Structural, Dielectric, Piezoelectric and Ferroelectric Characterization of NBT-BT Lead-Free Piezoelectric Ceramics

S Shanmuga Sundari1, Binay Kumar2, R Dhanasekaran1, 3

1Crystal Growth Centre, Anna University, Chennai-600025, India
2Crystal Lab, Department of Physics and Astrophysics, University of Delhi, Delhi-110007, India.
E-mail: rdhanasekaran@annauniv.edu (R. Dhanasekaran)

Abstract. Lead free piezoelectric 0.94(Na0.5Bi0.5)TiO3-0.06BaTiO3 (NBT-BT) ceramics were synthesized in MPB composition by conventional solid state reaction method. The crystalline nature of NBT-BT ceramic was studied by XRD and the size of the grains are determined by SEM. The X-ray diffraction results reveal that Ba2+ diffuse into the Na0.5Bi0.5TiO3 lattices to form a solid solution with a pure perovskite structure. Because of the strong ferroelectricity and MPB, the ceramics exhibit high piezoelectric properties: d33 = 206 pC/N. Td (depolarization temperature) and Tm (temperature at with the dielectric constant ε reaches a maximum) were observed through the phase transition in dielectric studies. In addition, the prepared ceramic exhibits relaxor characteristic, which probably results from the cation disordering in the 12-fold coordination sites. Pr and Ec of the prepared ceramics were determined from the P-E hysteresis loop.

1. Introduction

The ABO3 perovskite oxides are an important family of ferroelectrics which can readily undergo structural phase transitions involving both polar and non-polar distortions of the cubic lattice [1]. Among these, the lead based perovskites and its solid solution like PZN, PMN-PT, PZN-PT have been considered as the excellent materials for electromechanical devices such as actuators, sensors and transducers due to its ultrahigh piezoelectric and electromechanical properties. The toxicity of the lead in these materials is further enhanced due to its volatilization at high temperatures during calcinations and sintering. In near future, the lead based materials may be prohibited by law from the view point of sustainable development of the world. Hence more and more attention is focused on the lead free piezoelectric materials. In this context, Na0.5Bi0.5TiO3 (NBT) based materials have been proved to be one of the most promising lead free piezoelectric materials [2]. NBT is a ferroelectric complex having Bi3+ and Na+ on the A-site of ABO3 perovskite structure with a rhombohedral symmetry. It is having high Curie temperature of 320°C, remnant polarization Pr= 38 μC/cm2 and coercive field of Ec=73 kV/cm [3, 4]. The high coercive field makes the poling process difficult. Hence the attraction is moved towards its solid solutions like NBT-BT [5, 6], NBT-BLT [7] and KBT-NBT [8]. Takenaka et al [9] pointed out the existence of Morphotropic Phase Boundary (MPB) in NBT-BT solid solution at a composition around 94:06 by combining the rhombohedral NBT and

3 To whom any correspondence should be addressed
tetragonal BT. The existence of anomalously large dielectric constant values compared to other compositions makes the dielectric materials near an MPB interesting. A variety of actuation characteristics have been observed in NBT-BT depends on the phase ranging from ferroelectric to anti-ferroelectric coupled with large electrostrictive component [10, 11]. Temperature of dielectric maxima Tm is ranging from 200-300°C, depending on the concentration of BaTiO3 [12].

In the present work, the 0.94Na0.5Bi0.5TiO3-0.06BaTiO3 (NBT-BT) lead-free ceramics were prepared by conventional solid state reaction method and their structural, temperature dependence of dielectric properties and piezoelectric properties were studied systematically. The previously reported NBT-BT ceramics were prepared by using ball milling in the solid state reaction method. To see the effect of ball milling in the piezoelectric and ferroelectric properties as a initial step in this work NBT-BT ceramics were prepared without ball milling and the properties were seems to be increased. This may be due to the reduction of mechanical strain induced by the milling techniques. A detailed discussion about the dependence of dielectric constant on temperature was made. The effect of DC field on the piezoelectric properties was studied.

