

Stabilizing the Barium Titanate by Different Kinds of Zirconia

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Abstract

The addition of 30 mol% of different zirconia containing powders: cubic stabilized zirconia (8YSZ), tetragonal zirconia (TZ3Y), and TZ3Y+20 wt.% Al₂O₃ (3Y-20A) to barium titanate (BaTiO₃) was studied. X-ray diffraction analysis of the sintered compact made of these powder mixtures confirmed the presence of single phase perovskite-like structure. The microstructure of the sintered samples showed different grain sizes, for different kinds of zirconia additives. The relative permittivity and the dielectric loss of the sintered pellets were measured at zero and room temperatures. The highest relative permittivity was obtained for samples having 30 mol% TZ3Y. It was 5300 at zero temperature and 2250 at room temperature at 1kHz. The samples sintered at 1350°C showed lower values of the dielectric losses than those sintered at 1400°C.

Index Terms: Stabilized Barium Titanate Zirconate, solid-state reaction, dielectric properties.

1 INTRODUCTION

Perovskite type mixed oxides such as: PbTiO₃, Pb(Zr,Ti)O₃, Pb(Mg_{1/3} Nb_{2/3})O₃ ...etc. had been found to be extensively useful due to their excellent ferroelectric properties. However, in order to minimize the use of toxic lead, several other materials had been investigated [1,2]. Barium Titanate (BT) of Perovskite structure is a common ferroelectric material with a high dielectric constant, lead free, environmental friendly material, and widely utilized to manufacture electronic components [3,4]. Barium titanate powder can be mixed with various types of additives to control the grain size and to obtain better electrical characteristics of the ceramic. It has been found that the dielectric properties of polycrystalline barium titanate depend mainly on the grain size, the additive type and its concentration [6-8]. Many researchers studied the doping effect of different additives to barium titanate on the dielectric properties [9,10].

Zirconia is one of the most attractive additives that affect the dielectric behavior of BaTiO₃ ceramics. This behavior results from the substitution of Ti⁴⁺ (atomic weight of 47.9, ionic radius of 0.0745nm) with Zr⁴⁺ (atomic weight of 91.2, ionic radius of 0.086nm) [5]. BaTiO₃ at room temperature has a Perovskite tetragonal crystal structure with large barium ions (Ba²⁺) on the corners of the unit cell, oxygen ions (O²⁻) in the face centers forming an octahedral arrangement and an off-centered small titanium cation (Ti⁴⁺) [6]. Partial substitution of Ti⁴⁺ with Zr⁴⁺, which has a larger ionic radius, forms the solid solution BaZr_xTi_{1-x}O₃, 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 BaTiO₃. F. Moura et. al.[5] and V.Vinothini et al [10] reported that substitution of Zirconium for titanium in BaTiO₃, decreases

and shifts the Curie temperature. Moreover, Zr⁴⁺ ion is chemically more stable than Ti⁴⁺ 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 Ti⁴⁺ and Ti³⁺, and it would also decrease the leakage current of the BaTiO₃ system. Barium Zirconate Titanate (BZT) ceramics are attractive candidates for dynamic random access memories and tunable microwave devices, and dielectric material for the Multi-Layer Ceramic Capacitor (MLCC) [11].

Different powders were used for the preparation of BZT. V.Vinothini et al. [10] used a microwave assisted heating to synthesis nano-powders of BZT with a former requiring lower temperature and shorter times compared to the conventional heating (700°C/30min versus 900°C/5h for the conventional). Their 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.[11] prepared BZT, BaZr_xTi_{1-x}O₃ (x = 0.0-0.2), using a sol-gel process and sintering aid-1.5 wt.% Lithium oxide (Li₂O) at a firing temperature lower than that of the conventional method by about 30 % i.e. 900°C/4h, without any degradation of the electromechanical properties. They observed that the highest dielectric constant value (about 9500) was at x = 0.05 at temperature 103°C. The curie temperature of the peaks decreased with increasing zirconium fraction x, and reached about 40°C at x = 0.2.

