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Abstract

Polycrystalline BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ceramics ($x = 0.02-0.04$) were prepared by a combination of solid-state and mechanochemical process and characterized at room temperature by X-ray diffraction for phase composition. Their crystal structures were found to be of the cubic and tetragonal symmetries, respectively. The grain size and porosity which were determined using Field Emission Scanning Electron Microscope (FESEM) and densitometer, respectively showed decrease and increase of relative density respectively, with increase in doping concentration. The variations of dielectric constant and loss with frequency and temperature show a maximum dielectric constant of 1660 at room temperature for Ba(Ti$_{0.96}$Sn$_{0.03}$Zr$_{0.01}$)O$_3$. The remnant polarization ($P_r$) and coercive field ($E_c$) of BT were found to be 581.73 V/cm and 0.27 $\mu$C/cm$^2$. Increase in Sn content led to an increase in $P_r$ of 0.58, 3.07, 3.73 C/cm$^2$, and $E_c$ of 1766.8, 2855.7, 2661.1 V/cm, respectively and are expected to lead to a significant reduction in the thickness of the multilayer ceramic capacitors. Impedance spectroscopy of polycrystalline Ba (Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ in a wide frequency and temperature range showed Nyquist plots with presence of grain and grain boundary at 400°C and a negative temperature coefficient of resistance (NTCR) for Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$. The dielectric relaxation showed a non-Debye character.

Keywords: porous ceramics, barium titanate, doping, ferroelectrics, MLCC

1. Introduction

1.1. BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$

Barium titanate (BT) is one of the most basic and widely applied ferroelectric oxide materials with a perovskite-ABO$_3$ type crystalline structure. It is chemically and mechanically remarkably stable and exhibits ferroelectric properties from room temperature to just below the transition
temperature ($T_c$). It is easily prepared and used in polycrystalline ceramic form [1]. Due to its excellent dielectric, ferroelectric, piezoelectric, pyroelectric and optoelectric properties, it is extensively used in multilayer ceramic capacitors (MLCC), positive temperature coefficient of resistance (PTCR) thermistors, piezoelectric sensors, actuators, ferroelectric random access memories (FRAM) and electro-optic devices [2, 3]. Pure BT is an electric insulator with a large energy gap of 3.05 eV at room temperature. However, when doped with small metals, it becomes semiconducting and leads to possibilities of tailoring its properties for specific technological applications. Modified BT compositions are widely used in MLCCs due to its high dielectric constant and low loss [4]. Among the doped BT compositions, Ba(Ti$_{1-x}$Sn$_x$)O$_3$ (BST) system has drawn wide attention due to its manifestation of diffuse-type phase transition [5–7] and many dielectric applications with reduction of phase transition temperature toward room temperature [8, 9]. Zirconium-doped barium titanate with general formula Ba(Zr$_x$Ti$_{1-x}$)O$_3$ (BZT) has attracted great attention for its potential applications due to its high dielectric constant, relatively low dielectric losses, large voltage tunability of the dielectric constant, as well as a good chemical stability [10–12]. Partial replacement of titanium by tin, zirconium or hafnium generally leads to a reduction in $T_c$ and an increase in the permittivity maximum ($\varepsilon_{\text{max}}$) with increase in dopant content [13]. The substitution of isovalent cations Zr$^{4+}$ and Sn$^{4+}$ for Ti$^{4+}$ lead to the formation of barium titanate stannate zirconate compound which belongs to the class of complex perovskite structure having the general formula ABB$^{4-x}$O$_3$ (A, B, are the cation, B$^{4-x}$B$^{x}$ are the isovalent cation dopants and O$_3$ anion). These compounds have been widely studied owing to their very high and broad relative permittivity at the ferroelectric Curie point. Therefore, codoping of BT with two tetravalent ions Zr$^{4+}$ and Sn$^{4+}$ would be a good strategy to tailor the properties of porous BT ceramics.

There are challenges, however, one of which is in developing a dielectric layer of fewer than 10 μm with a large capacitance, a major requirement for MLCC miniaturization and electronic/microelectronic devices [14]. Reduction of the grain size of BT ceramics to the micron level leads to an increase in permittivity at room temperature. Further reduction of grain size to less than few hundred nanometers leads to a further decrease in permittivity. On the other hand, the presence of porosity can lead to dielectric permittivity that is lower than that of the solid material. It is thus one strategy to achieve lower dielectric constants for microelectronics devices. Thus, controlling porosity can yield a spectrum of dielectric constants from a single material [15]. Porosity plays a role in decreasing the Curie point for barium titanate ceramics with apparent density below 90% [16]. Manipulation of the volume ratio of porosity can lead to appropriate dielectric constant being obtained in a wide range. These advantages have been harnessed in the fabrication of materials with highly anisotropic dielectric constants with simultaneous introduction of aligned pores [17]. High material porosity is considered as an advantage only in few cases such as in materials that have resistance to temperature changes.