2. Experimental Procedures

The conventional solid solution method was used to prepare the NBT-BT ceramics. High purity (99.9%) Na2CO3, BaCO3, Bi2O3 and TiO2 were used as initial precursors. The oxide and carbonates were weighed according to the composition of 0.94Na0.5Bi0.5TiO3-0.06 BaTiO3. The precursors were subjected to the TG-DTA analysis using thermal analyzer SDT Q 600 at a heating rate of 10°C in inert atmosphere to know their melting behaviour. The carbonates and oxides were mixed homogeneously in ethanol medium and calcined at 850°C for 4 hours. The calcined powders were regrind and mixed with binder (Polyvinyl alcohol). After drying, pellets of the size 19mm dia and 1mm thickness were made by applying 6 tons of pressure using hydraulic pressure. The prepared discs were sintered at 1200°C for 4 hours. The radial and thickness shrinkage of the prepared ceramics were 17.6 and, 24.1% and no shape change is observed. The obtained ceramics were finely grind and subjected to powder XRD in the range of 10° to 80° of 2θ with the step angle of 0.02° and step time 1s using PANalytical diffractometer (CuKα radiation) to confirm the phase formation and crystalline nature. Surface morphology of the gold coated sintered samples was studied by scanning electron microscopy (S-3400). The variation of dielectric constant with temperature at different frequencies (100 Hz to 2 MHz) was studied from room temperature to 350°C using Agilent E4980A impedance analyser. The hysteresis loop was traced by using computer controlled P-E loop tracer. Ceramics were poled by applying a field 25 kV/cm at room temperature for 20 min. The piezoelectric co-efficient d33 (pC/N) was measured using Piezometer (PM300, Piezotest).

3. Results and discussion

Figure 1 shows the TG-DTA curves of the precursors of NBT-BT at the heating rate of 10°C/min. Three endothermic peaks were observed around 150, 553 and 1237°C. The first endothermic peak corresponds to the evaporation of H2O, the second endothermic peak corresponds to the decarbonation of Na2CO3 and BaCO3 and the third one corresponds to the complete melting of NBT-BT [13]. In addition, around 550°C there is a weight loss of 0% which is equivalent to the theoretical wt% of CO2 in the NBT-BT mixture. Based on the TG-DTA measurements the sintering temperature is chosen as 1200°C and the heating rate is 1°C/min. Though the complete melting is occurring around 1237°C the sintering temperature is chosen little bit lower temperature.

In NBT-BT the A-site is occupied by the Na+, Bi3+ and Ba2+, the B- Site is occupied by the Ti4+ ion. The Goldschmit tolerance factor t, gives the simple geometry packing of pervoskite structure which is described as [14],

$$t = \frac{R_{A} + R_{o}}{\sqrt{2}(R_{B} + R_{o})}$$
where $R_A$, $R_B$ and $R_O$ be the ionic radii of the A-site cation, B-site cation and $O^{2-}$ ion respectively. As a rule of thumb, a perovskite structure is stable only if the tolerance factor is in the range $0.8 < t < 1.1$; larger deviations of ‘t’ from unity generally prevent crystallization of a compound with the composition $ABO_3$ in the perovskite structure. In the present case the value of $t = 0.91$ has been estimated and it is within the limit of stable perovskite structure. However, ‘t’ is a necessary but not a sufficient condition for the formation of the perovskite structure [15]. The octahedron $BO_6$ is the basic unit of perovskite so the octahedral factor $R_B/R_O$ determines the stability of octahedron and governs the formability of perovskite structure [16]. For the perovskite formation the ratio of $R_B$ and $R_O$ should be in the range of 0.425. Here it is found as 0.44. Hence the formation of perovskite in the present system is well defined.

Figure 1 TG-DTA Curves for the precursors of NBT-BT.

Figure 2 X-ray diffraction pattern of NBT-BT ceramics.
Figure 2 shows the XRD pattern of the NBT-BT ceramics in the $2\theta$ range $10^\circ$ to $80^\circ$. It shows pure perovskite phase and no secondary phases are observed implying that Ba$^{2+}$ has diffused into the NBT lattices to form a solid solution [17]. The inset of figure 2 shows the XRD pattern in the $2\theta$ range $38^\circ$ to $42^\circ$ and $45^\circ$ to $48^\circ$. The rhombohedral symmetry of NBT-BT ceramic at room temperature is characterized by a $(0 \ 0 \ 3)$ / $(0 \ 2 \ 1)$ peak splitting between $38^\circ$ and $42^\circ$ and a single peak of $(2 \ 0 \ 2)$ between $45^\circ$ and $48^\circ$ [18]. Therefore, the structure of NBT-BT ceramic has rhombohedral symmetry with the space group $R3c$ characterized by $(0 \ 0 \ 3)$ / $(0 \ 2 \ 1)$ peak splitting at around $40^\circ$ [18, 19]. The lattice parameters are $a = b = c = 3.895$ Å and $\alpha = 89.41^\circ$.

