Grain size induced monoclinic (Cm) to rhombohedral ($R3c$) transformation in sodium potassium bismuth titanate ceramics

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ABSTRACT

Grain size effect on structure, remnant polarization and piezoelectric constant of lead-free $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics with grain sizes of 0.58, 0.85, 1.19 and 1.83 μm was investigated. Synchrotron X-ray diffraction in combination with Rietveld refinement was used to examine the structural changes. We have reported an existence of monoclinic (Cm) phase at room temperature and discussed the grain size (1.83 → 0.58 μm) induced structural transformation ($Cm \rightarrow R3c$) through both intrinsic polarization rotation and adaptive phase theory. Polarization vector in the $(1\bar{1}0)_{pc}$ monoclinic plane rotates towards $[111]_{pc}$ with the reduction of grain size. Better domain alignment and large polar variants results enhanced remnant polarization and piezoelectric constant in 1.83 μm sample.

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Sodium potassium bismuth titanate $(Na,K)_{0.5}Bi_{0.5}TiO_3$ (NKBT) is considered as one of the potential candidate for the replacement of PZT due to its comparable electromechanical properties with other NBT-based solid solutions [1–4]. Very recently, the highest piezoelectric constant (215 pC/N) was achieved in $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics by excess addition of Bi_2O_3 and K_2CO_3 for volatility compensation [5]. It has been reported that origin of such physical properties in NKBT ceramics attributed to the coexistence of rhombohedral ($R3c$) and tetragonal phases ($P4mm$) at Morphotropic Phase Boundary (MPB). After the discovery of low symmetry monoclinic phase (Cc) in pure $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and NBT-based piezoelectric materials such as $0.93Na_{0.5}Bi_{0.5}TiO_3 - 0.7BaTiO_3$ using high resolution transmission electron microscopy and neutron diffraction the above explanation has been suspicious and a complete structural investigation using synchrotron radiation is required to reveal the origin of electromechanical properties [6,7]. Origin of large piezoelectricity was well established in $Pb(Zr_{1-x}Ti_x)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3 - PbTiO_3$ and it is attributed to the existence of low symmetry monoclinic phase (M_A, M_B or M_C type) which acts as a bridge between rhombohedral and tetragonal phases [8,9]. However, grain size effect on structure

and its corresponding physical properties of such materials is quite important towards technological implications.

Grain size effect in the range of 0.1 to 10 μm was investigated on morphotropic PZT composition by Randall et al., and noticed that a significant reduction in the piezoelectric constant from 550 pC/N for 4 μm to 350 pC/N for 0.17 μm. This is due to the strong coupling between grain boundaries and domain wall in sub-micrometer sample that limits extrinsic contribution [10]. A drastic reduction in the remnant polarization from 24 $\mu C/cm^2$ to 2.7 $\mu C/cm^2$ with the reduction of grain size from 4 μm to 0.15 μm in $0.65Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.35PbTiO_3$ (PMN-PT) ceramics was reported [11]. Dielectric constant of $BaTiO_3$ is maximum ~ 5000 in the range of 0.8–1.1 μm and drops below 1000 with further reduction in grain size [12]. Reduction of dielectric constant in sub-micron sized sample is attributed to a "dilution effect" of non-ferroelectric grain boundaries [13,14]. Thus grain size effect on dielectric, ferroelectric and electromechanical properties couldn't be ignored in both lead and lead-free materials. Unfortunately, grain size induced structural transformation and its corresponding electromechanical properties are not much studied in lead-free ceramics, especially in sodium potassium bismuth titanate.

In the present work, we have presented an evidence for the existence of M_B type monoclinic phase using synchrotron X-ray diffraction in combination with Rietveld refinement. We also discussed the structural transformation from Cm to $R3c$ with the reduction of grain size through both polarization rotation as well as adaptive

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phase theory. Size dependent remnant polarization and piezoelectric constant were also investigated.