Various techniques have been introduced to make mesoporous and porous BaTiO$_3$ some of which include, development of soft-chemistry routes to produce nanoparticles or specially shaped materials, such as one-dimensional nanowires; sonochemical methods to prepare size-tunable BaTiO$_3$ crystals [18] and the introduction of biosynthesis methods to prepare BaTiO$_3$ nanopowders [19]. Mesoporous and porous materials have important features such as the
possession of large surface areas and nano size porous structures [20]. These features make the materials widely used in photo electronics, catalytic reactions and semiconductors among others [21, 22]. However, the high costs and difficulty in process control in these routes necessitated the development of alternative options for the synthesis of porous BaTiO$_3$ nanoparticles.

Mechanochemical synthesis can be used to reduce the grain size of porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) powder to nanosize. This is predicated on the fact that mechanical technique is superior to both the conventional solid-state reaction and wet-chemistry-based processing routes for several reasons as it uses low-cost and widely available oxides as starting materials compared to wet chemical routes which are extremely sensitive to environmental conditions such as moisture, light and heat [23, 24].

Complex impedance spectroscopy is a nondestructive method [25] that uses to distinguish the grain boundary from the grain-electrode effects which are usually the sites for trapping oxygen vacancies and other defects. Within a wide range of ceramics, an ionic, ionic plus electronic or electronic conduction is shown in these sites. It is also useful in establishing space charge polarization and its relaxation mechanism, by appropriately attributing different values of resistance and capacitance to the grain and grain boundary effects. It allows the contributions to the overall electrical property by various components in the material to be easily separated. Other workers have used impedance spectroscopy to study other materials [26, 27] to gain insight into electrical conduction mechanisms of the materials. In this work, we report the structural and electrical properties of porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) ceramics prepared by solid-state and mechanochemical technique. The effect of porosity on the ceramics material will be used to evaluate the materials and serve as guide in the choice for MLCC and thermistor applications.

1.2. Mechanochemical synthesis

Mechanochemical synthesis or high-energy milling is the preparation of powder by high-energy ball milling of elemental mixtures. The most important feature of this technique is that the formation of the product compounds flows from the reactions of oxide precursors by mechanical energy activation, rather than the heat energy necessitated in the conventional solid-state reaction process.

The solid-state reactions initiated by intensive milling in high-energy ball mills could be a good choice for the ceramic powder preparation. The area of contact between the reagent powder particles increases with the intensive milling. This is the consequence of reduction in particle size and permits fresh surfaces to come into contact. This permits the reduction to continue without the requirement for diffusion through the product layer. Alternatively, the particle refinement and consequent reduction in diffusion distances (due to microstructural refinement) can at least reduce the reaction temperatures significantly, even if they do not occur at room temperature. In general, the procedure of sintering is improved by liquid-phase sintering with titanium-rich composition at the temperature above 1320°C or by mechanical activation of precursors (BaCO$_3$ and TiO$_2$) [28–30]. In addition, particle size of ceramic powders is reduced by mechanical
treatment and produces nanostructured powders which are of primary interest in the current trend of miniaturization and integration of electronic components [31, 32].

1.3. Barium titanate (BaTiO$_3$) perovskite structure

The perovskite, ABO$_3$ type structure of BT is cubic (above 120°C) with Ba ion (larger A cation) located at the cube corners, Ti ion (smaller B cation) at the body center, and oxygen at the face centre, forming octahedra around each Ti ion. It is considered an FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice, while the smaller B cation occupies the octahedral interstitial sites in the FCC array. The Ba ion occupies the space formed between eight neighboring octahedra, giving the Ba, Ti and the oxygen ions coordination number of 12, 6 and 6, respectively. BaTiO$_3$ can accept the substitution of foreign cations on two distinct sites, the A-site (Ba) and the B-site (Ti). The stability of the perovskite compounds arises mainly from the electrostatic charge of the ions when perfectly integrated.

