***Paper ID:93***

# Synthesis and investigation of frequency-dependent dielectric behavior in potassium, strontium, and niobium-doped and co-doped barium titanate ceramics

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## Abstract

*$BaTiO_3$ (BTO) ceramic resistivity, dielectric properties and density generally restrict BTO's electronic applications. By doping with $K^+$, $Nb^{2+}$, and $Sr^{5+}$, this study attempts to improve the electrical behavior of BTO for the fabrication of $[(Ba_{0.88}Sr_{0.00}K_{0.03})O_3]$ (BSK0.02-TN) and $[(Ba_{0.87}Sr_{0.003})(Ti_{0.99}Nb_{0.03})O_3]$(BSK0.03-TN). Compared to BTO that had not been doped, doped samples exhibited higher bulk densities (BSK0.02-TN: 3.87 g/cm³ and BSK0.03-TN: 3.37 g/cm³) and resistivities ($2.998\times10^6$ and $1.72\times10^6$ Ω·cm). Impedance analysis revealed that dopants promote grain growth, reduce boundaries, and increase resistance. Furthermore, BSK0.03-TN had the highest dielectric constant and lowest optical absorption, indicating a potential for energy storage and capacitor technologies. Further characterization techniques, such as measuring the dielectric constant at varying frequencies and temperatures, as well as dielectric loss, will help confirm the potential of $K^+$, $Nb^{2+}$, and $Sr^{5+}$-doped BTO ceramics for advanced electronic applications.*

Keywords: BT ceramics, Dielectric constant, Impedance analysis, Material Science.

## 1. Introduction

Barium Titanate ($BaTiO_3$; BTO) is widely recognized as one of the most prominent ferroelectric materials, known for its exceptionally high dielectric constant, as reported by numerous researchers. Its unique properties make it highly suitable for a wide range of applications in electronic devices [1, 2]. In various studies, it has been found that the physical and electric properties of it are highly dependent on doping elements. The doping elements influence factors like grain size, density, and dielectric constant [3]. In that case, BTO ceramics have a higher concentration of donor dopants, leading to a higher dielectric constant with reduced dielectric loss. On the contrary, acceptor doping has a reverse effect on the dielectric properties- the dielectric constant was reduced while the dielectric loss was enhanced [1, 4].

Recent research has shown the effect of different doping elements on enhancing properties and optimizing material for advanced applications [5, 6]. In some studies, the effects of Sr doping have been demonstrated, though limited research has been conducted on K doping. Nb, however, has shown significant improvements in the performance of BTO [7, 8].

Notwithstanding these advancements, substantial gaps persist in comprehending the intricate interactions among various dopants in BTO ceramics. The synergistic effects of co-doping with Sr, K, and Nb remain inadequately comprehended, especially concerning their influence on the structural and electrical properties of ceramics. Moreover, although research has shown a degree of success in improving dielectric characteristics, discrepancies in findings attributable to fluctuations in dopant concentrations, preparation techniques, and sintering circumstances underscore the necessity for more comprehensive studies. The ambiguity, especially in multi-doped systems, constrains the customization of BTO ceramics for particular industrial applications.

The objective of this study is to investigate the effects of co-doping barium titanate with Sr, Nb, and K—specifically $[(Ba_{0.88}Sr_{0.1}K_{0.02})(Ti_{0.99}Nb_{0.01})O_3]$ (BSK0.02-TN) and $[(Ba_{0.87}Sr_{0.1}K_{0.03})(Ti_{0.99}Nb_{0.01})O_3]$ (BSK0.03-TN)—and to analyze their dielectric properties (at 1000 Hz) and resistivity characteristics.

## 2. Materials and methods

The preparation of pure BTO, (BSK0.02-TN), and (BSK0.03-TN) ceramic samples involved a solid-state sintering method. The experimental procedure involved the utilization of high-grade raw materials, namely $BaCO_3$ (purity >

99%, Merck Specialties, India), $K_2CO_3$ (purity > 99%, Merck Specialties, India), $SrCO_3$ (purity > 99%, SRL, India), $Nb_2O_5$ (purity > 99%, SRL, India), and $TiO_2$ (purity > 99%, Merck Specialties, India), in the correct stoichiometric proportions. The powders were weighed and then subjected to ball milling using ethanol (purity > 99%, Merck, Germany) as the milling medium. Yttria-stabilized alumina balls were utilized for this process, which lasted for 20 hours. Following milling, the resulting slurry was dried in an oven at 100°C for 24 hours. Subsequently, the desiccated powder was manually ground for 2 hours and then calcined at 900°C for 2 hours. Then, the powder was subjected to mixing with a binder consisting of 2-wt% polyvinyl alcohol. The resulting mixture was then crushed into disk-shaped pellets using an axial pressure of 2.5 tons. Subsequently, the manufactured pellets underwent a sintering process at a temperature of 1250°C for a duration of 4 hours. The entire procedure is illustrated in Figure 1. The sample pellets were analyzed using an impedance analyzer to evaluate their frequency-dependent dielectric behavior and resistivity.