Detailed experimental procedure for Bi^{3+} and K^+ compensated $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics was reported elsewhere [5]. Samples with different grain sizes were prepared by varying sintering time about 30, 60, 120 and 180 min. Samples sintered above 180 min were partially melted and thus it could not be considered for further investigations. Our previous investigation in $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) ceramics also suggests that no significant improvement was noticed with piezoelectric constant for prolonged sintering time [15]. Average size of the grain was estimated from field emission scanning electron microscope (FESEM, Quanta 250FEG, USA) using linear intercept method and they are 0.58, 0.85, 1.19 and 1.83 μm for 30, 60, 120 and 180 min respectively. High energy synchrotron diffraction experiments of all four samples were done in the beamline 11-1D-C at the advanced photon source, Argonne National Laboratory (USA). This beamline provides a monochromatic incident beam with a wavelength of 0.1174 (105.1 keV). Rietveld refinements were carried out using JANA 2006 program [16]. Relative densities of all the pellets are above 97%. Dielectric permittivity and loss factor as a function of frequency ($10^1 - 10^6 Hz$) and temperature were measured using HIOKI 3532-50 LCR meter. P-E loop measurements were carried out using ferroelectric tester (Radiant Technologies, USA). Poling field of 33 kV/cm was applied on well-polished pellets at room temperature

using high voltage D.C. power supply (H5KO2N, APLAB Ltd., India). Piezoelectric constants were measured using a d_{33} meter (YE2730A, APC International, USA).

Synchrotron X-ray diffraction pattern was recorded to examine the size induced structural changes. Full width at half maximum (FWHM) of the reflections were reduced with increase in the grain size from 0.58 μm to 1.83 μm as expected. Superlattice reflection (1/2{311}) at 2.86° (indicated with *) in 0.58 μm as shown in Fig. 1(a) due to $a^-a^-a^-$ tilting of oxygen octahedra should be accounted for rhombohedral $R3c$ phase [17]. Surprisingly, it diminishes with increase in the grain size and vanished at 1.83 μm that evidences size induced structural change.

Detailed structural investigation was carried out on all the samples (0.58, 0.85, 1.19 and 1.83 μm) using Rietveld refinement. Though pure NBT has been considered as a rhombohedral ($R3c$) system at room temperature, existence of monoclinic phase with Cc symmetry has also been resolved from high resolution synchrotron and electron diffraction studies recently [6,17]. Thus, rhombohedral ($R3c$) and monoclinic (Cc) structural models were considered for Rietveld fitting of sub-micrometer (0.58 μm) sample. Satisfactory profile fitting was obtained for ($R3c$) model and it is shown in Fig. 1(b). Goodness of the refinement parameter (χ^2), obtained for $R3c$ and Cc models was 1.97 and 2.36 respectively. Inset (i) of Fig. 1 (b) shows the best fitting of the superlattice reflection. While satisfactory fitting was obtained
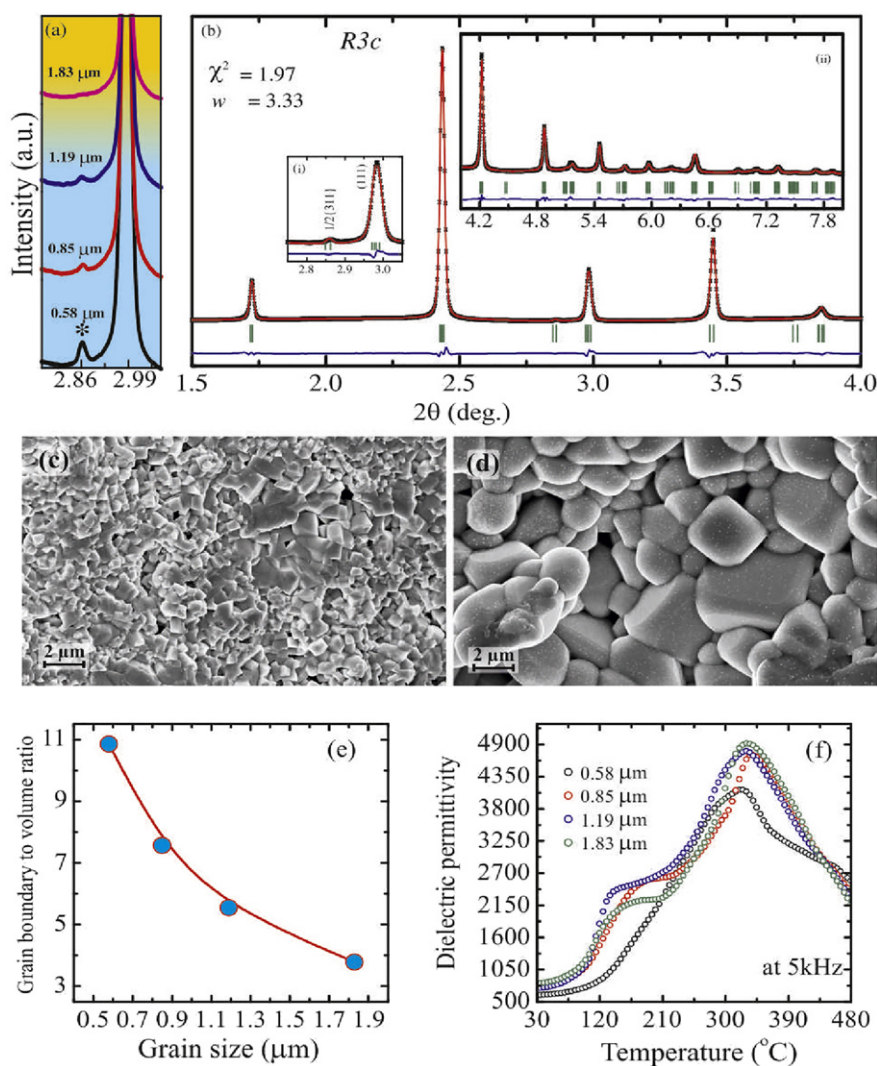