Figure 3 displays the SEM micrograph of a surface of NBT-BT ceramics. It shows that the prepared ceramic is relatively dense and pore free. The grain size is about 1.6 $\mu$m. The smaller grain size may be due to the substitution of Ba$^{2+}$ which inhibits the grain growth [20]. The variations of real part ($\varepsilon'$) of dielectric constant and dielectric loss (tan $\delta$) as a function of temperature for various frequencies (100 to 1.2 MHZ) are shown in Figs 4 and 5 respectively. The dielectric response exhibits the diffuse phase transition and it is observed by the shift of dielectric maxima ($\varepsilon'_{\text{m}}$) towards higher temperatures with increasing frequency. A similar diffuse phase transition has been observed in many ABO$_3$ type perovskites and bismuth layer-structured compounds [21, 22]. Also, a decrease of ($\varepsilon'_{\text{m}}$) with frequency is observed. The tan $\delta$ exhibited the frequency dependent phenomena. The loss is more at the higher frequency which may be associated with the other relaxation phenomena.

Figure 3 SEM micrograph of NBT-BT ceramics.

The prepared NBT-BT ceramic exhibits two dielectric anomalies at all frequencies as shown in figure 4. The first one corresponds to $T_d$, the depolarization temperature, where the transition from a ferroelectric state to anti-ferroelectric state exhibits, it can be derived from the first dielectric loss peak. The piezoelectric properties disappear at and after $T_d$. The second one is at $T_m$, it is the temperature at which $\varepsilon$ reaches a maximum value and corresponds to a transition from an anti-ferroelectric state to a paraelectric state. Lower dielectric peaks at $T_d$ exhibit strong frequency dependence, implying that ceramics undergo a relaxor phase transition at $T_d$. The higher dielectric peaks at $T_m$ for the ceramics are relatively broad, suggesting that the phase transition at $T_m$ is a diffuse phase transition. In NBT-BT ceramic Na$^+$, Bi$^{3+}$ and Ba$^{2+}$ are randomly distributed in the 12-fold coordination sites, so the observed diffuse phase transition behaviour at $T_m$ is reasonably attributed to the disordering of A-site cations [20]. The values of $T_d$ and $T_m$ in the present system are low when
compared to other lead free ceramics [23, 24], which favours their possible applications in the lead free world.

The temperature variation of $1/\varepsilon'$ at different frequencies is also an evidence for the existence of relaxor behaviour in ferroelectrics. Figure 6 shows the variation of $1/\varepsilon'$ as a function of temperature at 100Hz as an example and a similar nature is observed at all the examining frequencies. From figure 6 three temperature regions can be determined by, the $T_m$ where the ferroelectric transition can occur and the $T_{cw}$, Curie-Weiss temperature. The extrapolation of the linear behavior $T_{cw}$ on the temperature axis is used to determine the apparent Curie temperature $T_c$ [25]. Above $T_m$ a strong deviation from classical Curie-Weiss law ($1/\varepsilon' \propto T^{-1}$) is observed in all relaxor ferroelectric materials. The deviation can be described by the quadratic power law ($1/\varepsilon' \propto (T-T_m)^2$) [1]. The values of $T_c$, $T_m$ and $T_{cw}$ for various frequencies are listed in Table 1. The increase in difference between $T_{cw}$ and $T_m$ with frequency shows the broadening of the $T_m$ peak [26].

![Figure 4 Temperature dependence of $\varepsilon'$ for NBT-BT ceramics.](image)

![Figure 5 Temperature dependence of tanδ for NBT-BT ceramics.](image)
The diffuseness of the relaxor ferroelectrics can be further explained by fitting the dielectric data with the modified Curie-Weiss law [27],

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{1}{k(T - T_m)^\gamma}$$

(2)

where $\varepsilon_m$ is the dielectric maximum at the transition temperature ($T_m$), $k$ is a constant, $T$ is the absolute temperature and $\gamma$ is the degree of diffuseness. It is well known that $\gamma$ is equal to 2 for typical relaxor ferroelectrics and 1 for normal ferroelectrics.