T. Badapanda et al., [13] prepared the composition Ba_{1-x}

$x\text{Ti}_{2/3x}\text{Ti}_{0.75}\text{Zr}_{0.25}\text{O}_3$ (where $x=0, 0.01, 0.025, 0.05$), through the solid state reaction. They recorded a decrease of the permittivity, of the maximum peak, from 6000 at $x=0$ to values ranged from 1200 to 2000 for the other compositions, while the Curie temperature were 260, 290, 220, and 170°C at $x=0, 0.01, 0.025, 0.05$, respectively. Molokhia et al.[14], studied the dielectric constant and the dissipation factor for barium titanate doped with ytterbium oxide (Yb_2O_3) with different concentrations (0-6 mol%). They found that when adding 6 mol% of Yb_2O_3 , the dielectric constant of barium titanate decreased from 4000 for undoped barium titanate to 500 (at Curie temperature). The grain size decreased from 25.7 μm for undoped barium titanate to 1.9 μm , while the Curie temperature decreased to room temperature through the structure transformation from tetragonal to cubic.

The aim of this work is to study the effect of the addition of 30 mol% of 8YSZ, TZ3Y, and TZ3Y-20wt.% Al_2O_3 commercial powders to the barium titanate, on the dielectric properties.

2. Experimental Procedure:

Calculated amounts of commercial BaTiO_3 (from Alfa Aesar, Karlsruhe, Germany) were mixed with 30 mol% of either 8YSZ, TZ3Y, TZ3Y-20A (Tosoh, Japan) to prepare different samples having the composition: $\text{BaTi}_{0.7}\text{Zr}_{0.276}\text{Y}_{0.024}\text{O}_{2.988}$, $\text{BaTi}_{0.7}\text{Zr}_{0.291}\text{Y}_{0.009}\text{O}_{2.9955}$, and $\text{BaTi}_{0.7}\text{Zr}_{0.2328}\text{Y}_{0.072}\text{O}_{2.9673} + 20\text{wt}\% \text{Al}_2\text{O}_3$ 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 press (Hydraulic press-Perkin Elmer) to form pellets of 1cm diameter and 2mm thick. The pressed pellets were then sintered at 1350°C and 1400°C for 2hrs in air. X-ray diffractometer (XRD-3A, Shimadzu-Japan, $\text{CuK}\alpha$ -Ni filter) was used for phase analysis. The densities of the samples were determined by Archimedes method. The microstructures of the different samples were observed by the Scanning Electron Microscope (SEM), [JEOL - Japan, JSM 5400]. 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. In some samples carbon conductive sheet was used instead of the Pt paste for comparison. The dielectric properties of the sintered ceramics were investigated with RCL (Resistance-Capacitance-Inductance) meter (Philips, PM6304) over the temperature range from room temperature to 180°C with a frequency ranging from 500Hz to 100 kHz.

An equimolar mixture of BaCO_3 (99% purity, Aldrich Chemical Company, USA) powder and a very fine titanium dioxide (TiO_2) were used as the starting materials. The fine TiO_2 powder was prepared from TiCl_4 (Aldrich Chemical Co. Ltd., Gillingham-Dorset-England) by oxidation and hydrolysis. Slurry of BaCO_3 - TiO_2 powder mixture in alcohol was milled in the planetary mill (Retsch PM400-Fritsch, Germany) for 7.5h. The milling speed was set at 200 rpm. The milling was stopped for 5 min every 30 min of milling to cool down the mill. After milling the slurry was dried at 90°C for 20h in the drying Furnace (NEY Furnace, M-525). The dried powder was then crushed in agate mortar (Fritsch, Germany) followed by sieving using 112 μm sieve. The sieved powder was calcined in Carbolite Furnace, GPC 1300, UK at temperatures from 600 to 900°C for different times, with a heating rate of 10°C/min. The thermal analysis was studied using differential thermal analyzer (DTA-50), the thermo-gravimetric analyzer (TGA-50) and the

thermo-mechanical analyzer (TMA-50) from Shimadzu-Japan. X-ray diffractometer (XRD-3A, Shimadzu-Japan, $\text{CuK}\alpha$ -Ni filter) was used for phase analysis. Powder morphology, agglomerations, grain size and the as-fired surfaces of the sintered bodies were examined using a Scanning Electron Microscope (JEOL, JSM 5400, Japan).