Fig. 1. (a) Enlarged view of 1/2{311} superlattice reflection, (b) Rietveld fitting of 0.58 μm sample with rhombohedral $R3c$ structural model, (c & d) FESEM micrographs of 0.58 and 1.83μm samples respectively, (e) Grain boundary to volume ratio as a function of grain size and (f) Grain size dependent dielectric permittivity of $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics.

for single phase R3c model, we have also attempted for mixed phases (R3c + Cc) but no remarkable improvement in the profile fitting was observed. FESEM micrographs of 0.58 and 1.83 μm samples are shown in Fig. 1 (c & d). It is evidenced from the figure that the size and shape of the grains are strongly influenced as a function of sintering time. Fig. 1 (e) shows grain boundary area to grain volume ratio as a function of grain size. The ratio increases with decrease in grain size that favors interfacial stress. Temperature dependent dielectric permittivity for different grain sizes is shown in Fig. 1 (f). The dielectric permittivity increases with increase in grain size and a maximum of 4918 was obtained for 1.83 μm sample. Reduction in the dielectric permittivity is due to the dilution effect exerted by the increasing number of non-ferroelectric grain boundaries in sub-micron sized sample. Slight reduction in the phase transition temperature (330 to 320°C) is noticed while the grain size is decreasing from 1.18 to 0.58 μm. Upon cooling, the cubic to tetragonal phase formation is delayed due to large interfacial stress in sub-micron sized sample which results in reduction in the phase transition. Satisfactory profile fitting was obtained for 0.85 and 1.19 μm samples using rhombohedral R3c model and the refined lattice parameters are listed in Table 1. Plausible structural models such as rhombohedral (R3m), tetragonal (P4mm) and monoclinic (Cm & Pm) were considered for 1.83 μm sample instead of rhombohedral R3c due to the absence of superlattice reflection. Among these models, suitable profile fitting was obtained with R3m and Cm however satisfactory profile fitting with better goodness of refinement, Rw and Rwp values were obtained with monoclinic Cm as shown in Fig. 2.