1.4. Structural phase transitions in barium titanate

BT undergoes a series of structural phase transitions upon cooling from high temperature. In the temperature range of 1430–1620°C, barium titanate assumes a hexagonal structure. In the 130–1430°C range, BT is cubic and nonpolar (space group $Pm3m$), thus centrosymmetric and nonpiezoelectric. When the temperature is below the Curie temperature (130°C), the cubic structure (paraelectric) is slightly distorted to a tetragonal ($P4mm$) structure (ferroelectric) which is noncentrosymmetric, with an accompanying movement of Ti atoms inside the O$_6$ octahedra. In turn, oxygen ions all shift in the opposite direction [100]. Not only does this result in distortion of oxygen octahedron, but the opposite displacement of negative and positive charges within the unit cell leads to the formation of an electric dipole moment, and hence to the appearance of spontaneous polarization and ferroelectric properties. In the tetragonal phase, the direction of the vector of spontaneous polarization $P_s$ (i.e., polar direction) lies parallel to the direction of one of the original cubic directions. When the temperature is below 5°C, the tetragonal structure transforms to an orthorhombic ferroelectric phase ($C2mm$) with the polar axis parallel to a face diagonal, and the direction of spontaneous polarization transfers to a pseudocubic [110]. At as low as −90°C, it further transforms to a rhombohedral structure ($R3m$) with the polar axis along a body diagonal and is spontaneously polarized along a [111] direction.

The Goldschmidt tolerance factor for a perovskite structure (ABO$_3$) is given by the formula:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where $r_A$, $r_B$, and $r_O$ are the A-site, B-site, and oxygen ionic radii, respectively. There are three possible values of $t$: (1) $t \geq 1$: show ferroelectricity. (2) $t < 1$: This antiferroelectric perovskite. (3) $t = 1$: perfect cubic structure.
2. Experimental

2.1. Sample preparation

All samples used in this study were prepared by the conventional solid state and mechanochemical technique from fine powders of metal oxides or metal carbonates. The nominal purity of the initial powders, as well as their manufacturers are given in Table 1.

2.2. Synthesis of barium titanate (BaTiO$_3$) and Zr- and Sn-doped barium titanate

BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{0.04-x}$Zr$_{0.04}$)O$_3$ ($x = 0.02$–$0.04$) nanocrystalline powders were synthesized by a combination of solid-state reaction and high-energy ball milling technique. The starting materials were analytical grade high-purity (99.9%) oxide precursors, BaCO$_3$, ZrO$_2$, TiO$_2$ and SnO$_2$. Stoichiometric amounts of the oxides were weighed according to nominal composition and ball-mixed for 12 h in alcohol. The mixture was dried in an oven and calcined in an alumina crucible at 1050°C for 4 h in the air to yield BaTiO$_3$, Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$, Ba(Ti$_{0.96}$Sn$_{0.03}$Zr$_{0.01}$)O$_3$, and Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$ powders. The calcined powders were ball-milled in an isopropyl alcohol as wetting medium using SPEX 8000 Mixer/Mills (60 Hz model) at room temperature for 7 h. The milling was stopped for 15 min after every 60 min of milling to cool down the system. The slurry was put in an oven and dried at 90°C for 24 h. The milled powder was compacted at 5 ton to make pellets of size 15 mm in diameter and 1.5 mm in thickness using polyvinyl alcohol (PVA) as a binder. After burning off the binder (PVA), the pellets were sintered in a programmable furnace at temperatures of 1190°C for 2 h in alumina crucibles.

2.3. Characterization

Phase identification of calcined and sintered powders was carried out using X-ray diffractometer with monochromatic Cu-Kα radiation ($\lambda = 1.54178$ Å) under 40 kV/30 mA—over a 2θ range from 20 to 80° at a scanning rate of 2°/min. The experimental densities of the samples were calculated using Electronic Densimeter MD-3005 ALFAMIRAGE. The morphological studies of the sintered sample were carried out using field-emission scanning electron microscopy (FE-SEM) (JEOL 7600F) operated at 15 kV. The polarization-electric field (P–E) hysteresis

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Manufacturers</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCO$_3$</td>
<td>Merck, Germany</td>
<td>99.9%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Aldrich Chemical Company, Inc., U.S.A</td>
<td>99.9+%</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Strem, Chemicals, U.S.A</td>
<td>99.9%</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Strem, Chemicals, U.S.A</td>
<td>99.9%</td>
</tr>
</tbody>
</table>

Table 1. Precursors, purity level and manufacturers.
characteristics of the samples were determined using a Precision LC material analyzer (Radiant, U.S.A). The dielectric and impedance measurement was carried out for the sintered sample using an Agilent 4294 A Impedance Analyzer in the frequency and temperature range of 40 Hz–1 MHz and 30–400°C, respectively.

