

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 \rightarrow 0.58 μm) induced structural transformation (*Cm* \rightarrow *R3c*) through both intrinsic polarization rotation and adaptive phase theory. Polarization vector in the (1-10)_{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.

Keywords: Sintering, Synchrotron radiation, Piezoelectric ceramics, Piezoelectricity

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

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 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, R_w and R_{wp} 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 $(11\bar{0})$ 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]

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

Refined hexagonal lattice parameter could be converted to rhombohedral and it is $a_r = 3.9034 \text{ \AA}$. From Eq. (1), lattice parameters of adaptive monoclinic phase as $a_m = 5.5197 \text{ \AA}$, $b_m = 5.5207$ and $c_m = 3.9034 \text{ \AA}$. Surprisingly, the derived lattice parameters of adaptive monoclinic phase is well matched with the refined monoclinic parameters ($a_m = 5.5225 \text{ \AA}$, $b_m = 5.5207$ and $c_m = 3.9041 \text{ \AA}$) 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 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 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 $(1-10)_{pc}$ 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 $0.8\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3 - 0.2\text{PbTiO}_3$ 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 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 100Hz 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 $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$ 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 $\mu\text{C}/\text{cm}^2$ 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

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

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 $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$ 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 $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$

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 $(11\bar{1}0)$ 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 ($10^1 - 10^6\text{Hz}$) 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 ($\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$) 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 $\sim 1 \mu\text{m}$ denotes critical grain size of the sample. Improvement in the piezoelectric constant with increase in the grain size indicates the 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

This work was financially supported by Major Research Project (F. No. 39-476/2010 (SR)), University Grants Commission, New Delhi. Author MVGB thank Dr. N. V. Giridharan and D. Dhayanithi for providing P-E loop and dielectric facilities. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility

operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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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	
	<i>Rhombohedral (R3c)</i>	<i>Monoclinic (Cc)</i>
0.58	$a=5.5331, c = 13.5889$ $wR_p = 3.33, \chi^2 = 1.97$	$a = 9.5492, b = 5.4996, c = 5.5225$ $wR_p = 4.68, \chi^2 = 2.77$
0.85	$a = 5.5207, c = 13.5148$ $wR_p = 3.26, \chi^2 = 1.93$	$a = 9.5671, b = 5.5263, c = 5.5157$ $wR_p = 3.94, \chi^2 = 2.33$
1.19	$a = 5.5185, c = 13.5132$ $wR_p = 3.34, \chi^2 = 1.97$	$a = 9.5582, b = 5.5203, c = 5.5125$ $wR_p = 3.55, \chi^2 = 2.10$
	<i>Rhombohedral (R3m)</i>	<i>Monoclinic (Cm)</i>
1.83	$a = 5.5206, c = 6.7601$ $wR_p = 3.51, \chi^2 = 2.09$	$a = 5.5225, b = 5.5207, c = 3.9041$ $wR_p = 3.44, \chi^2 = 2.04$

Figure Caption:

