Mechanical Property Characterization of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ Ceramics

C. Efe, H. Yilmaz, Y. K. Tur, and C. Duran

***Abstract*—Bismuth based ferroelectric ceramics are drawing more attention due to being environmentally friendly. The studies are mainly focused on improving electrical properties of these ceramics, whereas studies on mechanical properties are scarce. Mechanical properties of solid solution of sodium bismuth titanate with barium titanate ($(Na_{1/2}Bi_{1/2})_{0.945}Ba_{0.055}TiO_3$) ceramics were studied and compared to those of PZT-4 ceramics. Three point bending strength, elastic modulus as well as indentation toughness were measured. It was found that the stress state with respect to the domain state plays an important role in determining the response to loading. An R-curve behavior was observed with increasing indentation load. The fracture toughness was found to be higher than PZT-4 ceramics. It was found that cracks encounter higher resistance to propagation when propagating in the poling direction.**

***Index Terms*—Ferroelectric material, NBT, mechanical property, R-curve.**

I. Introduction

Recently, lead-free piezoelectric materials are intensely studied due to being environmentally friendly. [1], [2] Among them, sodium bismuth titanate ($Na_{1/2}Bi_{1/2}TiO_3$, or NBT) and its various solid solutions have been drawing special attention as a new candidate for their lead based counterparts [3]. There is a great demand for reducing the adverse effect of lead. However, these studies are mainly focused on improving the electrical and electromechanical properties of this bismuth based piezoelectric material [4].

NBT is a ferroelectric material with A-site complex perovskite structure. Oxygen octahedrons are tilted giving NBT a rhombohedral symmetry at room temperature. However at this stoichiometry NBT has a low piezoelectric coefficient and a high coercive field (E_c = 73 kV/cm) restricting its uses severely. It is difficult to pole these ceramics due to the high coercive field. However, its solid solution with $BaTiO_3$ (BT) not only lowers the coercive field but also enhances the piezoelectric coefficient by forming a rombohedral-tetragonal morphotrophic phase boundary (MPB) at ~5 mol% BT (NBT-5.5BT) [5]-[8].

One big issue with NBT based piezoelectric ceramics is that the unipolar strain curve is hysteretic. That is, the increasing and decreasing strain paths are separated well apart, unlike lead based relaxor ferroelectrics [9]. It is one of the main restrictions on the widespread use of not only NBT based but also other piezoceramics. On the other hand, for vibration damping applications, being hysteretic is not a disadvantage.

Ferroelectrics are very useful in a variety of applications, so called “smart” applications. [10]- [12] They are handy in conversion of mechanical energy into electrical energy or vice versa. In most of these applications piezoelectric ceramics are subjected to severe stress conditions. These stresses may originate not only by mechanical means but also by applied electric fields because of the piezoelectric effect. Unfortunately, piezoelectric ceramics are brittle and have a rather low facture toughness. [13]- [17] Fracture behavior of piezoelectric ceramics is governed by the domain state with respect to the stress state. The understanding of the critical role of ferroelastic domains, non-180° domains, to crack propagation behavior is crucial. Therefore, it is important to know the mechanical properties of the candidate material to predict the service performance as well as to explore new application areas.

Electromechanical actuators couple electrical energy with mechanical energy or vice versa. Electric field induced strains are the response of an actuator to an applied electric field and expressed as the strain energy density which is defined as the energy per unit mass of actuator, given in equation (1),

$$e_{\max} = \frac{1}{rho}\frac{1}{4}\left[\frac{1}{2}E(s_{\max})^2\right] \tag{1}$$

where $e_{\max}$ is the maximum strain energy density, E is the actuators elastic moduli, $s_{\max}$ is the Maximum Field Induced Strain and rho is the actuators Density [18]. A maximum strain energy density is ensured with a low ceramic density and a high achievable strain and elastic modulus. NBT based piezoceramics have lower density than PZT (6 g/cm^3 vs. 7.5 - 8.5 g/cm^3) and comparable maximum strains at high electric fields, up to 0.25%. It is expected to have higher elastic modulus than PZT which is another factor in achieving high strain energy density. [18]