Figure 6 shows the graph between $\ln(1/\varepsilon - 1/\varepsilon_m)$ and $\ln(T - T_m)$ at 10, 50 and 1000 kHz. By fitting the experimental data to the Eq. (2) the $\gamma$ value is found to 1.69, 1.79 and 1.87 respectively, which fell into the prescribed region. The diffusivity $\gamma$ corresponds to a very broad relaxation and higher disorder, its value increase with increasing frequency suggests that the disorderness, i.e., polar-nanoregions are more involved at high frequencies [28]. The relaxation time of each peak was found to decrease with temperature and follows Arrhenius dependence, as shown in figure 8. The hopping between equivalent dipolar orientations is a thermally activated process, the relaxation time ($\tau$) can be expected to obey the Arrhenius law,

$$\tau = \tau_0 \exp \left( \frac{E}{k_B T} \right)$$

(3)
where $\tau_0$ is the reciprocal of attempt frequency, $\omega_0 k_B$ is the Boltzmann constant and $E$ is the activation energy. Figure 8 shows the plot between $\ln(\tau)$ and $1/k_B T$ for the prepared NBT-BT ceramic. After fitting the experimental data to the linear fit of the Eq. (3) the activation energy is found to be 0.22 meV. The low activation energy is discussed by Correa et al [29] for relaxor ferroelectrics and it suggests the glassy behaviour of the system.

![Figure 7 Dielectric permittivity data fitted with modified Curie-Weiss law for NBT-BT ceramics at various frequencies.](image)

![Figure 8 Plot between $\ln(\tau)$ and $1/k_B T$ for NBT-BT ceramics.](image)

The variation of imaginary part of the dielectric constant ($\varepsilon''$) as a function of temperature with different frequencies of NBT-BT ceramic is shown in figure 9. As the frequency increases the $\varepsilon''$ is found to increase and temperature at which the maximum of $\varepsilon''$ increases towards the higher temperature.
Frequency dependence of $\varepsilon''$ measured at different temperatures was analyzed using the power law as suggested by Jonscher [30]

$$\varepsilon''(f) \propto f^{n-1}$$  \hspace{1cm} (4)

where (0<n<1). Figure 10 shows the fitting of imaginary part of the dielectric constant to the Eq. (4) and the exponent $n$ is found to 0.72 and it is an intrinsic property of the material.

![Figure 9](image9.png)

**Figure 9** Temperature dependence of $\varepsilon''$ for NBT-BT ceramics at different frequencies.

![Figure 10](image10.png)

**Figure 10** plot between $\varepsilon''$ and frequency for NBT-BT ceramic at 290°C.

The poling temperature and time are fixed as constants and the piezoelectric coefficient ($d_{33}$) is measured as a function of applied dc field and the plot between $d_{33}$ and $E$ is shown in figure 11. It is found that the $d_{33}$ value is increasing with poling field. Further increase of poling field did not resulted
in a substantial enhancement of piezoelectric properties. Moreover, ceramics were electrically broken down when a poling field over 3.0 kV/mm was applied. Thus, the poling field of 2.5 kV/mm was preferred for the NBT-BT ceramics. Hence for the prepared NBT-BT ceramic the maximum field of 2.5 kV/cm is used and a corresponding $d_{33}$ value is 206 pC/N. By comparing the reported values [4- 6, 17, 31] the high $d_{33}$ and low $E_c$ are observed for the present system. The prepared NBT-BT ceramic is found to exhibit the P-E hysteresis loop as shown in figure 12. The NBT-BT ceramic exhibits remenant polarization $P_r= 2.79 \mu$C/cm$^2$, saturation polarization $P_s= 4.47 \mu$C/cm$^2$ and coercive field $E_c= 31.09$ kV/cm. Because of its high coercive field the hysteresis loop is flatted, slanted and not well developed.

The values of $E_c$ and $P_r$ is low when compared to [17, 32] the low $E_c$ facilitates the domain movement and leading to the increase in piezoelectric properties, the low $P_r$ is resulted from the large concentration of defects near the MPB, because the greater lattice distortion will be produced as the concentration of BT increases [13].
4. Conclusion

0.94(Na_{0.5}Bi_{0.5}) TiO_{3}-0.06 BaTiO_{3} (NBT-BT) ceramics were prepared by conventional solid state reaction method. The TG-DTA analysis indicated the proper sintering temperature as 1200°C. The X-ray diffraction studies confirm the formation of pure perovskite phase. The depolarization temperature $T_d$ shows a strong frequency dependence. The shift in $T_m$ toward higher temperature side as a function of frequency was observed suggesting the relaxor ferroelectric nature of NBT-BT ceramic. The modified Curie-Weiss law used to determine the diffusion parameter. The dependence of relaxation time on Arrhenius equation is studied. The influence of poling field on piezoelectric properties was studied and it is found that the $d_{33}$ value increases with poling field. The MPB where the number of possible spontaneous polarization directions increases and the low $E_c$ favours to increase the piezoelectric properties significantly. A well shaped P-E hysteresis can be obtained at high temperature where significant decrease in $E_c$ may occur.

