Ferroelectric and impedance response of lead-free (B0.5N0.5) TiO3-BaZrO3 piezoelectric ceramics

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Abstract. Lead-free piezoelectric (0.96B0.5N0.5TiO3)-0.04BaZrO3 (BNT-BZ4) was synthesized by using a solid-state reaction method. SEM micrograph shows dense microstructure. X-ray diffraction (XRD) indicated the formation of a BNB-BZ4 single phase having pseudocubic symmetry. A maximum value of remnant polarization (30 µC/cm2) and piezoelectric constant (112 pC/N) was observed for BNT-BZ4 ceramic. The temperature dependences of the dielectric properties of BNT-BZ4 were investigated in the temperature range of 25-600°C at various frequencies (0.1 Hz-1 MHz). The maximum dielectric constant value (εr) reaches a highest value of 4046 (at 10 kHz). The electrical properties were investigated by using complex impedance spectroscopy and provided better understanding of relaxation process.

1. Introduction
In the last few decades, there has been much interest in finding lead-free piezoelectric ceramics. Among lead-free candidate materials, Bismuth sodium titanate, Bi0.5Na0.5TiO3 (BNT), is one of the superior candidate material having excellent ferroelectric properties with a large remanent polarization (Pr = 38µC/cm2) and a relatively high Curie temperature (Tc = 320 °C) [1]. At room temperature BNT has an ABO3 perovskite structure with a ferroelectric rhombohedral phase. As temperature increases, BNT transform from rhombohedral to tetragonal and finally into cubic phase. The transition temperatures of rhombohedral-tetragonal phase (TR-T) and tetragonal-cubic phase (TT-C) are 300 and 540 °C, respectively [2]. On the other hand, BNT has drawbacks, such as a large coercive field (Ec) of approximately 7.3 kV/mm and a high conductivity, which causes problems in the poling process.

To improve the piezoelectric properties of BNT ceramics it is modified with other perovskite such as BaTiO3 (BT) [3, 4], BaZrO3 (BZ) [5], SrTiO3 (ST) [6, 7], (Bi0.5K0.5)TiO3 (BKT) [8, 9], NaNbO3 (NN) [10, 11], KNaNbO3 (KNN) [12]. These modifications reveal a significant enhancement in its piezoelectric and ferroelectric properties. However, previous reports are limited to the piezoelectric and the electromechanical properties, thus, the effects of doping and several solid solutions on the dielectric and the electrical properties are not fully understood.

In this work, 0.94(Bi0.5Na0.5)TiO3-0.04BaZrO3 (BNT-BZ4) attain a maximum ramanant polarization (Pr =30 µC/cm2) with a maximum static piezoelectric coefficient of (d33 = 112pC/N). However, little attention has been paid to impedance and conductivity studies of this material. In this study, we prepared...
BNT-BZ4 ceramics through a conventional solid-state reaction method and investigated the dielectric, electrical conductivity and impedance relaxations in the BNT-BZ4 ceramic.

2. Experimental
The 0.96(B0.5N0.5)TiO3-0.04BaZrO3 (BNT-BZ4) ceramics was fabricated by using conventional, solid-state reaction method with BaCO3 (99%), Na2CO3 (99.95%), Bi2O3 (99.90%), ZrO2 (99%), and TiO2 (99.90%) from Sigma Aldrich Co, were used as starting raw materials. Prior to measuring the weight, the powders were dried in an oven at 100 °C for 24 hrs. The dried powders were weighed according to the stoichiometric formula and ball-milled for 24 h in ethanol. The dried slurries were calcined at 850 °C for 2 h and ball milled again to dissociate the agglomerates. After drying, the powders were pulverized, passed through a sieve of 150 µm mesh and mixed with an aqueous polyvinyl alcohol (PVA) solution as a binder for granulation. The granulated powders were subsequently pressed into green disks with diameter of 10 mm and thicknesses of 2 mm. The green disks were embedded in the same compositional powder to minimize the evaporation of the volatile elements (Bi, Na) and sintered at 1160 °C for 2 h in air.

The crystal structure was characterized using an X-ray diffractometer (XRD, X’pert MPD 3040, Philips) while microstructure was examined through scanning electron microscope (SEM) JP/JSM5200 (Japan). To measure the electrical properties, silver paste was coated on both polished faces of the sintered samples and fired at 650 °C for 0.5 h to form electrodes. Dielectric constant and complex impedance data for the BNT-BZ4 ceramic were measured using an automatic acquisition system using an impedance analyzer (SI1260, UK) in 25-600°C temperature range with frequency range of 0.1 Hz - 1MHz.

3. Results and discussions
3.1. Phase and microstructure analysis
SEM micrograph of the polished and thermally etched surface of BZ-modified BNT ceramic is presented in Fig. 1. The composition is well sintered and have compact microstructures with an average grain size of 5 ~ 6 µm.

Figure 1. SEM micrographs of BNT-BZ4 ceramic.