3. Structural and electrical properties

3.1. Structural properties

Structural and dielectric properties were evaluated for both BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) ceramic, while thermistor application is explored in Ba (Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ceramic.

3.1.1. XRD analysis

Figure 1 shows the room temperature XRD patterns of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) ceramics. It is seen that all the compositions are of single-phase perovskite structure without any trace of secondary phase and imply that Sn$^{4+}$ and Zr$^{4+}$ entered the unit cell and maintained the perovskite structure as a solid solution. The enlarged XRD patterns of the ceramics in the range of 2$\theta$ of 44–46.5° clearly show that the crystal structure of the ceramic is cubic for BT with JCPDS file no. 96-150-7758 and space group $Pm-3m$ (Figure 2a). This is because the (200) and (002) peaks are not split [33] as reported by other workers [34, 35], whereas it is tetragonal for Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) (Figure 2b–d) with the splitting of the (200) and (002) characteristic peaks which are in agreement with the joint committee on powder diffraction standards (JCPDS file no.98-00-2020), similar result was obtained for $x = 0.04$ using conventional method by other workers [36]. It can also be noticed from Figure 2a–d that the positions of the diffraction peaks of the ceramics shift slightly to lower angle with increasing Sn content in the range of 2$\theta$ from 44 to 46.5°. This is attributed to the larger ionic radius of Sn$^{4+}$ (0.69 Å) and Zr$^{4+}$ (0.72 Å) as compared with that of Ti$^{4+}$ (0.60 Å) with results in a slight enlargement of crystal cell volumes and hence a shift of diffraction peaks toward lower angles.

3.1.2. Microstructure

Figures 3–6 show the FE-SEM images of porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) ceramic sintered at 1190°C for 2 h. All the samples are dense and have varying microstructural features with the presence of voids. The presence of voids in the FE-SEM images indicates that the pellets have a certain amount of porosity. The grain size and grain boundary can be seen very clearly in a nonagglomerated region and the grain size decreases with increasing Sn content. The difference among these four samples is attributed to the difference in Sn and Zr content since all of them have been processed under the same conditions. Further substitution of Sn caused the grain size to become smaller with more porous regions between them compared to porous BaTiO$_3$ sample. The average grain size of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ ($x = 0.02–0.04$) ceramics determined by using linear intercept technique is shown in Table 2.
grain size decreased from 199.65 to 89.28 nm with increase in Sn and this indicates that Sn is a grain growth inhibitor.

3.1.3. Density

The experimental or observed density of each sample was calculated using the Archimedes principle from (Eq. (2)): 

\[
\text{Density} = \frac{\text{Mass}}{\text{Volume}}
\]
where $M_a$ and $M_w$ are the respective weights in gram of the pellet measured in air and in water. $\rho_w$ is the density of pure water in g/cm$^3$. The theoretical density of the material was calculated using (Eq. (3)):

$$\rho_{\text{theo}} = \frac{n \times \text{cell mass}}{\text{cell volume}} = \frac{n \times M \times 6.02 \times 10^{-23}}{V} \text{g/cm}^3,$$

where $n$ is the number of atoms per unit cell, $M$ is the molecular weight of atoms constituting one unit of the chemical formula, and $V$ is the unit cell volume.
The experimental densities of the porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics prepared by High Energy Mechanochemical (HEM) method and conventional sintering vary from 93.6% to 89.0% of theoretical density. The relative density of BaTiO$_3$ is higher compared to the Sn-/Zr-doped samples. The increase of the tin content to x = 0.04 induced further densification which tends to inhibit the grain growth [37]. This increase in density is also evident in FESEM microstructures of Figures 3–6 which show a decreasing presence of porosity with increasing Sn content.

![Figure 3](image1.png)  
**Figure 3.** FESEM images of nanocrystalline BT sample at magnification of ×200,000.

![Figure 4](image2.png)  
**Figure 4.** FESEM images of nanocrystalline Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02) sample at magnification of ×200,000.
3.1.4. Porosity

The porosity of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics was calculated using (Eq. (4)):

$$\text{Porosity} = \left(\frac{d_{\text{calc}} - d_{\text{exp}}}{d_{\text{calc}}}\right) \times 100 \quad (4)$$

Figure 5. FESEM images of nanocrystalline Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.03) sample at magnification of ×200,000.