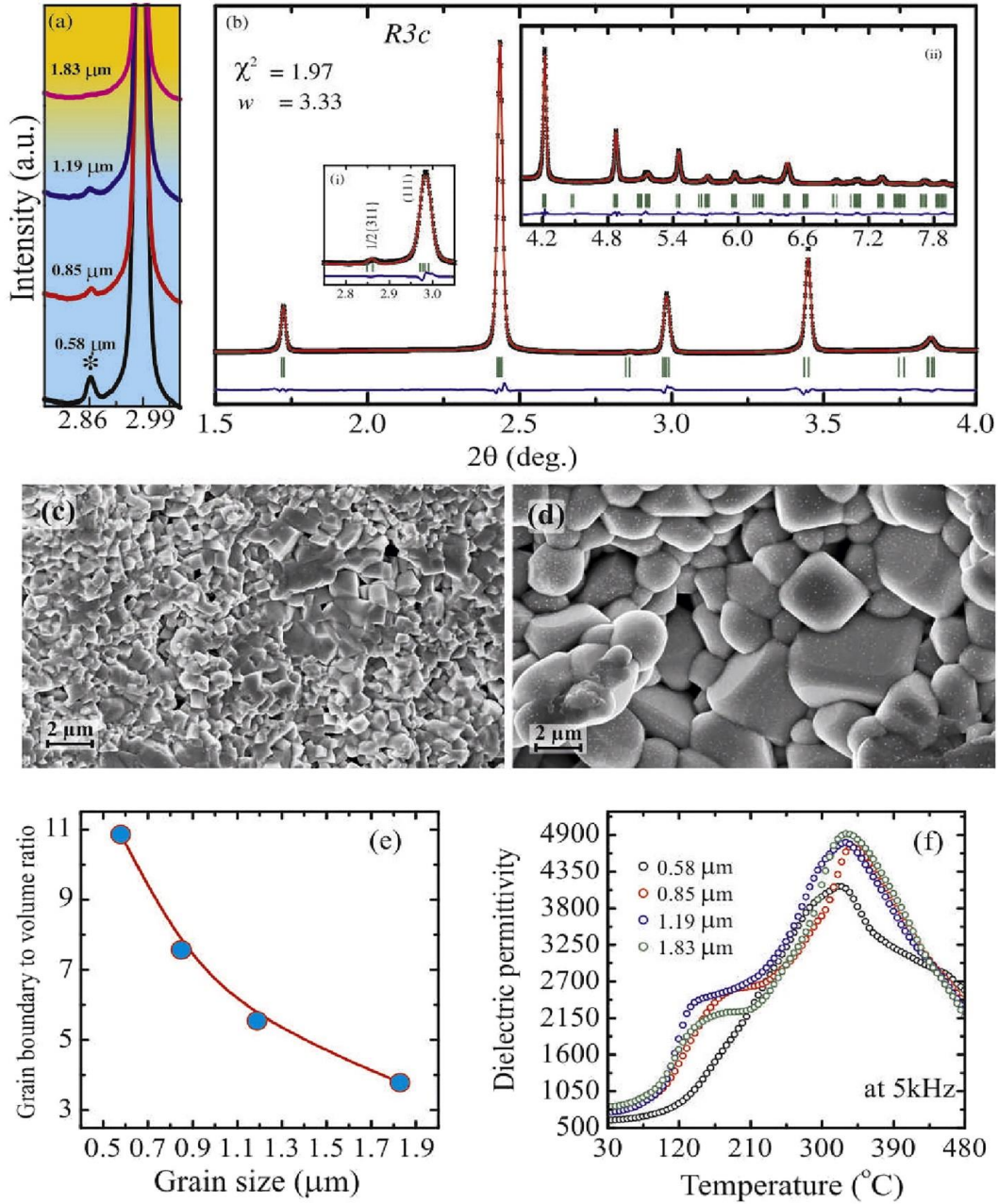


Fig. 1. (a) Enlarged view of $1/2\{311\}$ superlattice reflection, (b) Rietveld fitting of 0.58 μm sample with rhombohedral $R3c$ structural model, (c & d) FESEM micrographs of 0.58 and 1.83 μm samples respectively, (e) Grain boundary to volume ratio as a function of grain size and (f) Grain size dependent dielectric permittivity of $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$ ceramics.

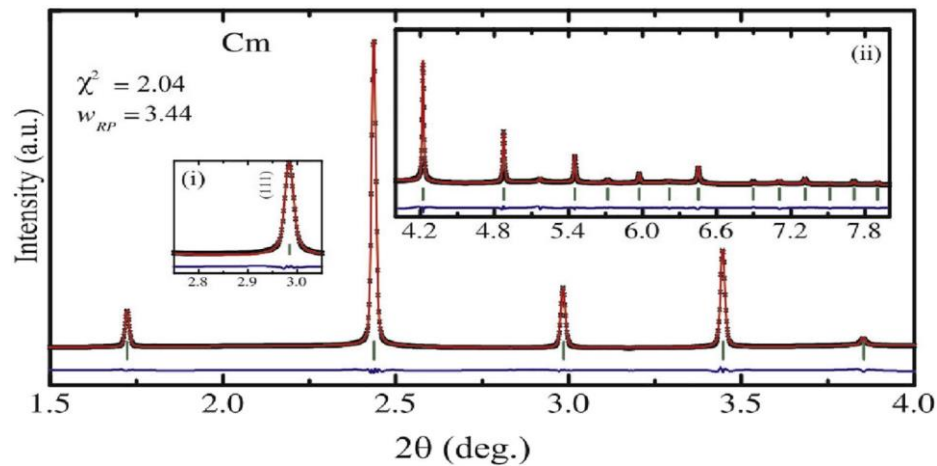


Fig. 2. Rietveld fitting of 1.83 μm sample using monoclinic Cm structural model.

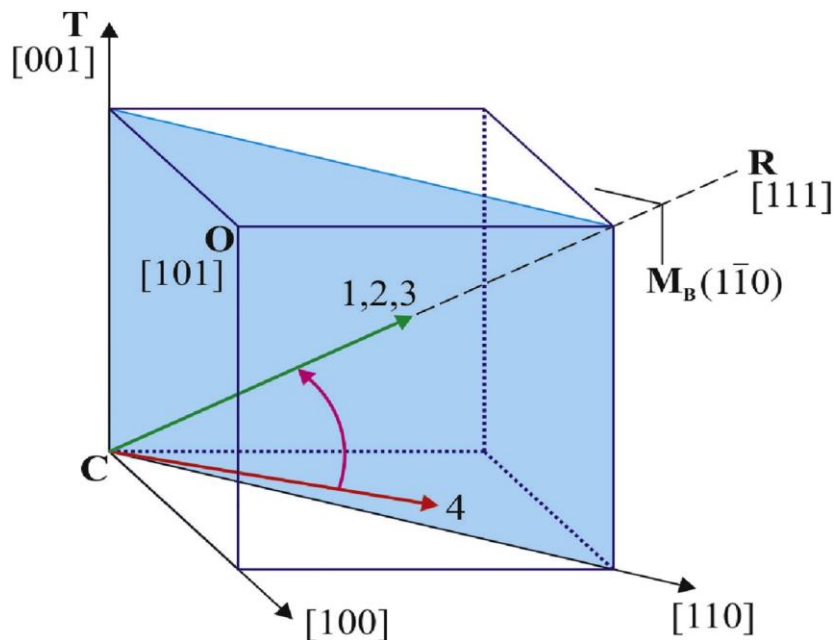


Fig. 3. Schematic of polarization rotation from monoclinic to rhombohedral on $(11\bar{0})$ pcplane with the reduction of grain size and 1, 2, 3 denote polar direction of rhombohedral ($R3c$) whereas 4 implies monoclinic (Cm) polarization vector; 1, 2, 3 and 4 correspond to 0.58, 0.85, 1.19 and 1.83 μm samples respectively.

