Effect of Sr$^{2+}$ doping on the phase transition of BaTiO$_3$ lead-free ferroelectric ceramics

Sarir Uddin$^{1,2,*}$, Sidra Hameed$^3$, Nisar Ali$^4$, Khaled Althubeiti$^5$, Abid Zaman$^6*$, Hussein Alrobei$^5$, Muhammad Mushtaq$^7$ and Fozia Sultana$^8$

1 Department of Physics, Government College Hayatabad, Peshawar 25000, Pakistan
2 Department of Physical and Numerical Sciences, Quutuba University of Science & Information Technology Peshawar 25000, Pakistan
3 Department of Physics, Government Post Graduate Jehanzeb College Swat 19230, Pakistan
4 Department of Chemistry, College of Science, Taif University, PO Box 11099, Taif 21944, Saudi Arabia
5 Department of Physics, Riphah International University, Islamabad 44000, Pakistan
6 Department of Mechanical Engineering, College of Engineering, Prince Sattam bin Abdulaziz University, Alkharj 11942, Saudi Arabia
7 Faculty of Materials Science, Beijing University of Technology, Beijing, 100124, People’s Republic of China
8 University of science and technology China, Hefei, Anhui, 230026, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: sariruddin@uop.edu.pk and zaman.abid87@gmail.com

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1. Introduction

Barium titanate (BaTiO$_3$) is a ferroelectric material with an ABO$_3$ type perovskite structure, where Ba$^{2+}$ is occupying the A-site, Ti$^{4+}$ occupying the B-site, and oxygen is holding the each face of the cubic structure [1]. There are four isomorphs of BaTiO$_3$ which is Rhombohedral, orthorhombic, tetragonal, and cubic. BaTiO$_3$ is durable in its tetragonal form at ambient temperature, but the cubic form retain its stability at temperature exceeding 120°C [2]. Furthermore, spontaneous polarization in BaTiO$_3$ happens when the temperature is reduced below 120°C (the Curie temperature, Tc), and the crystal undergoes a phase shift to the ferroelectric state with tetragonal structure. At 5°C, BaTiO$_3$ undergoes a second phase transition; below this temperature, the crystal retains its ferroelectric orthorhombic structure. Below ~60°C, a third phase change occurs due to the ferroelectric’s rhombohedral symmetry [3]. The three ferroelectric polymorphs of BaTiO$_3$ with non-zero electric dipole moments below Curie temperature (120°C) are tetragonal, orthorhombic, and rhombohedral phases. BaTiO$_3$ changes to a non-perovskite hexagonal phase at temperatures over 1429°C [4].

At Curie temperature, BaTiO$_3$ possess higher dielectric constant of about 1200. Barium Titanate has a relatively larger electromechanical coupling factor $k_p (∼ 0.50)$ [5]. Variations in the basic features of BaTiO$_3$-based compounds occur due to different substitutions in BaTiO$_3$ at the A and B sites [6–9]. Zhang et al [10] have investigated the sol-gel derived Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ bulk ceramics and thick films. According to their findings, thick films have a dielectric constant of 1209 and a loss tangent of 0.016 at 0°C, 10 kHz, while BST ceramics in bulk were found to have a 5510 of 0.02, respectively, at 0°C, 10 kHz. The nonlinear variation in
dielectric properties of $Ba_{x}Sr_{1-x}TiO_3$ ceramics under external DC bias field was actually described by Wei et al [11]. Kuwabara et al [12] had reported increases in the Curie point ($T_C$) of undoped and lanthanum (La) doped barium titanate ($BaTiO_3$) ceramics sintered at temperatures in the range of 1300°C–1450°C were observed. Both undoped and 0.3% La-doped $BaTiO_3$ ceramics showed almost the same $T_C$ behavior; their $T_C$ increased by 3.5°C as the sintering temperature was increased from 1300°C to 1450°C.

The purpose of this study is to investigate the effects of the substitution of $Sr^{2+}$ with $Ba^{2+}$ in the amounts of 0%, 40%, and 80 mol%, according to the stoichiometry of $Ba_{1-x}Sr_xTiO_3$ ceramics. The synthesis process were carried out by the conventional mixed oxide method. After the heat treatment, the samples were characterized in terms of structure, crystallite morphology, and phase transition.

2. Materials and synthesis

The solid state approach was used to manufacture solid solutions of $Ba_{1-x}Sr_xTiO_3$ ($x = 0, 0.4, 0.8$) ceramics. The stoichiometric ratios were used to weigh the starting ingredients of $BaCO_3$, $SrCO_3$, and $TiO_3$. In a horizontal ball mill with ethanol as a lubricant and zirconium balls as grinding media, the powdered materials were mixed and processed for 24 h. The slurry was dried in an oven and calcined at 850°C for 2 h and grounded with pistol and mortar manually to avoid agglomerations. The calcined powder were mixed with polyvinyl alcohol (PVA) and pressed into pellets with a diameter of 10 mm at a pressure of 100 MPa. The aforesaid pellets were calcined for 2 h at 1150°C, with heating and cooling rates of 5°C min⁻¹.