Therefore, it is crucial to know the mechanical behavior of piezoceramics even used for electrical applications. In this paper, crack growth behavior of indentation cracked NBT-5.5BT solid solution in the poled and unpoled state was reported. Hardness, elastic modulus, and fracture toughness of NBT-5.5BT piezoceramics were measured along with some electrical properties and compared to the properties of PZT-4 ceramics (hard). The effect of poling on the mechanical behavior was investigated. Quantitative knowledge on the mechanical properties of bismuth based NBT-5.5BT is limited, because similar studies are scarce in the literature. This research aims to fill the gap.

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II. Experimental Procedure

A. Materials and Sample Preparation

$(Na_{1/2}Bi_{1/2})_{0.945}Ba_{0.055}TiO_3$ (NBT-5.5BT) powders were synthesized using reagent grade TiO_2 (Degussa P25), Na_2CO_3 (Alfa Aesar), Ba_2CO_3 (Riedel de Haen) and Bi_2O_3 (Aldrich) powders. The powder mixture was first ball milled for 18 h in isopropanol using 3 mm ZrO_2 ball, then dried and calcined at 800°C for 2 hours. Hard PZT-4 powders (American Piezo Ceramics, USA) were used as-received. Phase purity was checked by an X-ray diffractometer (Rigaku Dmax 228, Japan). Discs (12 mm in diameter and 2 mm in thickness) for electrical property measurements, and bars ($l \times h \times w$ of 25 × 3 × 4 mm) for mechanical property measurements were first pre-shaped by uniaxial pressing and then compacted at 95 MPa by cold isostatic pressing. NBT-5.5BT samples were sintered at 1200°C for 6 h in air. PZT-4 samples were sintered at 1260°C for 4 h. A double crucible arrangement and PbO-ZrO_2 atmosphere powder were used to control evaporation of lead.

For electrical property studies, the surfaces of the samples were polished down to 1 µm using diamond paste and colloidal silica. Silver electrodes were applied to the parallel faces of the bar and then baked at 600°C for 30 min. Hysteresis loops were measured using a bipolar triangular wave at a period of <5 sec (Radiant- Precision, USA). The poling was carried out in silicon oil bath at 120°C for 15 min. Piezoelectric charge coefficient (d_{33}, Pennbaker Americanpiezo) was measured the next day of poling.

Mechanical property measurements were carried out for both unpoled and poled samples in the perpendicular and parallel directions to the poling electric field (electric field direction). Average of 5measurements were reported. Young's modulus was measured by the resonance frequency method according to the ASTM Standard C1259-94 (Grindo-Sonic System, Belgium). Flexural strength was measured by three point bending test at a crosshead speed of 0.25 mm/min with a lower span of 25 mm following ASTM C1161-90 (Universal Testing Machine, Model 5569, Instron Ltd.). Hardness was measured by Vickers indentation (Instron Wolpert Tester 2100) at 5, 10, and 20 N loads for NBT-5.5BT samples, and at 10, 20, and 50 N loads for hard PZT samples.

B. Results and Discussion

Electrical characterization of NBT-5.5BT and PZT-4 samples were done before carrying out the mechanical tests. PZT-4 was chosen to compare the properties of NBT-5.5BT. Fig. 1 shows the hysteresis loop of PZT-4 samples. The loops embody the characteristic behavior of hard PZT ceramics: a pinched loop with a low remnant polarization. Acceptor dopants (e.g., Fe^{3+}) occupying the B-site in the perovskite structure are compensated by oxygen vacancy formation. The defects form a couple ($2Fe'_{(Ti,Zr)}$ - $V^{\bullet\bullet}_O$) which prevents the domain wall motion during the hysteresis cycle. The result is a pinched hysteresis loop, which is named as hard PZT. Estimated remnant polarization (P_r) and coercive field (E_c) values are 5 µC/cm^2 and 8 kV/cm, respectively. In the same figure the hysteresis loop of the NBT-5.5BT ceramic was also shown. Estimated P_r and E_c were 33 µC/cm^2 and 38 kV/cm, respectively. This sample exhibits a well-saturated hysteresis loop. The piezoelectric coefficients, d_{33}, of NBT-5.5BT and PZT-4 were 110 pC/N and 290 pC/N, respectively.