3. Results and Discussion

3.1. XRD Analysis

Figure (1,a-c) shows the XRD patterns of the different samples sintered at 1350°C: (a) pure BaTiO_3 , in which the main peaks detected belong to the tetragonal BaTiO_3 phase[14], (b) cubic phase of: $\text{BaTi}_{0.7}\text{Zr}_{0.276}\text{Y}_{0.024}\text{O}_{2.988}$ due to the addition of 30 mol% of 8YSZ, (c) cubic phase of: $\text{BaTi}_{0.7}\text{Zr}_{0.291}\text{Y}_{0.009}\text{O}_{2.9955}$ due to the addition of 30 mole % of TZ3Y. (d) cubic phase of $\text{BaTi}_{0.7}\text{Zr}_{0.2328}\text{Y}_{0.072}\text{O}_{2.9673}$ due to the addition of 30 mole % of (TZ3Y -20 wt% Al_2O_3).

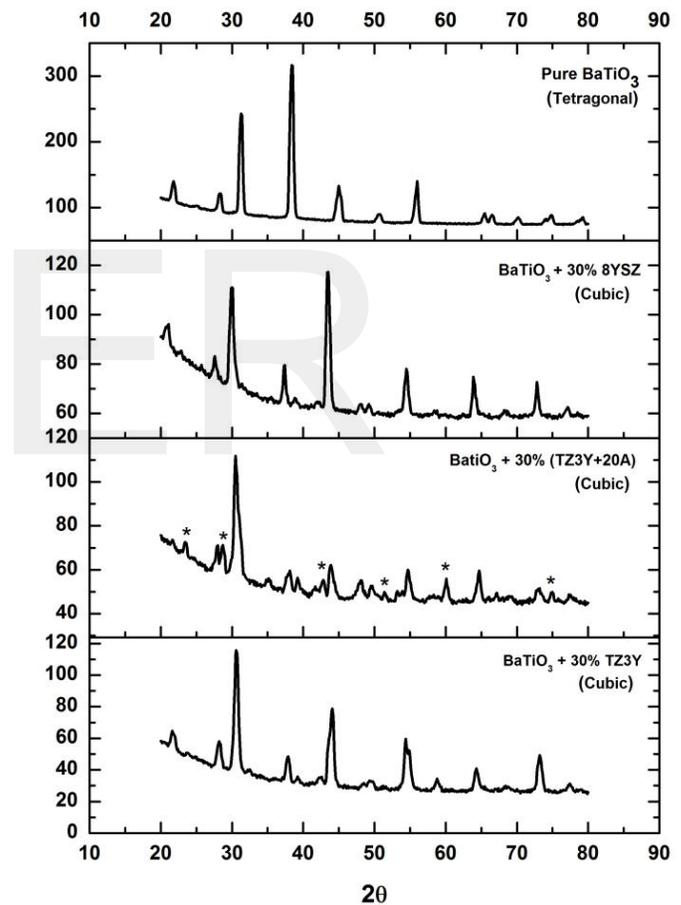


Figure 1: XRD patterns of the sintered barium titanate: pure and with 30 mol% of different additives sintered at 1350°C.

The small remarked peaks are referred to the formation of the BaAl_2O_4 compound, and the monoclinic $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$ phase. This is in agreement with the results obtained by Jiansirisomboon et al.[15], who studied the addition effect of nano particles of Al_2O_3 to the barium titanate and detected the formation of BaAl_2O_4 and $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$ phases due to the reaction between BaTiO_3 and Al_2O_3 .

3.2. Sintered Densities

For all the studied samples, the densities were measured by the Archimedes method and the relative density was calculated. The variation of densities of the sintered samples with the sintering temperature, are given in Table 1. It is clear that the sample densities increased with increasing the sintering temperature for all studied compositions.

Table (1): Variation of the densities of the sintered samples with the sintering temperatures.

