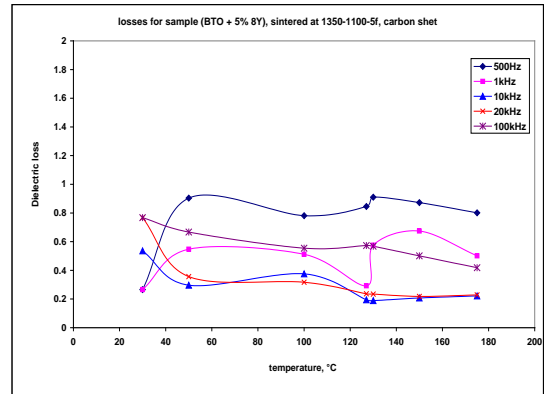
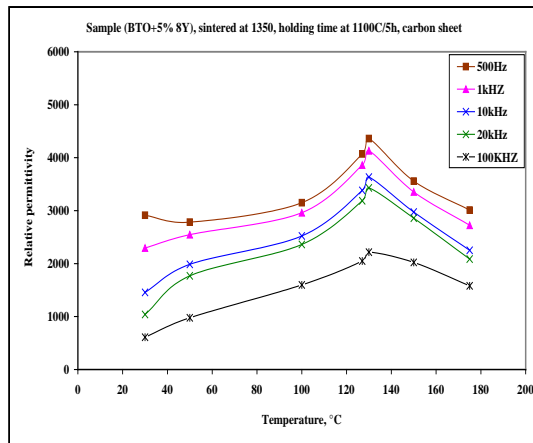
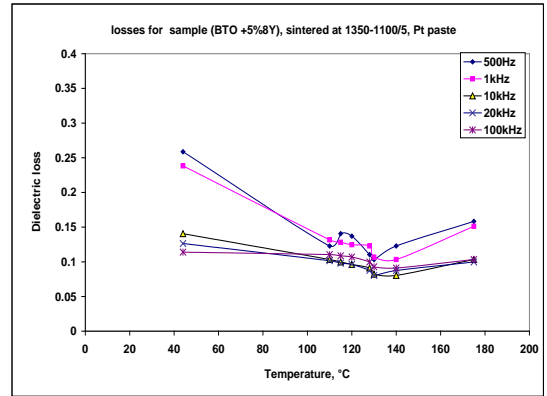
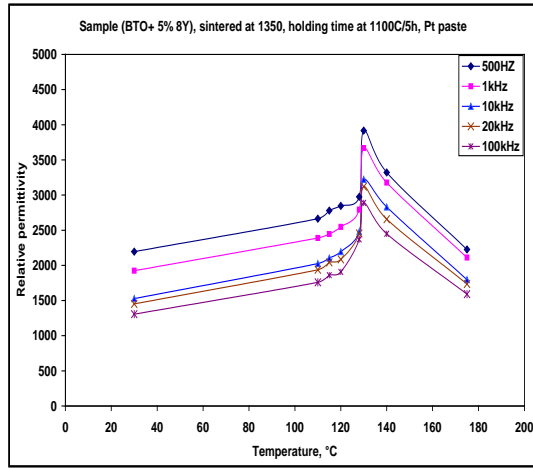


Figure (4-b): Dielectric losses of $BaTi_{0.95}Zr_{0.05}Y_{0.004}O_3$ sintered at $1350^{\circ}C$