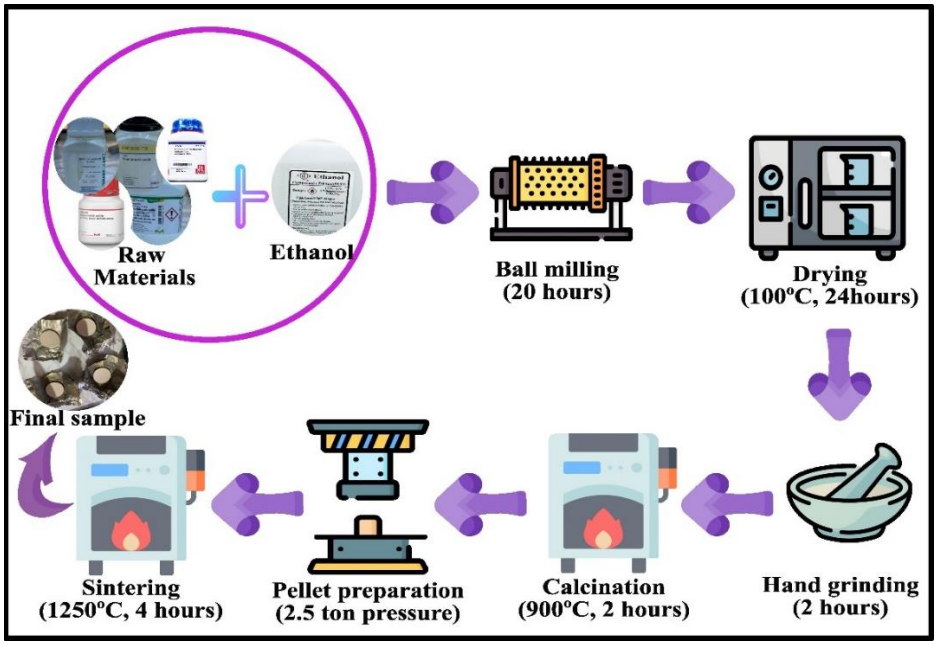



**Figure 1.** Flowchart of ceramic sample preparation.

## 3. Characterization of the samples

### Physical characterization

The physical property and the bulk density of the ceramics according to ASTM-C29/C29M standards. The bulk density (ρ) of the samples was calculated using the formula:

$$\rho = \frac{M}{V} \tag{1}$$

Where M is the mass of the sample (g), V is the volume of the sample ($cm^3$). For a cylindrical sample, the volume is given by:

$$V = \pi r^2 h \tag{2}$$

Here, r is the radius of the cylinder (cm), and h is the height of the cylinder (cm).

### Electrical characterization

The electrical properties of the synthesized ceramic samples were examined using an impedance analyzer (Wayne Kerr 6500B series, UK) with a 500mV input signal. Specifically, resistivity and dielectric constant as functions of frequency were measured, providing insights into the frequency-dependent behavior of the ceramics.
The electrical resistivity ($\rho_r$) of the samples was measured at 1000 Hz using the following equation [9]:

$$\rho_r = R\frac{A}{L} \tag{3}$$

Where R is the measured resistance (Ω), A is the cross-sectional area of the sample ($m^2$), and L is the distance between the electrodes (m).
The dielectric constant of the samples was measured at 1000 Hz. The capacitance value (C) was measured to determine the dielectric constant, and it was calculated using the following equation [10]:

$$\kappa = \frac{CD}{€A} \tag{4}$$

Here, κ is relative permittivity (dielectric constant), C denotes capacitance (Farads, F) of the capacitor, D is distance between the plates (in meters, m), € is permittivity of free space (also known as the vacuum permittivity), which is a constant approximately equal to 8.854 x $10^{-12}$ $Fm^{-1}$ and A is the area of one of the plates (in square meters, $m^2$).

## 4. Result analysis

### Bulk density analysis

Table 1 reflects the bulk density of pure BTO, which is 3.44 $gcm^{-3}$, while that for the sample, BSK0.02TN, is 3.87 $gcm^{-3}$ and BSK0.03TN is 3.37 $gcm^{-3}$. The slight increase in the bulk density of the co-doped sample BSK0.02TN compared to pure BTO and BSK0.03TN is most likely because several factors act in concert. The higher barium content in (BSK0.02TN), with barium being heavier than potassium, adds to the overall mass, increasing the bulk density. Additionally, the lower potassium content reduces structural disturbances and lattice defects, which allows for improved grain packing. Furthermore, fewer lattice defects result in better densification during sintering, which enhances the compactness of the material. Generally, doping with Sr, K, and Nb can improve sintering characteristics by reducing porosity and increasing grain growth, hence increasing the bulk density. Considering factors such as optimized composition, Sr and Nb are responsible for the increase of bulk density in BS-K0.02-TN.