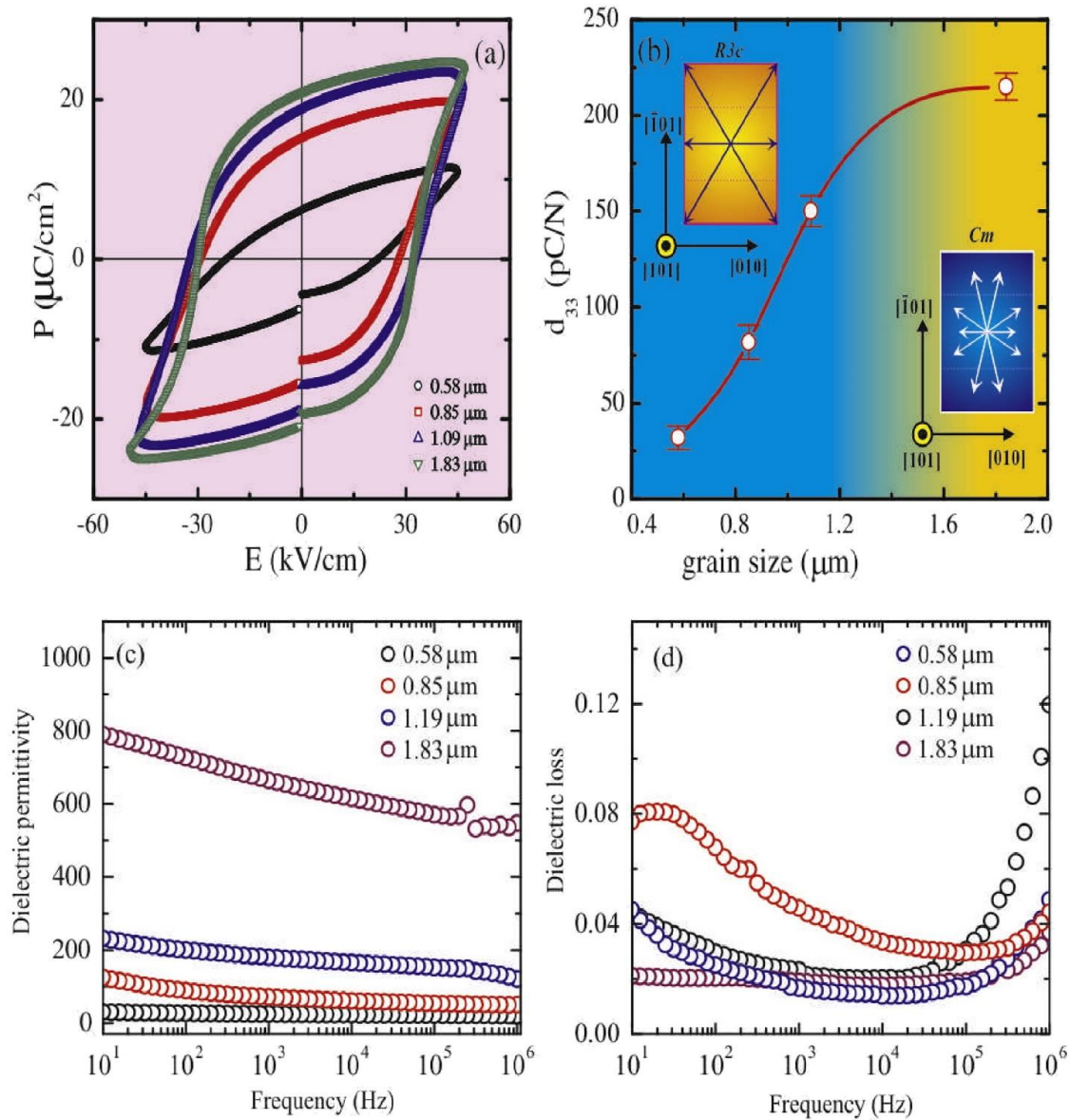


Fig. 4. (a) $P - E$ loop of $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$ ceramics for 0.58, 0.85, 1.19 and 1.83 μm (at 40 kV/cm) (b) piezoelectric constant as a function of grain size, inset shows possible polar variants in $R3c$ and Cm , (c & d) frequency ($10^1 - 10^6\text{Hz}$) dependent dielectric permittivity and loss respectively recorded at RT.

Graphical Abstract