3. Characterization

The analysis of phases was governed by an x-ray diffractometer (XRD). The thermal properties were examined by Thermo gravimetric analyzer (TGA). A scanning electron microscope (SEM) was used to examine the microstructural and chemical compositional properties. An impedance analyzer was used to determine the dielectric characteristics (HP4282A).

4. Results and discussions

4.1. Phase analysis

The phase analysis of the samples were carried out through the XRD Technique. Figure 1 reveal the crystallographic array of $Ba_{1-x}Sr_xTiO_3$ (BST) ceramics composition calcined at 850°C and sintered at 1200°C. The XRD pattern indicates that the sample shows good crystallinity and all the diffraction peaks are well consistent with the single phase $BaTiO_3$ perovskite structure [13]. Moreover, the composites assigned to space group pm-3m are well-matched with PDF #39–1395. It is revealed that $Ba^{2+}$ is replaced by $Sr^{2+}$ at the A-site of $ABO_3$ perovskite structure. Moreover, with the increasing of strontium content ($x$) in $Ba_{1-x}Sr_xTiO_3$ the peaks in XRD spectra gradually shifted to lower angle. It is due to that ionic radii of $Ba^{2+}$ ions ($r = 1.61 \text{ Å}$) are larger than that of $Sr^{2+}$ ions ($r = 1.44 \text{ Å}$) at the 12-fold coordinated A-site of the perovskite following the Bragg’s diffraction law ($2dsin\theta = m\lambda$) [14, 15]. The enlarged (1 0 0) diffraction peaks with angles from 31.5° to 33.5° are given in figure 1(b) to clearly show the phase evolutions.

4.2. TGA analysis

Thermo-Gravimetric Analysis plot of as-obtained composite $BaTiO_3$ ceramics from ambient temperature to 1000°C at a heating rate of 5°C min⁻¹ is shown in figure 2. The graph depicts two parts of the mass-loss process. The first losses were discovered between 200 and 400°C (about 14%). This could be due to water and other organic solvents evaporating from the surface. The second loss, which occurs between 650°C and 800°C (approximately 11%), is attributed to composites crystallization and CO₂ group emission from solid state solution [16].

4.3. Microstructure analysis

The microstructure of the synthesized BST composites were investigated through Scanning Electron Microscopy. Figure 3 displays shows the SEM micrograph of $Ba_{1-x}Sr_xTiO_3$ samples that were annealed at 850°C and 1200°C for 2 h in air. SEM scans reveal a thick microstructure with no visible holes. The grains have a spheroidal shape, ranging in size from $2 \times 3 \text{μm}^2$ to $3 \times 5 \text{μm}^2$, which was compatible to prior research [17, 18]. The grain size of the as-obtained samples were found to be decrease somewhat as $Sr^{2+}$ was increased. The EDX...
4.4. Phase transition analysis

Figure 4 illustrate the variation in dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) with temperature at various frequencies of Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics. The dielectric phase transition with temperature was studied by the temperature dependent properties as shown in figure 4. The anomalies in the dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) versus temperature curves indicated the Curie point and the phase transition from polar ferroelectric phase to non-polar paraelectric phase of Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics. Figure 4 indicated that the Curie point is decreased with increasing Sr$^{2+}$ content in Ba$_{1-x}$Sr$_x$TiO$_3$ composition consistent with previous reports [7, 19, 20]. The value of the dielectric constant decreased with increasing Sr$^{2+}$ content which may be attributed to the substitution of relatively smaller ion of Sr$^{2+}$ for Ba$^{2+}$ in the perovskite structured Ba$_{1-x}$Sr$_x$TiO$_3$ [14]. A frequency dispersion is indicated in the dielectric constant and dielectric loss versus temperature curves which is attributed to the different cations (Ba, Sr) at A-site of the perovskite structured as obvious in figure 4(a) [21, 22].
5. Conclusion

In this particular study, the Solid state (mixed oxides) technique was used to construct single phase $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) ceramics. The XRD patterns are matched with PDF $\#39–1395$, space group $\text{pm-3m}$. The A-site of the $\text{ABO}_3$ perovskite structure reveals that $\text{Ba}^{2+}$ is replaced by $\text{Sr}^{2+}$. The SEM scan revealed a microstructure, that was thick and void of obvious pores. The morphology of the grains was found to be spheroidal, ranging in size from $2 \times 3 \mu \text{m}^2$ to $3 \times 5 \mu \text{m}^2$. The thermal properties were used to investigate the dielectric phase change with temperature, and it was discovered that when the $\text{Sr}^{2+}$ concentration in

![Figure 3. SEM micrograph of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ composites](a)-(c) x = 0, 0.4, 0.8, (e) EDX spectrum.]
Ba$_{1-x}$Sr$_x$TiO$_3$ mixture increases, the Curie point decreases. It was also found that the value of the dielectric constant decreased with increasing Sr$^{2+}$ content in Ba$_{1-x}$Sr$_x$TiO$_3$ composition.

Figure 4. Variation in dielectric constant and dielectric loss with temperature at various frequencies of Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics (a) $x = 0$, (b) $x = 0.4$, (c) $x = 0.8$. 

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

Abid Zaman https://orcid.org/0000-0001-9527-479X
Asad Ali https://orcid.org/0000-0002-3768-8748

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