**Table 1.** Comparison of bulk density, resistivity, and dielectric constant of BTO and doped samples.

| Compositions | Bulk density ($gcm^{-3}$) | Resistivity Ω·cm | Dielectric Constant (at 1000Hz) |
|---|---|---|---|
| BTO | 3.44 | $1.50 \times 10^6$ | 184.00 |
| (BSK0.02-TN) | 3.87 | $2.998 \times 10^6$ | 506.55 |
| (BSK0.03-TN) | 3.37 | $1.72 \times 10^6$ | 588.80 |

### Resistivity analysis

The resistivity values (Table 1) indicate that pure BTO has a resistivity of $1.50 \times 10^6$ Ω·cm. In comparison, the (BSK0.03-TN) sample increases resistivity to $1.72 \times 10^6$ Ω·cm, while the (BSK0.02-TN) sample exhibits a still higher resistivity of $2.998 \times 10^6$ Ω·cm. This increase in resistivity may be ascribed to substitution by $Ba^{2+}$ with $K^+$ $Sr^{3+}$, and $Nb^{2+}$ ions creating crystal structure distortions and defects acting as scattering centers for charge carriers. The highest resistivity was found for (BSK0.02-TN). It is believed that K, Sr & Nb increase grain growth rate and simultaneously reduce the area of grain boundary (as well as imperfections that induce conductivity), resulting in the increment of resistivity.

### Dielectric constant analysis

The dielectric constant of BTO, (BSK0.02-TN), and (BSK0.03-TN) was measured at 1000 Hz (depicted in Figure 2). The pure BTO sample exhibited a dielectric constant of 184.00, while an immense increase in the dielectric constants was observed for the doped compositions. BSK0.02-TN showed a dielectric constant of 506.55, while in BSK0.03-TN, the value further increased to 588.80. The increased dielectric constant due to doping might be ascribed to an enhanced polarization mechanism with lattice distortions and defects created due to the doping of Sr, K, and Nb. The observed trend, viz., BSK0.03TN > BSK0.02TN > BTO, shows increased polarizability in the doped compositions. The trend BSK0.03TN > BSK0.02TN > BTO for increased lattice distortion, generation of defects, and enhanced polarization mechanisms due to the higher doping levels of Sr, K, and Nb shows that the material is more polarizable with an electric field.

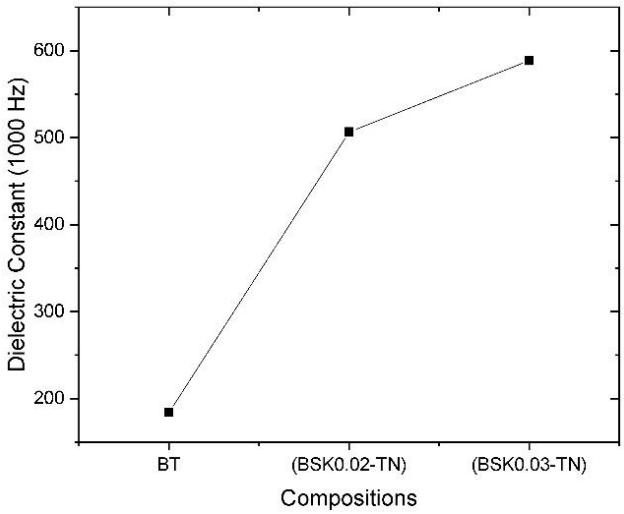



**Figure 2.** Dielectric Constant (1000 Hz) vs different compositions of ceramic samples.

## 5. Conclusion

The present study successfully concludes with the solid-state synthesis and comprehensive electrical characterization (resistivity and dielectric constant) of BTO-based ceramics doped with Sr, K, and Nb. The obtained results showed that the doping BTO significantly modifies its physical and electrical characteristics. The resultant doped compositions exhibited high values of dielectric constants and resistivity as compared to pure BTO. Among others, the BSK0.03-TN composition exhibited the highest dielectric constant due to grain growth rate and simultaneous reduction of the area of grain boundary with the Sr, K, and Nb doping. Consequently, promising BTO-based ceramics for electronic applications were obtained, which included high dielectric constants. In fact, further optimization of the doping and sintering processes is needed to realize such properties in practical applications. The results obtained in this work will contribute to the experience already available in the use of dopants for the tuning of BTO ceramic properties - an important task in the development of modern electronic components.

## 6. Acknowledgement

The authors acknowledge Md. Manwar Hossain, Technical officer, Department of Glass & Ceramic Engineering, Rajshahi University of Engineering & Technology (RUET).

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