However, as per adaptive phase theory, the satisfactory monoclinic profile could also be due to the existence of rhombohedral nano-twins in the sample. According to adaptive diffraction theory by Wang, M_A or M_B type monoclinic phases can be thought of as a combination of two {100} or {110} type rhombohedral nano-twins respectively, whose resultant polarization vector lies on (1$\bar{1}$0) plane [18]. Existence of {100} and {110} type rhombohedral twins in NKBT ceramics was reported recently using transmission electron microscope (TEM) around MPB [19] and thus we have presumed that why not the obtained monoclinic distortions in the diffraction pattern could be the formation of such nano-twins. Accordingly, we have derived the monoclinic (C_m) lattice parameters from the rhombohedral one using the equation given below [18]

$$a_m \simeq \sqrt{2}a_r\left(1 + \frac{1}{2}cos\alpha_r\right), \ b_m \simeq \sqrt{2}a_r\sqrt{1 - cos\alpha_r}, \ c_m \simeq a_r \qquad (1)$$

Refined hexagonal lattice parameter could be converted to rhombohedral and it is $a_r = 3.9034$ Å. From Eq. (1), lattice parameters of adaptive monoclinic phase as $a_m = 5.5197$ Å, $b_m = 5.5207$ and $c_m = 3.9034$ Å. Surprisingly, the derived lattice parameters
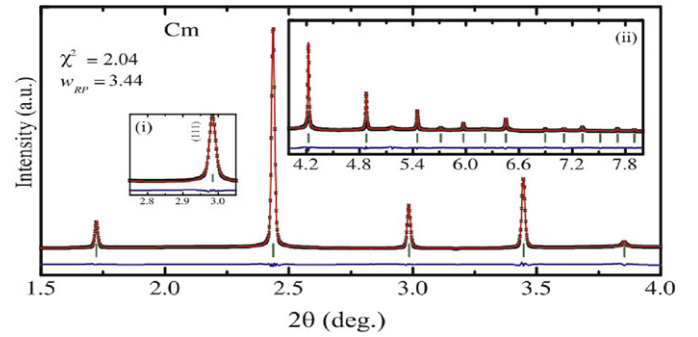

Fig. 2. Rietveld fitting of 1.83 μm sample using monoclinic Cm structural model.

of adaptive monoclinic phase is well matched with the refined monoclinic parameters ($a_m = 5.5225$ Å, $b_m = 5.5207$ and $c_m = 3.9041$ Å) which implies that obtained monoclinic like feature in the diffraction pattern obeys adaptive phase theory. Recently, Rao and Ranjan also established the monoclinic features in $Na_{0.5}Bi_{0.5}TiO_3$ ceramics in terms of intrinsic polarization rotation and adaptive phase theory [17].

As per intrinsic polarization rotation theory, ferroelectric distortion with polarization vector in the (1$\bar{1}$0)$_{pc}$ plane rotates as a function of external stimuli such as temperature, electric field, pressure, and composition, without leaving the plane towards one of the three high symmetry directions such as [001]$_{pc}$, [011]$_{pc}$ and [111]$_{pc}$ which leads to the formation of tetragonal (P4mm), orthorhombic (Amm2) and rhombohedral (R3c) [20]. In this point of view, structural transformation from monoclinic to rhombohedral with the reduction of grain size from 1.83 to 0.58 μm could be considered as a result of intrinsic polarization rotation as depicted in Fig. 3. Similar observation was reported in $0.8Pb(Mg_{2/3}Nb_{1/3})O_3 - 0.2PbTiO_3$ ceramics, whereas the polarization rotates within the monoclinic plane (M_B and M_A) and finally reached a rhombohedral phase (R3m) when the size of the grains reduced from 4 μm to 100 nm [21]. Though we could explain the structural transformation using adaptive phase theory as well
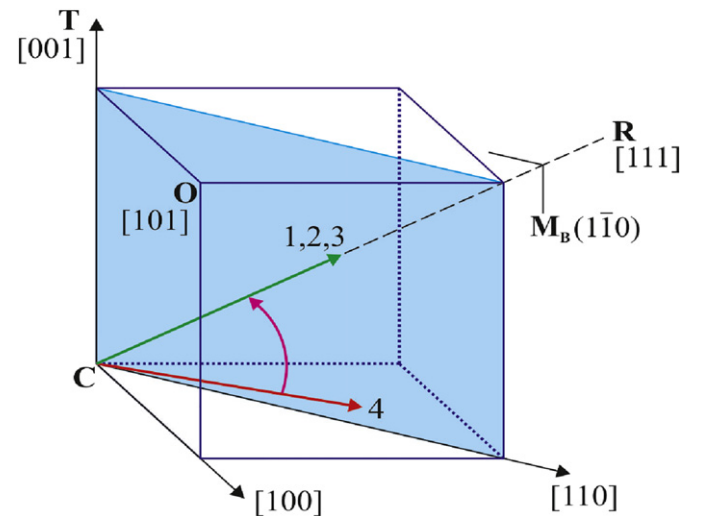
Table 1
Structural parameters obtained from Rietveld refinement for 0.58, 0.85, 1.19 and 1.83 micrometer samples.

