

# Synthesis and characterization of structural and electrical properties of Zirconium doped Barium Titanate ceramics

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**Abstract:** - Ba Ti<sub>0.90</sub> Zr<sub>0.10</sub>O<sub>3</sub> (BZT10), Ba Ti<sub>0.85</sub> Zr<sub>0.15</sub>O<sub>3</sub> (BZT15) Ba Ti<sub>0.80</sub> Zr<sub>0.20</sub>O<sub>3</sub> (BZT20) ceramics were fabricated by conventional solid-state route with different concentrations. The synthesized samples were subjected to structural, morphological & electrical characterization. The samples were calcined at 850 °C and sintered at 1250 °C. The dominance of the tetragonal phase with space group *P4mm* was confirmed by the XRD patterns. The lattice parameters and crystalline behavior were investigated. Ba Ti<sub>0.85</sub> Zr<sub>0.15</sub> O<sub>3</sub> showed the highest relative density (~ 85%), crystallinity (~ 96%) with better crystalline nature and tetragonality. A homogeneous grain size of < 1 μm was reported in SEM. The comparison of current density, resistance with applied voltage was denoted by I-V characteristics. The analysis confirmed that all the synthesized samples were pure ferroelectric material with high resistivity. Thus, zirconia doped barium titanate ceramics with suitable current density, resistance could be attractive materials for ceramic capacitors and electronic device applications.

**Key Words:** — *Solid-state reaction, crystalline, tetragonal, scanning electron microscopy, ferroelectrics, capacitor.*

## I. INTRODUCTION

Barium titanate is an oxide of the perovskite family that comprises any material with an ABO<sub>3</sub> structure. It is an abundant mineral discovered in 1839 [1]. BaTiO<sub>3</sub> was first intentionally synthesized during World War II for the production of a high dielectric constant material for capacitor application in the mid-1940s [2]. The primordial reports were based on doping studies of TiO<sub>2</sub> with BaO, which produced ceramic materials with ameliorated dielectric permittivity. The mixed oxides were fabricated as early as 1941, The high permittivity was found with dielectric constant ( $\epsilon_r \geq 1000$ ), ten times greater than any other ceramic known at that time, such as TiO<sub>2</sub> ( $\epsilon_r=110$ ) [3]. It was established that this marked improvement came from the ferroelectric behavior of the BaTiO<sub>3</sub> crystal. From the time of its discovery, it has been widely exerted in the electronic industry for the sake of its high dielectric constant and ferroelectric behavior [4].

It belongs to the perovskite (ABO<sub>3</sub>) family of compounds, which are significant electronic materials.

Owing to its high dielectric constant and low loss characteristics, barium titanate has been used in applications such as capacitors and multilayer ceramic capacitors (MLCC). Besides these, the wide variety of electrical phenomena exhibited by BaTiO<sub>3</sub> makes it applicable as sensors, actuators, resonators, filter- duplexers, voltage-controlled oscillators, antennas, current limiters, constant temperature heaters, thermistors, dynamic random access memories (DRAMs). Applications include phonograph pickups, the band-pass filters, and control of oscillator frequencies in communication equipment, sonic delay lines, sonar, high-voltage step-up transformers, ultrasonic cleaning, medical ultrasound uses, industrial nondestructive inspection, watches, etc [5].

The basic structure of barium titanate with the titanium ion occupying the octahedrally coordinated site and the Ba ion in the twelve coordinated sites in a high-temperature *P4mm* cubic symmetry. The ferroelectric phase at room temperature is tetragonal with oxygen and titanium ions shifting to produce a spontaneous polarization. Its tetragonality results from the outward displacement of Ti<sup>4+</sup> ions from the centrosymmetric position in the TiO<sub>6</sub> octahedra categorized as a displacive type ferroelectric. BaTiO<sub>3</sub> is highly stable chemically and mechanically. Its ferroelectric nature at and above room temperature has attained great importance as it can be easily prepared and used in the form of a ceramic polycrystalline sample [2].