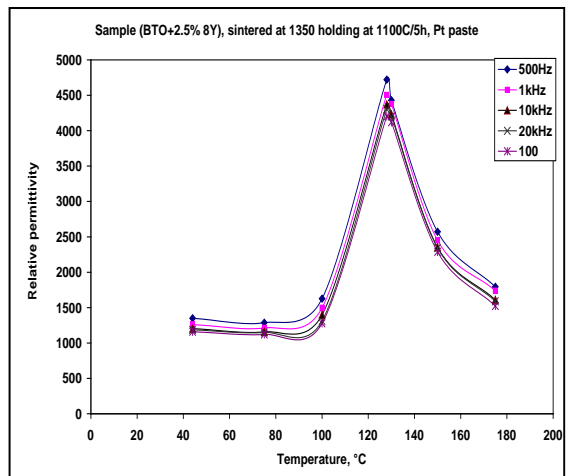
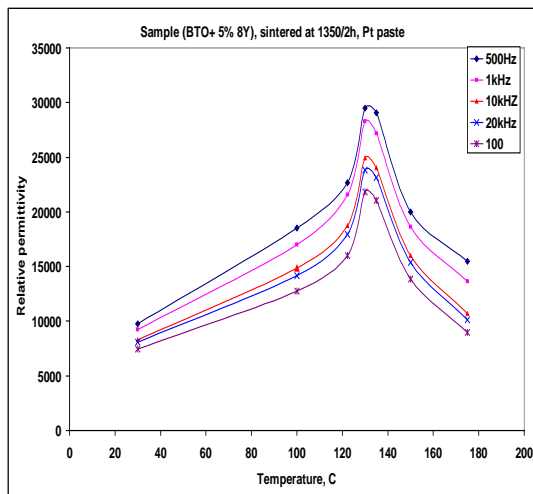
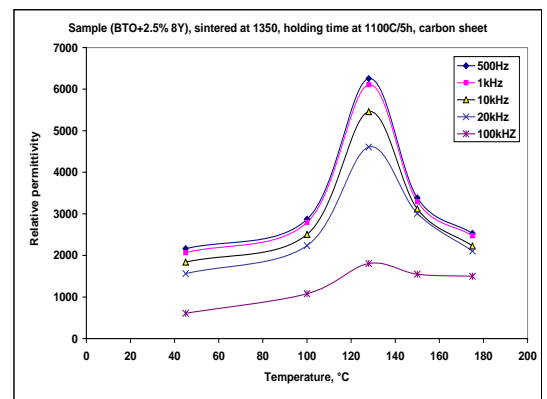


Figure (4-a): Relative permittivity of $BaTi_{0.95}Zr_{0.05}Y_{0.004}O_{3-\delta}$ sintered at $1350^{\circ}C$



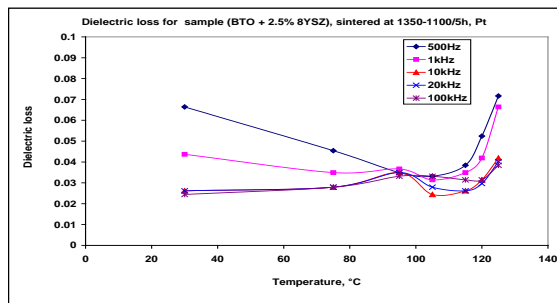


Figure (5): Relative permittivity and dielectric losses of $\text{BaTi}_{0.975}\text{Zr}_{0.025}\text{Y}_{0.002}\text{O}_3$ sintered at 1350°C

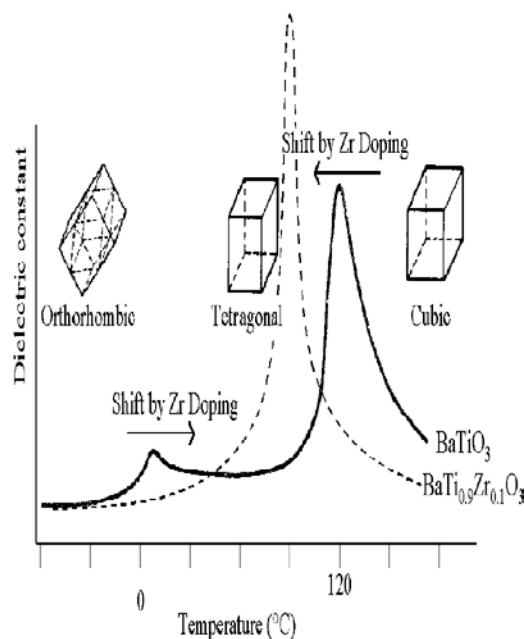


Figure (6): Schematic diagram showing the effect of Zr doping of BaTiO_3 on the dielectric properties⁽⁷⁾