Sample	Density (ρ), g/cm ³ Sintered at		
	1350°C	1375°C	1400°C
BaTiO ₃ +30 mol% 8YSZ	5.15	5.29	5.29
BaTiO ₃ +30 mol% TZ3Y	5.1619	5.19	5.24
BaTiO ₃ + 30 mol.% (TZ3Y+20A)	4.747	4.99	5.11
BaTiO ₃	6.028	6.03	----

3.3. Microstructure of the sintered samples

The microstructure was examined by scanning electron microscope (SEM). Micrographs of the different stabilized samples are shown on Figure (2). These micrographs show relatively dense and homogeneous materials. For both sintering temperatures (1350, 1400°C), the pure tetragonal barium titanate and the samples having 30mol%8YSZ have the greatest grain size while the sample with 30 mole% TZ3Y has the smallest grain size. On the other hand, the samples sintered at 1400°C showed some grain growth surrounded by small grains. The samples with 30 mol% (TZ3Y +20A) have grains greater than those containing 30 mol% TZ3Y.

3.4. Electrical Properties

Figures (3, 4) represent the impedance spectroscopy of the different samples sintered at 1350°C for 2 hrs, and measured at 500°C and 600°C respectively. Figure (3-a) shows the real resistance v.s imaginary resistance at different frequencies, and Figure (3-b) shows the imaginary resistance v.s frequencies from 0.1 kHz to 10 MHz). From the figure it can be seen that the resistance values of pure barium titanate are very small compared to those obtained for the samples stabilized by 30 mol% of the different additives.

The resistance values of the sample with 30 mol% (TZ3Y-20A) are greater than those for the samples stabilized with 30 mol% TZ3Y. On the other hand, samples stabilized with 30 mol% 8YSZ show the lowest resistance values among the doped samples. The maximum values of capacitance of the different samples correspond to frequencies between 1 kHz and 10 kHz at 500°C, while at 600°C the correspond to frequencies were between 10 kHz and 30 kHz, for all stabilized samples. For the pure barium titanate samples, the frequency at the maximum capacitance was 0.4 kHz and 4 kHz at 500°C and 600°C respectively.

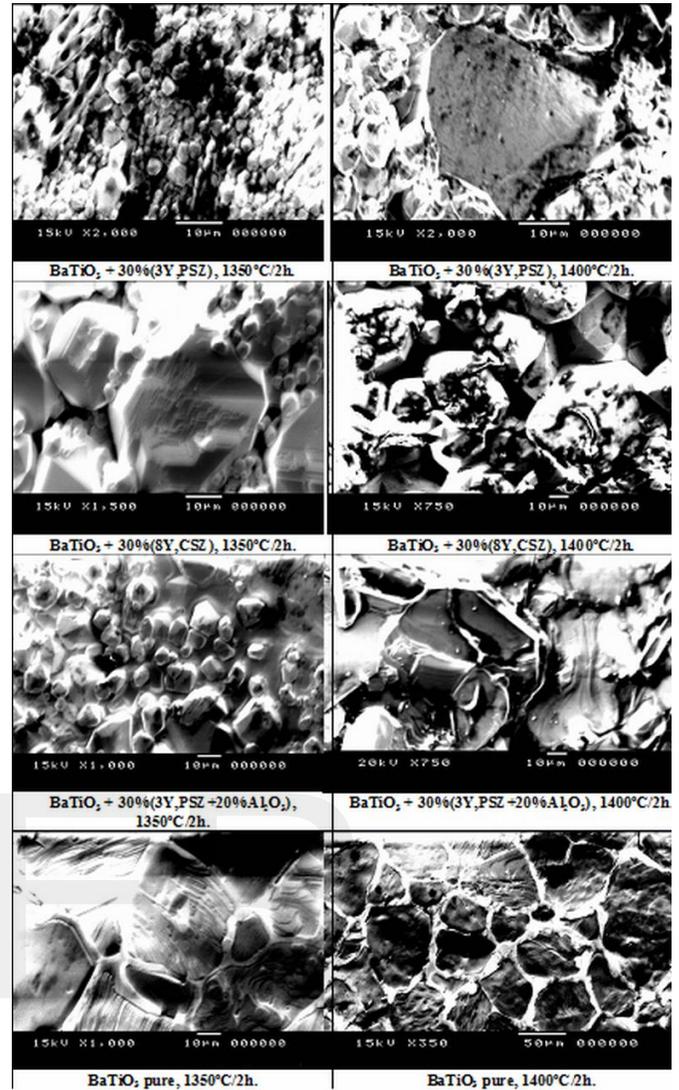
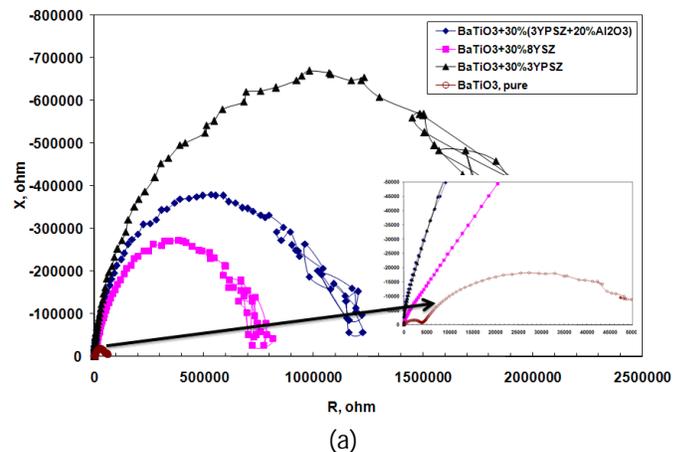