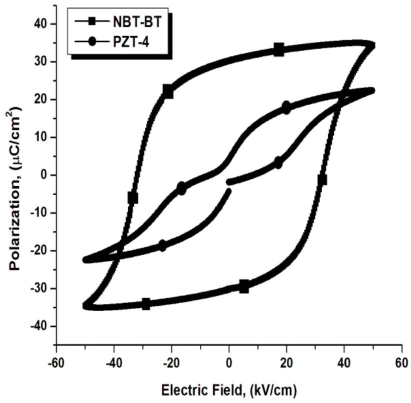


Fig. 1. Hysteresis loops of NBT-5.5BT and PZT-4 ceramics.

3-point bending strength of poled and unpoled NBT-5.5BT and PZT-4 ceramics have been measured. Loading configuration with respect to poling direction was shown in the drawing in Fig. 2. The sample surfaces were named as perpendicular face, Fig. 2.a (the face perpendicular to the poling direction, or electroded face) and parallel face, Fig. 2.b (the face parallel to the poling direction, side face). The measurements from the perpendicular face were taken after gently removing the electrode from it, to exclude its effect on the results. Bending strengths were slightly different for the same sample depending from which face they were measured, that is, they were poling direction dependent. It was the highest when measured from the face perpendicular to the poling direction, Fig. 2.a and the least when measured from the face parallel to the poling direction, Fig. 2.b. An intermediate average value was observed for the unpoled samples irrespective to the measurement face. For NBT-5.5BT, the bending strength from the perpendicular face was 165 MPa and from the parallel face was 155 MPa, even though the difference was within the measurement errors. The unpoled sample had a value of 160 MPa which was somewhat in between. For PZT-4, the bending strength from the perpendicular face was 150 MPa and from the parallel face was 140 MPa, and the unpoled sample had a value of 143 MPa which was also in between.

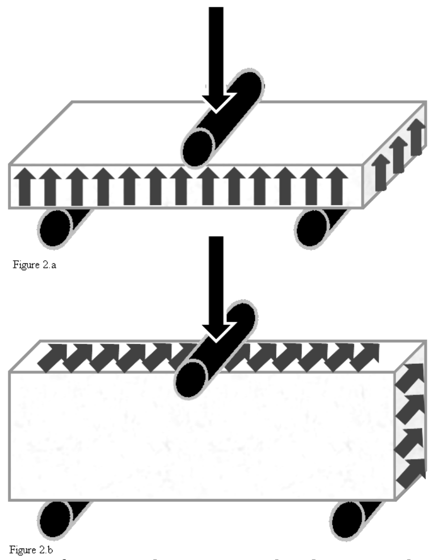


Fig. 2. Loading configuration during 3-point bending strength measurement. Arrows indicate poling direction (electric field direction).
a) Perpendicular face b) Parallel face

Stiffness values of rod shaped samples along the length were also measured using resonans frequency method. For unpoled NBT-5.5BT and PZT-4 stiffness values of 123 and 83 GPa were measured, respectively. NBT-5.5BT was found to be ~50% stiffer than its lead based counterparts.

Vickers indentation was used to measure the hardness of both ceramics. For NBT-5.5BT samples 5, 10 and 20 N and for PZT-4 samples 10, 20 and 50 N loads were used to measure the hardness. The hardness of NBT-5.5BT was 4.7 GPa and for PZT-4 was 3.7 GPa, respectively. However, hardness values were the same irrespective to the surface from which it was measured. No poling direction dependency was observed.

Using the so far reported mechanical values and equation. 1, it is possible to calculate and compare the maximum strain energy density of the relevant ceramics. Taking the maximum strain as 0.25 and 0.2% for NBT-5.5BT and PZT-4, respectively, the maximum strain energy density of NBT-5.5BT was about three times bigger than that of PZT-4.