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Various dopants such as Strontium, Niobium, Lanthanum, Zirconium, etc. have been incorporated in BaTiO<sub>3</sub> and their effect on its properties studied on being doped with donors, e.g. trivalent ions (La) at Ba site and isovalent/pentavalent ions at Ti site, BaTiO<sub>3</sub> becomes semiconducting. This has been associated with the presence of Ba<sup>2+</sup> vacancies or the conversion of Ti<sup>4+</sup> to Ti<sup>3+</sup> to create a charge balance. The compensation mechanism also leads to an increase in conductivity thereby rendering insulating pure BaTiO<sub>3</sub> semiconducting on doping [3,4,5]. Conventionally, BaTiO<sub>3</sub> powders are manufactured at high temperatures, by solid-state reaction, or from chemically derived precursors such as by sol-gel emulsion method. The present work, hence, aims at preparing Barium Titanate (BaTiO<sub>3</sub>) with Zirconium (Zr) doped fine powders through solid-state reaction sintered at a comparatively lower temperature (1250 °C) and investigation of its structural electrical properties. The electrical property is characterized by I ~ V characteristics to find out its insulating properties.

## II. EXPERIMENTAL PROCEDURE

Ba Ti<sub>0.90</sub> Zr<sub>0.10</sub> O<sub>3</sub> (BZT10), Ba Ti<sub>0.85</sub> Zr<sub>0.15</sub> O<sub>3</sub> (BZT15) Ba Ti<sub>0.80</sub> Zr<sub>0.20</sub> O<sub>3</sub> (BZT20) solid solutions were prepared by the conventional solid-state reaction method. Chemicals required for the experiment were BaCO<sub>3</sub> (purity > 98.5%, Merck Specialties, India), ZrO<sub>2</sub> (purity > 98.5%, Merck Specialties, India), TiO<sub>2</sub> (purity > 98.5%, Merck Specialties, India) powder, which was weighed and mixed according to those composite formulas using ethanol and milled in a ball mill (G91-e.J. Payne, UK) for 20 hours. Then the slurry was poured in biker & dried in drier (JISICO, J-s300S, Japan) for 24 hours. After drying, the powders were ground in a mortar pestle for 3 hours. Then, the mixtures were calcined in an alumina crucible at 850 °C for 2 h in the air in a furnace (Nabertherm GMBH). After that, the powder was shaped using a pellet press (Retsch Pellet Press PP 25).

The pressure required to shape the tablets was 2.5 tons. Then the tablets were sintered at 1250 °C for 2.5 h in the air in a furnace (Nabertherm GMBH). Microstructures of the sintered samples were examined by scanning electron microscope (ZEISS-EVO 18, UK). X-ray diffraction (XRD, Bruker D8 Advanced, Germany) was employed to examine the phase identification. To determine the electrical properties of the samples, an electrometer was used.

## III. RESULTS AND DISCUSSIONS

### 3.1 Density analysis

Several properties such as particle size distribution of the powder, the sintering temperature, morphology, dielectric properties have a great impact on the density. The volume of the unit cell was calculated from the lattice parameters obtained from XRD data and then used to calculate the theoretical X-ray density. The sintered pellet density was calculated experimentally using a slide caliper to measure the dimensions of the pellet (radius and thickness). The bulk density of sintered pellets was calculated by dividing their mass by volume [5]. It can be seen from Table.1 that the density of the BZT15 sample is relatively higher, and the density of the BZT ceramic sample increases with increasing Zr<sup>4+</sup> ion content, and the reason for increasing is that higher Zirconium enhances the nucleation sites, diffusion & mass transfer is easier [5]. The SEM micrograph Figure.1 denotes the grain size which is related to density. The reason for the lower density of BZT20 than BZT15 is described in SEM analysis. Porosity is present in the BZT20 sample, which leads to a decrease in density. The probability of defects occurring in the growth process of the grains is large, resulting in a phenomenon of lower density [6]. The decrease of the density of the BZT10 sample is due to the decrease of grain size with the lower Zr<sup>4+</sup> ion content.

### 3.2 Scanning Electron Microscopy analysis

Figure.1 shows the morphology and grain size of the BZT ceramics, sintered at 1250°C for 9 hours. These images exhibit fairly homogeneous, fine, and regular grains size which increases with increasing Zr content. In the fact, the BZT10 grains have the quasi quadratic form which is enhanced to the octahedral form for BZT15 & BZT20 indicating better homogeneity and densification [5]. This study indicates an increase in grain size with the increasing Zr content. It is due to grain boundary mobility & reduction of grain boundary width [6]. It results in the increment of diffusion co-efficient. The average grain size is less than 1.0 μm. Zr-O bond has higher bond energy than the Ti-O bond (Zr-O bond 776.1 kJ/mol, Ti-O bond 672.4 kJ/mol). Zr<sup>4+</sup> replaces Ti<sup>4+</sup> to provide higher energy with the increase of Zr<sup>4+</sup> content. So the ion mobility decreases with the increase of Zr content, which is not conducive to the movement of grain boundaries. The grain size is reduced [7]. For this reason, the density of BZT20 is lower than BZT15 mentioned in Table.1.