F. Moura et al.⁽⁴⁾ reported that Zirconium is an effective substituent in BaTiO_3 to decrease and shift the Curie temperature. Moreover, Zr^{4+} ion is chemically more stable than Ti^{4+} ion and has a large ionic size to expand the perovskite lattice. Therefore, the substitution of Ti by Zr would depress the conduction by electronic hopping between Ti^{4+} and Ti^{3+} , and it would also decrease the leakage current of the BaTiO_3 system. It was reported that an increase in the Zr content induces a reduction in the average grain size, decrease the dielectric permittivity ϵ_r maintaining a low and stable leakage current^(4,5).

V. Vinothini et al.⁽⁹⁾ reported that BaTiO_3 at room temperature has a Perovskite tetragonal crystal structure with large barium ion (Ba^{2+}) on the corners of the unit cell, oxygen ions (O^{2-}) in the face centers forming an octahedral arrangement and an off-centered small titanium cation (Ti^{4+}). Partial substitution of Ti^{4+} with Zr^{4+} , which has a larger ionic radius, forms the solid solution $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$, with an associated increase in the lattice parameter and consequent change in the crystal structure, phase transition temperatures and the dielectric properties compared to pure BaTiO_3 . Previous research performed using submicron-sized powders had suggested that BZT remains tetragonal at Zr additions up to 0.2 mol. %, then change to pseudo monoclinic over the range 0.2 – 0.6 mol. % before

becoming rhombohedral at Zr substitution levels up to ~ 20 mol. %. Above 20 mol.% of Zr additions, BZT is cubic at room temperature⁽⁹⁾. While pure BT undergoes a sharp ferroelectric to paraelectric (tetragonal to cubic) transition at 130°C , BZT ceramics with up to 10 mol.% of Zr exhibit a similar behavior with a shift in the phase transition temperature from 130°C to 110°C ⁽⁷⁾, that is in agreement with our results. V.Vinothini et al.⁽⁹⁾ also added that these phase transition temperatures and phase boundary compositions will be dependent on the crystallite size of the primary particles. As the particle size is reduced to approximately that of the domain size of around tens of nanometers, the particles tend to stabilize to the nearest high symmetry crystal structure (cubic), presumably because of the high surface energy. The critical particle size at which this occurs is still unknown and seems to vary depending on the synthesis route used⁽⁹⁾. V.Vinothini et al.⁽⁹⁾ used a microwave assisted heating to synthesis a nanopowders of BZT with a former requiring lower temperature and shorter times compared to the conventional heating ($700^\circ\text{C} / 30 \text{ min}$, versus $900^\circ\text{C} / 5 \text{ h}$ for the conventional), and added that the microwave synthesized BZT compositions were found to have well crystallized, finer nanoparticles with less agglomeration and higher dielectric permittivity compared to the conventionally prepared powders.

N. Binhayeeniyi et al.⁽¹⁰⁾ prepared BZT, $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.0 - 0.2$), using a sol-gel process and sintering aid – 1.5 wt% Lithium oxide (Li_2O) and a firing temperature lower by about 30 % to $900^\circ\text{C} / 4 \text{ hrs}$, without any degradation of the electromechanical properties. They⁽⁸⁾ observed a highest dielectric constant beak for $x = 0.05$ at temperature 103°C , about 9500. The curie temperature of the beaks decreased with increasing zirconium values, x , and reached about 40°C at $x = 0.2$.

3. SEM Analysis

SEM micrographs in the back scattered electron mode show the microstructure of the sintered samples, are shown on Figure (7). These micrographs show a relatively dense and homogeneous material. The grain growth of the samples sintered at 1350°C , with holding time for 5 hrs at 1100°C , is higher than that for the samples sintered at 1350°C for 2 hrs.

P.Zheng et al.⁽¹¹⁾ studied the grain-size effects on the dielectric and piezoelectric properties of poled BaTiO_3 ceramics and concluded that dielectric and piezoelectric constant increases significantly at room temperature with the reduction of the average grain size. This can explain the high permittivity constant of the sample sintered at 1350°C for 2 hrs measured at room temperature, Figure (3-a).