Figure 2. SEM micrographs of the sintered samples.



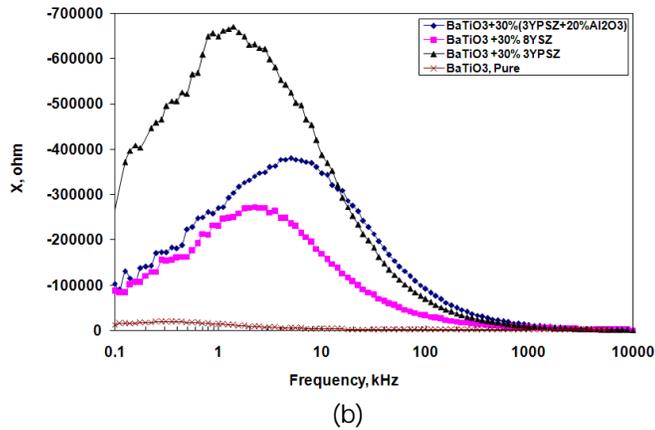


Figure 3. Impedance spectroscopy of the studied samples at 500°C.

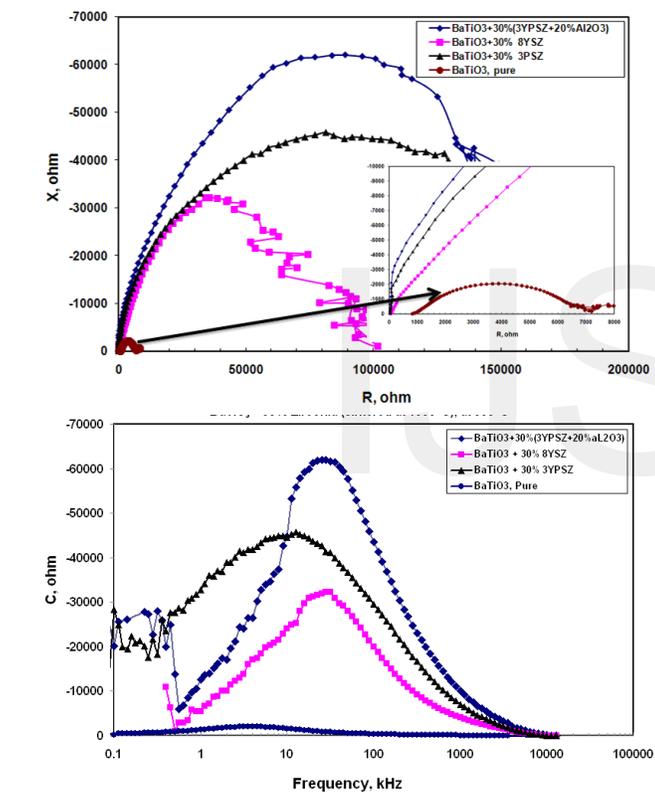


Figure 4. Impedance spectroscopy of the studied samples at 600°C.

Figure (5-a,b) gives the relative permittivity and the dielectric loss measured at zero and room temperature of the different samples sintered at 1350°C. It can be seen that, samples having 30 mol% TZ3Y showed the highest values of the relative permittivity at 1kHz, it reached 5300 at zero temperature and 2250 at room temperature (~27°C). While samples having 30 mol% TZ3Y +20A showed the lowest values of the relative permittivity at the same frequency, were about 580 at zero temperature and 330 at room temperature (measured at 1kHz).