Figure 6. FESEM images of nanocrystalline Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.04) sample at magnification of ×200,000.
The macroporous structure of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{x}$Zr$_{0.04-x}$)O$_3$ \((x = 0.02–0.04)\) ceramics exhibited a porosity of 6.3–10.9% \[Table 2\]. Porosity increased from 6.3 to 12.8% at Ba (Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ and then decreased to 10.9% with increase in Sn concentration, respectively. The increase of the relative density and decrease of porosity with Sn concentration enhance the density of the ceramics with reduction of pores. It can be seen from the FESEM image in \textbf{Figures 3–6} that the pores vary in sizes in all the samples. Pores are composed of macropores in the grain boundary or nanopores in the grains, but in all the samples, only macropores are visible.

3.1.5. Effect of porosity on dielectric properties

Porosity in BT ceramics can be considered as a secondary phase and indicates its degree of densification. Pores in BT ceramics are usually formed by incomplete sintering or using sacrificial pore formers and exist in between the grains. Porosity decreases strength, because pores reduce the true cross section area of a BT ceramics and also pores act as stress concentrating notches. In many cases, different densities within a ceramic are used to provide a wide continuous range of dielectric constants. The relative permittivity decreases with increasing material porosity as reported by other workers \[38\]. Porosity of a ceramic material is a serious defect in high-voltage insulating systems \[39\]. Enhanced electric field in the pores increases the probability of bond breakage on the pore walls and leads to the lowering of the overall breakdown strength \[40\].

3.2. Dielectric properties

3.2.1. Variation of dielectric constant and loss tangent with frequency

The real ($\varepsilon'$) part of relative permittivity and $\tan \delta$ in the frequency range of 40 Hz–1 MHz of porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{x}$Zr$_{0.04-x}$)O$_3$ \((x = 0.02–0.04)\) ceramics at room temperature is shown in \textbf{Figures 7} and \textbf{8}, respectively. It can be seen that the value of dielectric constant is higher at lower frequencies and decreases with increase in frequency. The decrease of dielectric constant with increasing frequency means that the response of the permanent dipoles decreases as the frequency increases and the contribution of the charge carriers (ions) toward the dielectric constant decreases \[41, 42\].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical density (d_{\text{th}}) (g/cm$^3$)</th>
<th>Experimental density (d_{\text{exp}}) (g/cm$^3$)</th>
<th>Relative density (%)</th>
<th>% porosity</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>6.02</td>
<td>5.639</td>
<td>93.6</td>
<td>6.3</td>
<td>144.53</td>
</tr>
<tr>
<td>Ba(Ti$<em>{0.96}$Sn$</em>{0.02}$Zr$_{0.02}$)O$_3$</td>
<td>6.17</td>
<td>5.382</td>
<td>87.2</td>
<td>12.8</td>
<td>199.65</td>
</tr>
<tr>
<td>Ba(Ti$<em>{0.96}$Sn$</em>{0.03}$Zr$_{0.01}$)O$_3$</td>
<td>6.19</td>
<td>5.418</td>
<td>87.5</td>
<td>12.4</td>
<td>84.54</td>
</tr>
<tr>
<td>Ba(Ti$<em>{0.96}$Sn$</em>{0.04}$)O$_3$</td>
<td>6.18</td>
<td>5.502</td>
<td>89.0</td>
<td>10.9</td>
<td>89.28</td>
</tr>
</tbody>
</table>

\[Table 2\]. Physical properties of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{x}$Zr$_{0.04-x}$)O$_3$ \((x = 0.02–0.04)\) ceramics.
The $\varepsilon_0$ for BT has a value of only 1550 at room temperature which is lower than that of the sample prepared by conventional solid-state reaction route [43, 44]. The observed lower value is as a result of the smaller grain size of the ceramics [45, 46]. With the reduction of crystallite size that corresponds to the width of the domain wall, pinning would be formulated inside the grains and the domain wall motion would be inhibited. The domain wall mobility reduction leads to the decrease of the switching rate, hence lowering the dielectric constant. The presence of tin in the material also decreases the dielectric constant of $\text{Ba(Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ [47, 48]. The observed lowering of the dielectric constant for $\text{Ba(Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ could be considered as a combined effect of the presence of Sn and the nanocrystalline nature of the grains.