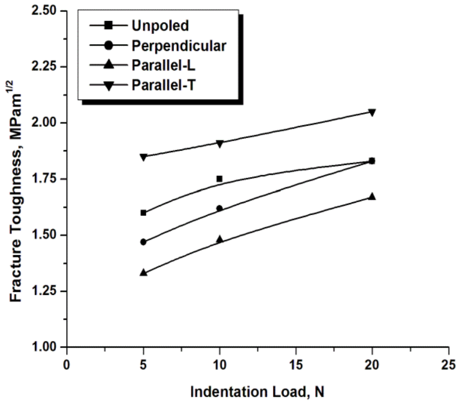
Fracture toughness of NBT-5.5BT and PZT-4 were calculated using the indentation toughness method [19]. In this method, immediate post-indentation crack sizes were measured and it was confirmed that crack lengths were comparable to the indentation diagonal length, confirming the presence of Palmqvist type crack in which case the fracture toughness was calculated using equation (2).

$$K_{IC} = 9.052 \times 10^{-3} H^{\frac{3}{5}} E^{\frac{2}{5}} d l^{-\frac{1}{2}} \tag{2}$$

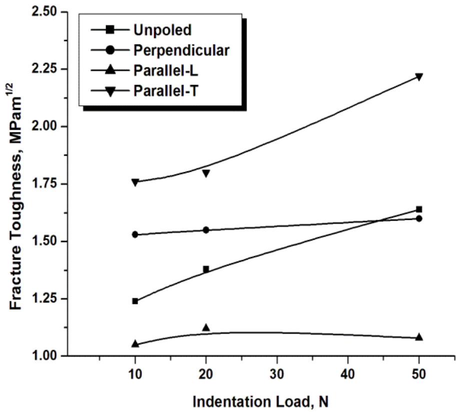
where H is the Vickers hardness, E is Young's modulus, d is the diagonal of the indentation, and l is the crack length emanating from the indent corners [19]. As stated in Equation (2), the calculated fracture toughness is inversely related to the square root of crack length at the corner of the indent. For the unpoled piezoceramics, a slight increase in fracture toughness with increasing indentation load was observed; confirming the presence of R-curve behavior. Fig. 3.a and Fig. 3.b give the fracture toughness measurement results for unpoled NBT-5.5BT and PZT-4 ceramics, respectively. It was found that the calculated fracture toughness of unpoled PZT-4 increased from 1.2 MPam$^{1/2}$ at 10 N load to 1.6 MPam$^{1/2}$ at 50 N load. On the other hand, the toughness of unpoled NBT-5.5BT was found to be slightly higher than hard PZT-4, quantitatively, toughness values of 1.6 and 1.8 MPam$^{1/2}$ were calculated at 5 and 20 N indentation loads, respectively. The relevant crack images from which the toughness values were calculated were given in Fig. 4a. and Fig. 5a., for NBT-5.5BT and PZT-4, respectively. For the unpoled ceramics there would be equal contribution to toughness in all directions because of random distribution of domains, i.e., equal probability of domain switching.

As a result, any difference in crack lengths and, therefore in toughness, were not expected. There was no macroscopic anisotropy in fracture properties.

As for the results from the poled samples, the indent images taken from the poling surface were shown in crack images Fig. 4b. and Fig. 5b. Since the polarization direction is perpendicular to the image plane,(perperndicular face in Fig. 6.) again, any anisotropy in fracture properties is highly unlikely. The stress state and the domain state were identical in all crack propagation directions. There is equal contribution of domain switching to the toughness in the longitudinal and transverse direction.



(a)



(b)

Fig. 3. a). Indentation fracture toughness of NBT-5.5BT ceramics measured from different direction w.r.t. the poling direction. b). Indentation fracture toughness of PZT-4 ceramics measured from different direction w.r.t. the poling direction.