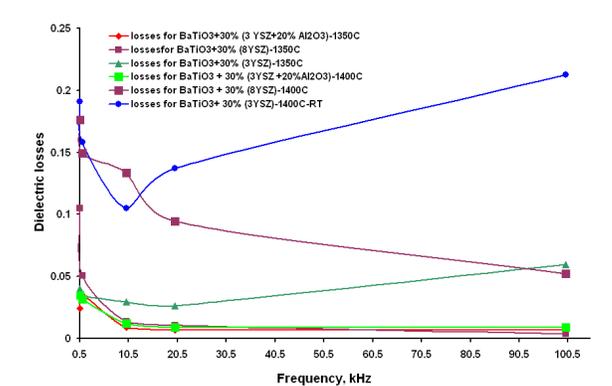
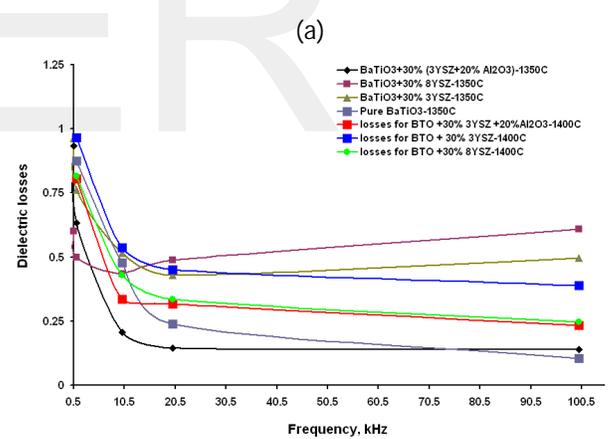
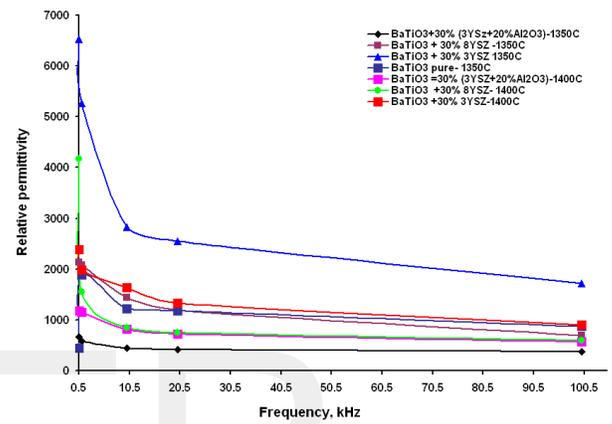
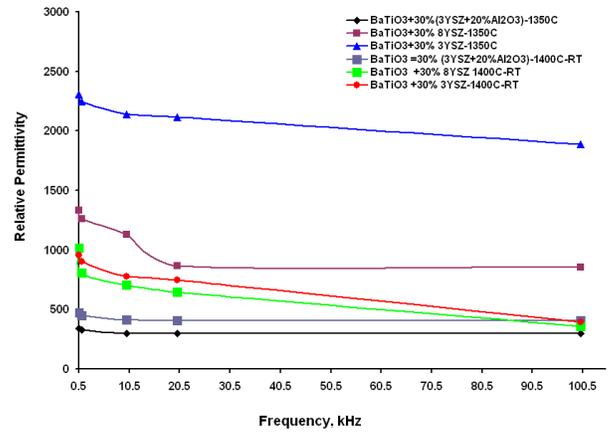


Figure 5. Relative permittivity and dielectric losses of the studied samples sintered at 1350°C: (a) near zero tempera-

ture, and (b) at room temperature.

The relative permittivity of the samples having 30 mol% of 8YSZ was about 2070 at 1kHz and that of the pure barium titanate was 1890 at 1kHz. The dielectric losses values, at all frequencies, are generally much higher near zero temperature than they are at room temperature. It was found that, the samples sintered at 1350°C show lower values of the dielectric losses than those sintered at 1400°C.