Grain size (μm)	Rietveld lattice parameters	
	Rhombohedral (R3c)	Monoclinic (Cc)
0.58	a=5.5331, c = 13.5889	a = 9.5492, b = 5.4996, c = 5.5225
	wR_P = 3.33, χ² = 1.97	wR_P = 4.68, χ² = 2.77
0.85	a = 5.5207, c = 13.5148	a = 9.5671, b = 5.5263, c = 5.5157
	wR_P = 3.26, χ² = 1.93	wR_P = 3.94, χ² = 2.33
1.19	a = 5.5185, c = 13.5132	a = 9.5582, b = 5.5203, c = 5.5125
	wR_P = 3.34, χ² = 1.97	wR_P = 3.55, χ² = 2.10
	Rhombohedral (R3m)	Monoclinic (Cm)
1.83	a = 5.5206, c = 6.7601	a = 5.5225, b = 5.5207, c = 3.9041
	wR_P = 3.51, χ² = 2.09	wR_P = 3.44, χ² = 2.04

Fig. 3. Schematic of polarization rotation from monoclinic to rhombohedral on (1$\bar{1}$0)$_{pc}$ plane with the reduction of grain size and 1, 2, 3 denote polar direction of rhombohedral (R3c) whereas 4 implies monoclinic (Cm) polarization vector; 1, 2, 3 and 4 correspond to 0.58, 0.85, 1.19 and 1.83 μm samples respectively.

as intrinsic polarization rotation, detailed investigation in the nano-regions is required to confirm the monoclinic (Cm) to rhombohedral ($R3c$) transformation.

Room temperature polarization (P) recorded at $100 Hz$ as a function of electric field (E) for different grain sizes is shown in Fig. 4 (a). Significant difference in shape of the $P − E$ loop is noticed below micron sized samples. Ellipse-like loop was obtained for 0.58 μm sample whereas in 1.83 μm sample has well defined square-like loop. Remnant polarization of $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics for 0.58, 0.85, 1.19 and 1.83 μm (at 40 kV/cm) are 6.12, 15.2, 18.8 and 25 $\mu C/cm^2$ respectively. Earlier, a model was proposed by Avrami for effect of grain size on ferroelectric properties [22]. Based on this model, fraction of grains contributing to polarization reversal can be written as

$$f = f_0 \left[1 - exp\left(\frac{-G_a d^3}{k_B T} \right) \right] \qquad (2)$$

where G_a and d represent grain anisotropy energy density and grain size respectively. Eq. (2) clearly reveals that fraction of grains is directly proportional to grain size. Hence, number of grains contributed in polarization reversal increases with an increase in grain size which favors ferroelectric behavior. Limited number of domain variants and large number of grain boundaries in sub-micron sized samples result reduction in the remnant polarization.

Fig. 4(b) shows piezoelectric constant, d_{33} as a function of grain size in $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics. Drastic reduction in the d_{33} values below sub-micrometer is noticed and the values are 32, 70, 150 and 215 pC/N for 0.58, 0.85, 1.19 and 1.83 μm respectively. Though the $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics has rhombohedral phase up to

1.19 μm, distinct reduction in the piezoelectric constant is seen and it is believed to be the impediment of domain wall motion in submicron sized samples. As discussed above, the M_B-type monoclinic phase with Cm symmetry whose polarization vector lies on $(1\bar{1}0)$ plane continuously rotates in between rhombohedral [111] and tetragonal [001] upon poling seems to be the reason for excellent piezoelectric constant for 1.83 μm. Room temperature dielectric permittivity and dielectric loss as a function of frequency ($10^1 − 10^6 Hz$) for all the samples are shown in Fig. 4 (c) and (d) respectively. Dielectric permittivity increases with grain size and reduced slightly at higher frequencies. Dielectric loss of the samples are less than five percentage except 0.85 μm sample which shows dielectric quality of the samples.