Fig. 2 shows the room temperature XRD pattern of BNT-BZ4 ceramic. The X-ray pattern depicts the formation of a single phase without any trace of secondary phase. This indicates that BZ is successfully diffused into BNT to form a complete solid solution. The intensity of the peaks exhibit a pseudo-cubic symmetry having no characteristic peak splitting in the 2θ range of 39° - 41° and 45° - 48°.
3.2. \textit{P–E} ferroelectric hysteresis

The ferroelectric response at room temperature of BNT-BZ4 is shown in Fig. 3. The hysteresis curve showed that ceramic exhibits typical ferroelectric behavior with a maximum remanent polarization ($P_r$) and coercive field ($E_c$) values of $30 \mu\text{C/cm}^2$ and $3.6 \text{kV/mm}$, respectively. In addition, a maximum static piezoelectric coefficient ($d_{33}$) of $112 \text{ pC/N}$ is obtained for BNT-BZ4 ceramic. The significant improvement observed in $d_{33}$ is attributed to a large $P_r$ and a lower $E_c$. This is because a lower $E_c$ enables the ceramics to be more easily poled, while a large $P_r$ favors piezoelectricity.

3.3. Dielectric constant and impedance response

Fig. 4 shows the temperature dependence of dielectric constant ($\varepsilon_r$) of BNT-BZ4 ceramics at different frequencies (0.1 Hz ~ 1MHz) from 25-600°C. It has been observed that dielectric constant increases with increase in temperature up to a maximum value ($\varepsilon_r$) and then it decreases. The maximum dielectric constant ($T_m$) reaches a highest value of 4046 (at 10 kHz). In addition, the dielectric curve revealed that with increasing in measuring frequency, the observed dielectric constant decrease similar to other BNT-based relaxor ferroelectric materials [6]. The decreasing trend of ($\varepsilon_r$) from low frequency to high frequencies may be due to the active presence of all types of polarization at low frequency i.e., electronic, ionic, orientational and space charge polarization; however, at high frequencies, some of these contributions lagged behind and did not follow the field variation and became inactive. At high frequencies, all other modes of polarization fade away and electronic polarization becomes the dominant mode of polarization; therefore, $\varepsilon_r$ decreased at high frequencies.
Figure 4. Temperature dependence of the dielectric constant and loss of BNT-BZ4 ceramics with different frequencies range.

Fig. 5 shows the frequency dependence of the real part $Z'$ (i.e., resistance) of the complex impedance for temperatures ranging from 50°C to 600°C which calculated by using the basic formula given below

$$Z^* = Z' - jZ''$$

Complex impedance $Z^*$ = $Z' - jZ''$ ..............(1)

It is observed that the magnitude of $Z'$ decreases with increase in both frequency as well as temperature, which indicates the possibility of an increase in the ac conductivity [13]. However, the $Z'$ values for all temperatures combine at high frequency, which can be attributed to the release of space charge as a result of reduction in barrier properties of the material with rise in temperature [14] and may be a responsible factor for the enhancement of ac conductivity of the material with temperature at high frequencies. Also at low frequencies, the $Z'$ values decrease with increasing temperature, and the compound exhibits a negative temperature coefficient of resistance (NTCR)-type behavior like that of semiconductors [15].

Figure 5. Variation of the real part of impedance of the BNT-BZ4 with frequency at different temperatures.
Fig. 6 shows the imaginary part of the impedance ($Z''$) as a function of frequency with temperatures ranging from $50 \, ^\circ C$ to $600 \, ^\circ C$. At low temperature the values of $Z''$ monotonically decrease on increasing frequency without getting any peak. However with increasing temperature, $Z''$-frequency plot show peaks at certain frequency ($f_{\text{max}}$) which shifts toward higher frequency as well as the broadening of the peak. The magnitude of $Z''$ at the peak ($Z''_{\text{max}}$) decreases with increase in temperature and the corresponding $f_{\text{max}}$ shifts towards higher frequency. The behavior may be considered due to the temperature dependence of electrical relaxation phenomena on the material [16].

![Figure 6](image_url)

**Figure 6.** Variation of the imaginary part of the impedance of BNT-BZ4 with frequency at different temperatures.

4. **Conclusion**
A lead-free piezoelectric $0.96(B_{0.5}N_{0.5})TiO_3-0.04BaZrO_3$ (BNT-BZ4) was synthesized by using a solid-state reaction method. SEM morphology confirmed that the composition is well sintered and have compact microstructures with an average grain size of $5 - 6 \mu m$. X-ray diffraction pattern reveals single phase with an ABO$_3$ perovskite structure. A maximum value of dielectric constant ($T_m$) 4046 (at 10 kHz), remnant polarization ($P_r$) $30 \mu C/cm^2$ and a piezoelectric constant ($d_{33}$) 112 pC/N were obtained for BNT-BZ4 ceramic. The ac conductivity data showed negative temperature coefficient of resistance character and of relaxation process. The resistances decrease with a rise in temperature.

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