### 3.3 X-Ray Diffraction analysis

The properties of perovskite oxides are profoundly linked to their crystal structure. Enormous research is being carried out to design and synthesize new perovskites. For the development of lattice parameters, the investigation of the BaTiO<sub>3</sub> compound with assorted dopants has great significance [7,8]. In this research work, it is attempted to experiment with crystallographic analysis via the x-ray diffraction method. The presence of peaks at  $2\theta = 22.14^\circ, 32^\circ, 39^\circ, 45.34^\circ, 50.98^\circ,$  and  $56.30^\circ$  was attributed to BaTiO<sub>3</sub>, according to the JCPDS card no.05-0626. Peaks at  $2\theta = 30.4^\circ, 40.3^\circ, 47.1^\circ, 53.1^\circ$  etc were attributed to ZrO<sub>2</sub> [JCPDS card no. 17-923] [9]. X-ray diffraction patterns for elemental analysis of materials were carried out. XRD patterns were ascertained in the 2-theta ( $2\theta$ -degree) range of  $20^\circ - 60^\circ$  at room temperature. Figure.3 (a) shows the comparison of XRD patterns of BZT samples. All of the compositions were calcined at  $850^\circ\text{C}$  & sintered at  $1250^\circ\text{C}$ . Here, the overall XRD patterns indicate that the decreasing zirconium peaks and evolution of BaTiO<sub>3</sub> peaks are attributed to homogeneous single-phase perovskite structures [10], [11]. The peaks of all the XRD patterns are successfully indexed with the tetragonal structure of the BaTiO<sub>3</sub> crystal belonging to the *P4mm* space group. In figure.3 (b) variation of sharpness of (110) diffraction peaks is shown. The maximum intensity (110) diffraction peak shifted towards a higher/ lower angle. Pure BaTiO<sub>3</sub> show (110) peak at  $2\theta = 32^\circ$ . Diffraction peak shifts at a lower angle ( $\sim 30.75^\circ$ ) for Zirconium doping at (BZT). Shifting of angle demonstrates the variation of lattice parameters [12]. In another way, it can be said that the transformation factor from tetragonal towards cubic phase.

### 3.4 Electrical property analysis

Figure.5. shows the dependence of leakage current on the applied electric field. It is observed in the graph that the leakage current increases with increasing voltage because of the inclusion of Zirconium. Electrical properties are strongly influenced by the sample preparation & composition. Especially the sintering and cooling atmospheres are very important [7]. It is found that most of the current is channeled through small pores in the inter-granular boundaries [13]. Existence of barrier layers of high resistivity separating the grains. The nature of the curve is dependent on an intergranular barrier, grain length, space charge limited conduction, Schottky barriers between the grains [14], [15]. Along with the barrier effects, the negative differential resistance in the bulk of the samples may play a significant role [16]. I-V characteristics of the samples were found to have a nonlinear characteristic,

which indicates good insulating properties of the ferroelectric ceramics [17]. In I ~ V curve there is first a low-voltage Ohmic region, then the current rises rapidly as a result of the reduction in barrier height by the voltage [18]. A horizontal portion (plateau) or a portion with a negative differential resistance portion with an exponential rise in the current is shown. Then finally the current becomes nearly linear in the field since the barriers have become small and the voltage is determined largely by the ohmic drop within the grains [18].

## IV. CONCLUSION

The present work is aimed at synthesizing doped barium titanate using the solid-state method. The objective is to study the effect of structural & electrical properties of the synthesized powders. The properties of the synthesized material are characterized. In SEM analysis, all the samples are in a few micro ranges, from  $0.743 \mu\text{m}$  to  $0.853 \mu\text{m}$ . In X-ray diffraction analysis, all the samples exhibit single-phase perovskite structures. BZT15 indicates better crystalline behavior than any other sample. The expansion of crystal volume in BZT is occurred due to the substitution of Zr<sup>4+</sup> with Ti<sup>4+</sup>. As Zr has a higher ionic radius than Ti. By doing this, the lattice parameter and tetragonality are decreased, crystallite size and crystallinity increase. The strain & dislocation density is lowest for the BZT15 sample. In I~V characteristics show a non-linear change of the current density with applied voltage. The resistance of BZT15 is  $5.08\text{E}^{+10} \Omega$ . At applied voltage 100V.

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