Phase pure ($Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$) ceramics with different grain sizes such as 0.58, 0.85, 1.19 and 1.83 μm were prepared by varying the sintering time. Microstructure of the grains are strongly influenced by sintering time. Rietveld refinement reveals that the rhombohedral phase with $R3c$ space group is stabilized up to 1.19 μm and it transformed to monoclinic (Cm) at 1.83 μm. In the present work, we have reported the existence of low symmetry monoclinic phase at room temperature and the grain size induced structural transformation has been explained by both intrinsic polarization rotation and adaptive phase theory. However, exact underlying mechanism can be established only by detailed investigation of the symmetry within the nano-domains. Strong energy barrier between grain boundary and domain wall limits polarization reversal in sub-micron sized samples. Drastic increment in the piezoelectric constant at $\sim 1 \mu m$ denotes critical grain size of the sample. Improvement in the piezoelectric constant with increase in the grain size indicates the
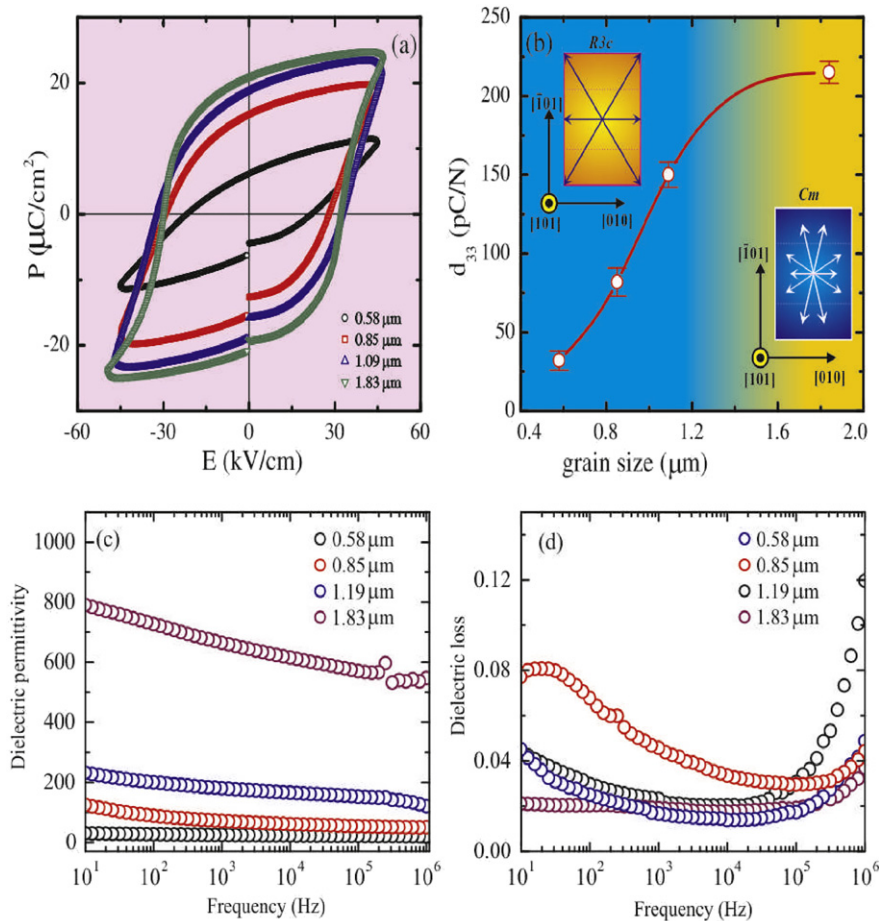

Fig. 4. (a) $P − E$ loop of $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ceramics for 0.58, 0.85, 1.19 and 1.83 μm (at 40 kV/cm) (b) piezoelectric constant as a function of grain size, inset shows possible polar variants in $R3c$ and Cm, (c & d) frequency ($10^1 − 10^6 Hz$) dependent dielectric permittivity and loss respectively recorded at RT.

facilitation of domain wall motion and maximum of 215 pC/N was obtained for 1.83 μm sample. This work provides evidence for the monoclinic phase at MPB composition in NBT-based system similar to that of Pb-based MPB systems.