The increase of dielectric constant from 1563 to 1671 (Table 3) in porous $\text{Ba(Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.02})\text{O}_3$ and $\text{Ba(Ti}_{0.96}\text{Sn}_{0.03}\text{Zr}_{0.01})\text{O}_3$, respectively, may be as a result of decrease of grain size and porosity of the sample. The frequency-independent behavior of $\varepsilon$ for $\text{Ba(Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.02})\text{O}_3$ and $\text{Ba(Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ beyond 1000 Hz indicates the reduction of the contribution of the charge carriers toward the dielectric permittivity $\varepsilon'$ and tends to a static value at all temperatures as a result of absence of space charge effects [49]. Further, the $\varepsilon'$ exhibits high value which reflects the effect of space charge polarization and/or conducting ion motion. The best sample is $\text{Ba(Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.01})\text{O}_3$ because it exhibited high real dielectric relative permittivity of 1671, loss of 1.63 and low porosity of 12.4% among the doped samples. This shows that the sample $\text{Ba(Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.01})\text{O}_3$ can be used for MLCCs and energy storage application.
The variation of $\tan \delta$ with frequency is shown in Figure 8. Similar to the behavior of $\varepsilon'$ with frequency, the dielectric loss exponentially decreases with decreasing frequency to almost zero for porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$ but rises beyond $10^5$ Hz for Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ and Ba(Ti$_{0.96}$Sn$_{0.03}$Zr$_{0.01}$)O$_3$, respectively. In the lower frequency region, a decrease in the value of $\tan \delta$ is observed which is due to the dominance of space charge polarization and interface effects at lower frequencies. However, for porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{0.02}$)O$_3$ at a frequency of $10^5$ Hz, frequency-independent behavior of these parameters is observed. The values of $\tan \delta$ of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ($x = 0.02 – 0.04$) are shown in Table 3. The decrease of $\tan \delta$ in BaTiO$_3$ from 0.8 to 0.43 and from 1.6 at $x = 0.03$ to 0.43 at $x = 0.02$ clearly indicates that loss tangent shows a decreasing tendency with increase of zirconium content in agreement with literatures [50]. The dielectric losses were a combined result of electrical conduction and orientational polarization of the matter [51].

Table 3. Ferroelectric properties of the samples at room temperature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$P_i$ ($\mu$C/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>0.592</td>
<td>0.295</td>
<td>1.934</td>
</tr>
<tr>
<td>BTSZ1</td>
<td>1.766</td>
<td>0.576</td>
<td>1.411</td>
</tr>
<tr>
<td>BTSZ2</td>
<td>2.930</td>
<td>3.117</td>
<td>4.680</td>
</tr>
<tr>
<td>BTSZ3</td>
<td>2.894</td>
<td>3.726</td>
<td>5.120</td>
</tr>
</tbody>
</table>

Figure 8. Frequency dependence of dielectric loss ($\tan \delta$) of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$ ($x = 0.02–0.04$) at 30°C.
3.2.2. Variation of dielectric constant and tangent loss with temperature

The variation of dielectric constant and tangent loss as a function of temperature for porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics measured from room temperature to 150°C at the frequency of 100 Hz is shown in Figures 9 and 10, respectively. From Figure 9, it is clear that the maximum dielectric constant of porous BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) is at room temperature and decreases with increase in temperature, though less than that reported in CuO-modified Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics synthesized using solid-state reaction [44] except for porous BT where the dielectric constant was observed to decrease from 30 to 70°C and then increased sharply at 90°C. Thereafter, it falls to the lowest level at 110°C, thus indicating a phase transition. For porous Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics, the phase transition seems to be shifted toward lower room temperature with increase in doping concentration as reported by other workers [52]. The shifting of transition temperature ($T_c$) to a lower value can be explained by the larger radius of Sn$^{4+}$ (0.69 Å) and Zr$^{4+}$ (0.72 Å), compared to Ti$^{4+}$ (0.605 Å). Uchino et al. have suggested that with decreasing grain size, $T_c$ was shifted downward toward room temperature, eventually tending toward 0 K at some critical particle size [53].