Our results are in a good agreement with the results of T. Badapanda et al.[13], they prepared the ceramics $Ba_{1-x}Ti_{0.75}Zr_{0.25}Y_{2x/3}O_3$ and found a great effect of Y_2O_3 content on the curie temperature and the peak values. The curie temperature changes from 265K for $x=0$ to 290, 220, and 180K for $x=0.01, 0.025$ and 0.05 respectively. While the peak values of the permittivity decreased from about 6000 to 1300, 2000, and 1400 for the same values of x , which means that the barium titanate zirconate is very sensitive to the small values of Y_2O_3 content.

Studies [1,12] on the effect of zirconium addition to barium titanate (BZT) showed that the zirconia addition shifted the curie point (from 130°C to about 90°C), as shown in Figure (6). Addition of zirconia particles into barium titanate can form a core-shell structure, which can exhibit temperature-stable dielectric behavior (7). When ZrO_2 content is less than 10 mol%, BZT ceramics show normal ferroelectric behavior and dielectric anomalies due to cubic to tetragonal (T_c), tetragonal to orthorhombic (T_2), and orthorhombic to rhombohedral (T_3) phase transitions [4]. It was reported that an increase in the Zr content induces a reduction in the average grain size, decreases the dielectric permittivity ϵ_r and maintain a low and stable leakage current [4,5], in accordance with present results.

Figure (7) shows the relative permittivity of the pure $BaTiO_3$, it has a peak at ~130°C and values between 1400 and 1500 at RT.

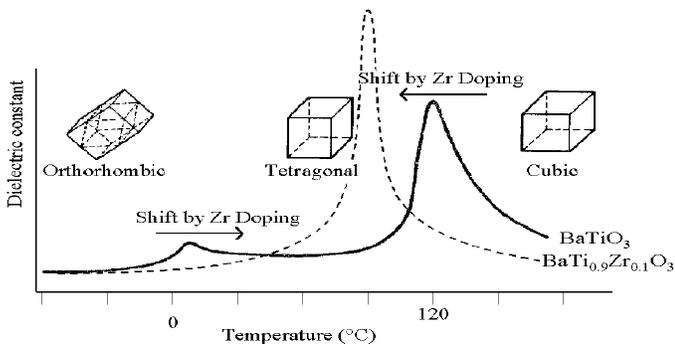


Figure 6. Schematic diagram showing the effect of Zr doping of $BaTiO_3$ on the dielectric properties[7].

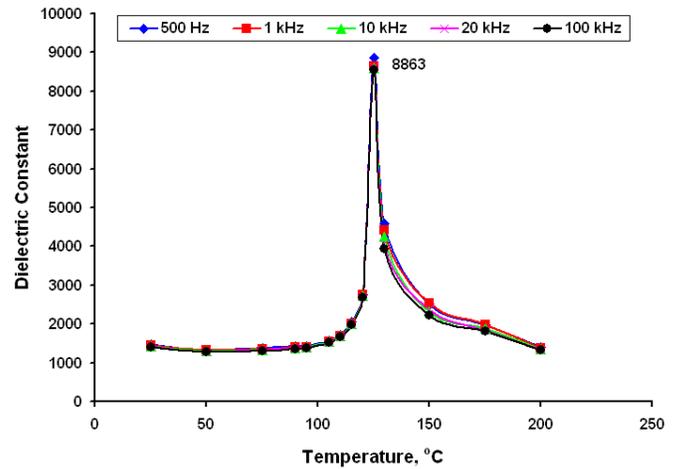


Figure 7. The relative permittivity of the pure $BaTiO_3$.

4. Conclusions

The addition of 30 mol% of different zirconia powders was studied and the following conclusions could be drawn:

1. Samples of BZT containing 30mol% of different additives of zirconia: 8YSZ, TZ3Y, TZ3Y+20A were prepared by solid state reaction. The room temperature X- ray diffraction patterns of the sintered samples showed single cubic phase structure.
2. The microstructure observations by scanning electron microscope (SEM) showed a different attitude of grain growth for each kind of zirconia added to Barium titanate, however all samples had very small grains compared to the pure barium titanate.
3. The dielectric constants measured for the different samples showed that $BaTiO_3$ doped with TZ3Y samples have the highest permittivity, while samples doped with TZ3Y-20A have the lowest one.

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