Acknowledgments

References

[1] A. Sasaki, T. Chiba, Y. Mamiya, E. Otsuki, Jap. J. Appl. Phys. 38 (9S) (1999) 5564.
[2] O. Elkechai, M. Manier, J.P. Mercurio, Phys. Status Solidi A 157 (1996) 499.
[3] G.O. Jones, J. Kreisel, P.A. Thomas, Powder Diffract. 17 (2002) 301.
[4] Y.R. Zhang, J.F. Li, B.P. Zhang, C.E. Peng, J. Appl. Phys. 103 (2008) 074109.
[5] M. Veera Gajendra Babu, S.M. Abdul Kader, M. Muneeswaran, N.V. Giridharan, D. Pathinettam Padiyan, B. Sundarakannan, Mater. Lett. 146 (2015) 81.
[6] E. Aksel, J.S. Forrester, J.L. Jones, P.A. Thomas, K. Page, M.R. Suchomel, Appl. Phys. Lett. 98 (2011) 152901.
[7] D. Maurya, A. Pramanick, K. An, S. Priya, J. Appl. Phys. 113 (2013) 114101.
[8] R. Guo, L.E. Cross, S.E. Park, B. Noheda, D.E. Cox, G. Shirane, Phys. Rev. Lett. 84 (2000) 5423.
[9] A.K. Singh, D. Pandey, Phys. Rev. B 67 (2003) 064102.
[10] C.A. Randall, N. Kim, J.-P. Kucera, W. Cao, T.R. Shrout, J. Am. Ceram. Soc. 81 (1998) 677.
[11] M. Algueró, J. Ricote, R. Jiménez, P. Ramos, J. Carreaud, B. Dkhil, J.M. Kiat, J. Holc, M. Kosec, Appl. Phys. Lett. 91 (2007) 112905.
[12] P. Zheng, J.L. Zhang, Y.Q. Tan, C.L. Wang, Acta Mater. 60 (2012) 5022.
[13] L. Curecheriu, S.-B. Balmus, M.T. Buscaglia, V. Buscaglia, A. Ianculescu, L. Mitoseriu, J. Am. Ceram. Soc. 95 (2012) 3912.
[14] V. Buscaglia, M.T. Buscaglia, M. Viviani, L. Mitoseriu, P. Nanni, V. Trefiletti, P. Piaggio, I. Gregora, T. Ostapchuk, J. Pokorny, J. Petzelt, J. Am. Ceram. Soc. 26 (2006) 2889.
[15] M. Muthuramalingam, D.E. Jain Ruth, M. Veera Gajendra Babu, N. Ponpandian, D. Mangalaraj, B. Sundarakannan, Scr. Mater. 112 (2016) 58.
[16] P.W. Stephens, J. Appl. Crystallogr. 32 (1999) 281.
[17] B.N. Rao, R. Ranjan, Phy. Rev. B 86 (2012) 134103.
[18] Y.U. Wang, Phy. Rev. B 76 (2007) 024108.
[19] I. Levin, I.M. Reaney, E.M. Anton, W. Jo, J. Rodel, J. Pokorny, L.A. Schmitt, H.J. Kleebe, M. Hinterstein, J.L. Jones, Phy. Rev. B. 87 (2013) 024113.
[20] D. Vanderbilt, M.H. Cohen, Phys. Rev. B 63 (2001) 094108.
[21] J. Carreaud, J.M. Kiat, B. Dkhil, M. Algueró, J. Ricote, R. Jiménez, J. Holc, M. Kosec, Appl. Phys. Lett. 89 (2006) 2906.
[22] J. Hao, W. Bai, W. Li, J. Zhai, J. Am. Ceram. Soc. 95 (2012) 1998.