In Figure 10, the dielectric loss of Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) beyond 70°C becomes almost independent and later merges at higher temperature, except for BaTiO$_3$ which rapidly increases with increase in temperature beyond 90°C. This sharp increase in dielectric loss in the

![Figure 9. Temperature dependence of dielectric constant of nanocrystalline BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$(x = 0.02–0.04) ceramics measured at 100 kHz.](image-url)
high temperature region in BaTiO$_3$ may be attributed to the increased mobility of charge carriers arising from defects or vacancies in the sample [54]. In porous BaTiO$_3$ sample, the minimum in the dielectric loss is coincident with the maximum of dielectric anomaly. Therefore, we conclude that porous BaTiO$_3$ sample undergoes a structural phase transition. The loss tangent of porous Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics decreases with increasing Zr content due to the chemical stability of Zr$^{4+}$ compared to that of Ti [55].

3.3. Ferroelectric properties

The polarization versus electric field (P-E) hysteresis loops of BaTiO$_3$ and Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04) ceramics measured at room temperature and 1 kHz with different Sn concentrations are shown in Figure 11. The results are presented in Table 3. The polarization hysteresis loop is not fully saturated which may be due to leakage current. The P-E loops become larger and broader as the Sn content (x) increases which show the ferroelectricity of the Ba(Ti$_{0.96}$Sn$_x$Zr$_{0.04-x}$)O$_3$ (x = 0.02–0.04). The increase in Remnant polarization is due to the decrease in the dielectric property and decrease of the porosity of the sample with an increase in Sn doping [56]. The performance parameter of BT is very close to that of the reported values ($P_s$ of 2.0 μC/cm$^2$, $E_c$ of 5 kV/cm) for the ceramic sample [57] and lower than the one obtained by the same synthesis route ($P_s$ of 2.0μC/cm$^2$, and coercive field ($E_c$) of 1060 V/cm) [35]. The decrease of $E_c$ for 2.8 to 2.6 kV/cm for Ba(Ti$_{0.96}$Sn$_{0.03}$Zr$_{0.01}$)O$_3$ to Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$ may be
attributed to the reduction in grain size and indicates that Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$ may be useful for switching applications. BaTiO$_3$ samples have cubic phase and ferroelectric tetragonal phase (Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$, Ba(Ti$_{0.96}$Sn$_{0.03}$Zr$_{0.01}$)O$_3$, and Ba(Ti$_{0.96}$Sn$_{0.04}$)O$_3$) as evident from XRD result. Polarization reversal of a ferroelectric domain is much easier inside a larger grain the comparison to that in a smaller grain [58]. Oxygen vacancies may affect domain wall motion by a screening of the polarization charge. A formation ion of mechanical barriers against the domain walls by oxygen vacancies, that is, domain wall pinning, might also stabilize the domain configuration.

3.4. Complex impedance

Figure 12 shows the variation of the real ($Z'$) and imaginary ($Z''$) part of impedance (inset) with frequency from 200 to 400°C. It is observed that the magnitude of $Z'$ decreases with increase in frequency at different temperatures which is an indication of an increase in dc conductivity. The coincidence of $Z'$ and $Z''$ values at higher frequencies at all temperatures indicates a possible release of space charge [59] and a consequent lowering of the barrier properties of the material [60]. Further, at low frequencies, the $Z'$ values decrease with rise in temperature, that is, they show negative temperature coefficient of resistance (NTCR) behavior similar to semiconductors [61].
Figure 13 shows the complex impedance plots ($Z^*$) or Cole-Cole plots, that is, plotting imaginary part $Z_0^\prime\prime$ against the real part $Z_0^\prime$ of complex impedance $Z^* = Z^\prime + jZ^\prime\prime$ of BTSZ ceramic, performed at 200, 250, 300 and 350°C over a wide frequency range (40 Hz to 1 MHz). From Figure 13, it is observed that with the increase in temperature, the slope of the lines decreases and the curve moves toward real ($Z_0^\prime$) axis indicating an increase in conductivity of the sample.

At temperature 400°C, two semicircles are formed (Figure 14) representing resistance for grain ($R_g$) and grain boundary ($R_{gb}$) effect in the material having centers lying below the real axis confirming the presence of the non-Debye type of relaxation phenomenon in the materials [62]. Hence, grain and grain boundary effects in Figure 14 could be separated at these temperatures. The high-frequency semicircle corresponds to a bulk contribution, and the low-frequency semicircle corresponds to the grain boundary effect [63]. The value of bulk resistance ($R_g$) in the high-frequency range and grain boundary resistance ($R_{gb}$) in the low-frequency range obtained from the intercepts of the semicircular arcs formed at 400°C on the real axis ($Z_0^\prime$) is 44.08 and 148.4 kΩ, respectively (Figure 14). The observed data were modeled on an equivalent circuit having a series combination of two parallel resistor-capacitor elements (inset of Figure 14) [64, 65]. The real ($Z^\prime$) and imaginary ($Z^\prime\prime$) parts of total impedance of the equivalent circuit are defined as:
Figure 13. Plot of $Z'$ versus $Z''$ (Nyquist or Cole-Cole plots) for nanocrystalline Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ceramic data taken over a wide frequency range of 40 Hz to 1 MHz at 200–350°C.