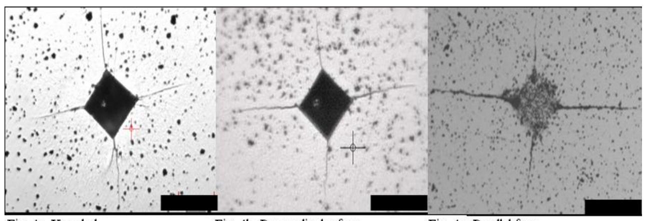


Fig. 4a. Unpoled Fig. 4b. Perpendicular face Fig. 4c. Parallel face

Fig. 4. Crack images of NBT-5.5BT.

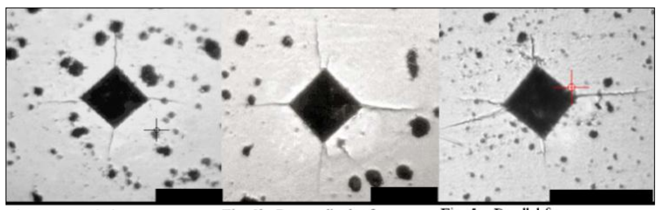


Fig. 5a. Unpoled Fig. 5b. Perpendicular face Fig. 5c. Parallel face

Fig. 5. Crack images of PZT-4.

The fracture toughness values for NBT-5.5BT and PZT-4 ceramics were calculated as 1.8 and 1.6 MPam$^{1/2}$ at 20 and 50 N loads, respectively.

The toughness values calculated from the poled sample and from the perpendicular face were isotropic and in between the upper and lower values of calculated toughnesses from the side face at all indentation loads. The same trend is true irrespective to the kind of samples under investigation.

On the other hand, for the images given in Fig. 4.c and Fig. 5.c, there was a clear difference in crack propagation lengths. The images were taken from the side face, i.e. parallel to the poling direction as shown in Fig. 6. The crack lengths were much shorter in the poling direction as compared to the ones in the direction perpendicular to the poling field. The calculated toughness values were inversely proportional to the crack lengths. So, as the crack propagates in the longitudinal direction on the side face, that is perpendicular to the poling direction, less energy absorbing mechanism were active as compared to the one that propagates in the parallel (transverence) direction. As the crack propagates parallel to the poling direction, the switching of ferroelastic domains (non-180 domains) took place making its progress difficult. Therefore, the calculated fracture toughness values differ, revealing the anisotropy in fracture properties. Closely looking at the calculated toughness values from the parallel face, it is clearly seen that the fracture toughness in the poling direction from the side face for the PZT-4 and NBT-5.5BT samples were 2.2 and 2.0 $MPam^{1/2}$ at 20 and 50 N loads, respectively. On the other hand, again from the same face but in the longitudinal directional the toughness values for PZT-4 and NBT-5.5BT were 1.1 and 1.7 $MPam^{1/2}$ at 50 and 20 N loads, respectively. The later one is the case where there is minimum contribution of energy absorption due to the domain switching. Jacop and Hoffman had studied toughness of NBT ceramics and found that the reported lead free NBT ceramics have higher fracture toughness than PZT ceramics. [17] The anisotropy in fracture toughness is more pronounced for PZT-4 after poling. There is a big difference in K_{IC} values measured from the side face in the longitudinal and transverse direction.

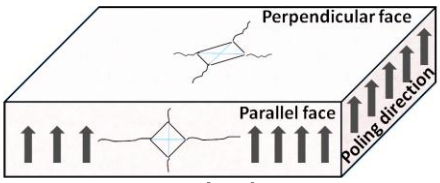


Fig. 6. Poling directions.

III. Conclusion

The mechanical properties of lead free piezoelectric ceramic, namely NBT-5.5BT, were studied and compared to that of PZT-4 ceramics. An R-curve behavior was observed with increasing indentation load. The fracture toughness values of NBT-5.5BT was found to be higher than that of PZT-4 ceramics. Furthermore, the crack lengths at the corners of the indent were different depending on the poling direction, revealing the anisotropy in fracture toughness. It was found that crack encounter higher resistance to propagation when propagating in the poling direction.

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