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References

[1] G.A. Samara 2003 *J. Phys. Condens. Matter* **15** R367
[2] G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya and N.N. Krainik 1961 *Sov. Phys. Solid State* **2** 2651
[3] J. Suchanicz, K. Roleder, A. Kania and J. Handerek 1988 *Ferroelectrics* **77** 107
[4] B.J. Chu, D.R. Chen, G.R. Li and Q.R. Yin 2002 *J. Eur. Ceram. Soc.* **22** 2115
[5] A. Herabut and A. Safari 1997 *J. Am. Ceram. Soc.* **80** 2954
[6] X.Y. Zhou, H.S. Gu, Y. Wang, W.Y. Li and T.S. Zhou 2005 *Mater. Lett.* **59** 1649
[7] D. Lin, D. Xiao, J. Zhu and P. Yu 2006 *J. Eur. Ceram. Soc.* **26** 3247
[8] K. Yoshii, Y. Hiruma, H. Nagata and T. Takenaka 2006 *Jpn. J. Appl. Phys.* **45 (5B)** 4493
[9] T. Takenaka, K. Maruyama and K. Sakata 1991 *Jpn. J. Appl. Phys. Part 1* **30** 2236
[10] Y.M. Chiang, G.W. Farrery and A.N. Soukhojak 1928 *J. Appl. Phys.* **73** 3683
[11] S. A. Sheets, A.N. Soukhojak and N. Ohashi 2001 *J. Appl. Phys.* **90(10)** 5287
[12] G.W. Farrey 2000 *Electromechanical properties of alkaline bismuth single crystals* in department of materials Science and Engineering, Cambridge: Massachusetts Institute of Technology 84
[13] Qinhui Zhang, Xiangyong Zhao, Renbing Sun and Haosu Luo 2011 *J. Phys. Status Solidi A.* **208** 1012
[14] F.S. Galasso 1990 *Perovskites and High Tc Superconductors* New York Gordon and Breach
[15] Chonghe Li, Kitty Chi Kwan Soh and Ping Wu 2004 *J. Alloy Compd.* **370** 40
[16] G.S. Roher 2001 *Structure and Bonding in Crystalline Materials* Cambridge New York University Press
[17] Chenggang Xu, Dunmin Lin and K.W. Kwok 2008 *Solid State Sciences* **10** 934
[18] Q. Xu, S. Chen, W. Chen, S.Wu, J. Lee, J. Zhou, H. Sun and Y. Li 2004 *J. Alloy Compd.* **381** 221
[19] J. Kreisel, P. Bouvier, B. Dkhil, P.A. Thomas, A.M. Glazer, T.R. Welberry, B. Chaabane and M. Mezouar 2003 *Phys. Rev. B.* **68** 014113
[20] K. Ramam and S.H. Luis 2006 *Phys. Status Solidi.* **203** 2119
[21] Y.M. Li, W. Chen, Q. Xu, J. Zhou, X. Gu and S. Fang 2005 *Mater. Chem. Phys.* **94** 328
[22] S. Shannigrahi, P.N.P. Choudary, H.N. Acharya and T.P. Sinha 1999 *J. Phys. D: Appl. Phys.* **32** 1539
[23] Xin-Yu Liu, Chang-Rong Zhou and Zhao-Hui Shan 2007 Bull. Mater. Sci. 30 579
[24] Huidong Xie, Li Jin, Dezhong Shen, Xiaoping Wang and Guangqiu Shen 2009 J. Cryst. Growth 311 3626
[25] A. Pelaiz-Barranco, I. Gonzalez-Carmenate and F. Calderon-Pinar 2005 Solid State Commun. 134 519
[26] F. Xia and X. Yao 1999 J. Mater. Sci. 34 3341
[27] K. Uchino and S. Nomura 1982 Ferroelectr. Lett. Sect. 44 55
[28] R. Martinez, V. Ashok Kumar, D. A. Sanchez, R. Palai and R. S. Katiya 2010 J. Appl. Phys. 108 084105
[29] M. Correa, A. Kumar, R. S. Katiyar and C. Rinaldi 2008 Appl. Phys. Lett. 93 192907
[30] A. K. Jonscher 1996 Universal Relaxation Law London Chelsea Dielectrics Press
[31] Hui-dong Li, Chu-de Feng and Wen-long Yao 2004 Mater. Lett. 58 1194
[32] Qing Xu, Sujuan Wu, Shutao Chen, Wen Chen, Joonghee Lee, Jing Zhou, Huajun Sun and Yueming Li 2005 Mater. Res. Bull. 40 373