Figure 14. Plot of $Z'$ versus $Z''$ (Nyquist or Cole-Cole plots) for nanocrystalline Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ceramic data taken over a wide frequency range of 40 Hz to 1 MHz at 400°C.
\[ Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \]  
\[ Z'' = R_g \left[ \frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] + R_{gb} \left[ \frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \right] \]  
where \( R_g \) and \( C_g \) are the grain resistance and grain capacitance, \( R_{gb} \) and \( C_{gb} \) are the grain boundary resistance and grain boundary capacitance at the interfacial regions, respectively, and \( \omega \) is the angular frequency. The semicircles in the impedance spectrum have a characteristic peak occurring at a unique relaxation frequency \( (\omega_{\text{max}} = 2\pi f_{\text{max}}) \) which can be expressed as \( \omega_{\text{max}} RC = \omega_{\text{max}} \tau = 1 \), where \( f_{\text{max}} \) is the frequency at the maximum of semicircle. Therefore,

\[ f_{\text{max}} = \frac{1}{2\pi \tau} = \frac{1}{2\pi RC} \]  

where \( \tau \) is the relaxation time. The respective capacitances (\( C_g \) and \( C_{gb} \)) due to the grain and grain boundary effects can be calculated using Eq. 7. The values of \( R_g, R_{gb}, C_g \) and \( C_{gb} \) obtained from Cole-Cole plots at 400°C are 44.17 kΩ, 148.43 kΩ, 3.23 × 10^{-10} Farad and 1.71 × 10^{-8} Farad, respectively. The corresponding relaxation times due to both the bulk and grain boundary effect (\( \tau_g \) and \( \tau_{gb} \)) have been calculated using Eq. 7 to be 1.42 × 10^{-5}s and 2.55 × 10^{-3}s, respectively.

Moreover, the results showed a higher value of \( R_{gb} \) as compared to \( R_g \) as a result of a lower concentration of oxygen vacancies and trapped electrons in grain boundaries. This is due to the loss of oxygen during high temperature sintering process which again greatly influenced the conduction and dielectric relaxation behavior of the material. High temperature sintering leads to the formation of oxygen vacancies as \( 2O_x^0 \rightarrow O_2(g) + 2V_0^+ + 4e^- \). Nevertheless, when the temperature is slowly cooled to room temperature in air, a reoxidation process occurs as \( 2V_0^+ + O_x^0 + 4e^- \rightarrow O_2(g) \) and leads to the formation an insulating grain boundary and highly conductive oxygen-deficient grains [66].

### 4. Conclusion

In this study, porous BaTiO_3 and Ba(Ti_{0.96}Sn_{0.02}Zr_{0.04-x})O_3 (x = 0.02–0.04) ceramics with nanocrystalline structure were obtained by mechanochemical synthesis method. The effects of the porosity of the ceramics on their microstructural and dielectric properties were investigated. It was found that porosity of the ceramics could be tailored by varying the dopant content. With increase of Sn content, porosity decreased from 12.8 to 10.9%. X-ray analysis confirms the cubic and tetragonal structure at room temperature for pristine and Zr and Sn codoped barium titanate, respectively. FESEM images indicated that the particles possess a porous structure. The temperature dependence dielectric study revealed a normal ferroelectric behavior in the material. Room temperature dielectric constant increased with Sn and Zr content, while
Dielectric loss decreased. Electrical parameters such as the real part of impedance ($Z'$), the imaginary part of impedance ($Z''$) as a function of both frequency and temperature have been studied through impedance spectroscopy. Nyquists plots of Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ceramic show both bulk and grain boundary effects at 400°C which indicates the NTCR behavior of the sample. Therefore, Ba(Ti$_{0.96}$Sn$_{0.02}$Zr$_{0.02}$)O$_3$ ceramic is considered as a promising low-cost material for thermistor applications. The electrical relaxation process occurring in the material has been found to be temperature dependent.

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