4. Conclusions

- (1) The barium zirconate titanate (BZT) ceramics prepared through a solid state reaction between barium titanate and 8Y-cubic stabilized zirconia, sintered at 1300°C were investigated.

- (2) The room temperature X- ray diffraction patterns of the sintered samples show the presence of a single phase structure. The dielectric properties of the different samples had been elucidated by RCL meter as a function of temperature.
- (3) The dielectric constants measured for the different samples showed clear increase of the dielectric constant with some decrease of the curie temperature.
- (4) The microstructure observations by scanning electron microscopy (SEM) revealed that the grain growth depend on the heating schedule used for the sintering.

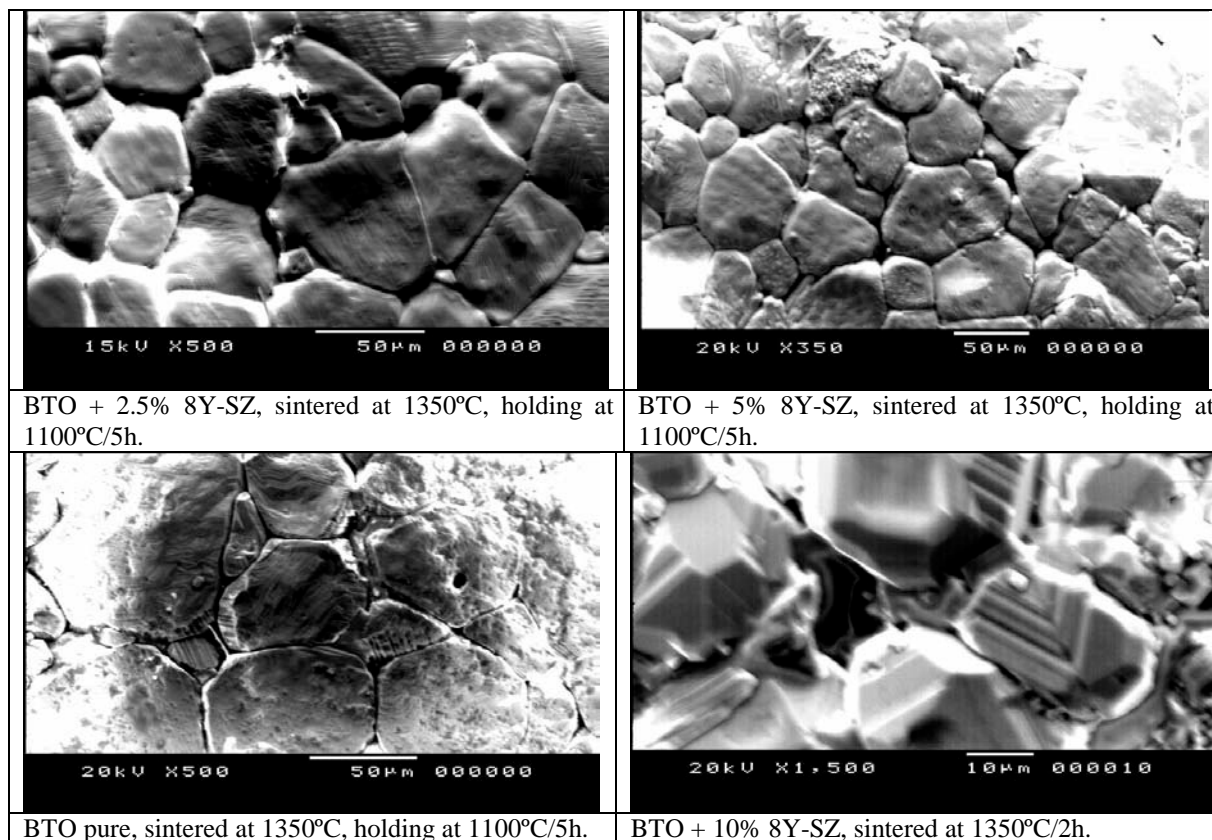


Figure 7: Microstructure by SEM of the different sintered samples

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