ROLE OF (NA, BI) EXCESS MOL% ON DIELECTRIC, FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF NA$_{0.5}$BI$_{0.5}$TIO$_3$ CERAMIC

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ABSTRACT

Lead free ceramics based on $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ with different excess mol% of Na/Bi volatiles were synthesised by sol-gel method. The x-ray diffraction and Raman spectra analyses reveal that excess mol% of Na/Bi volatiles cause local disorders without disturbing the whole perovskite structural symmetry of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics. The surface morphology of samples is improved in terms of homogeneity and density with excess to that of without excess of Na/Bi volatiles. The excess of Na/Bi at x = 0.02 leads to stoichiometric composition with compact crystal growth and improved properties such as DC resistivity ($\rho_{DC}=4.9x10^{11}$ ohm-cm), dielectric, ferroelectric ($P_r=20.5$ $\mu C/cm^2$) and piezoelectric ($d_{33}=97pC/N$) properties. The compositional fluctuations induced by Bi loss and higher Na/Bi excess concentration for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ samples with x = 0 and x > 0.02 are observed to affect ferroelectric and piezoelectric properties.

KEYWORDS: Lead free ceramic; Sol-gel process; Raman spectra; Dielectric properties; Ferroelectric properties

I.   INTRODUCTION

Lead based perovskite oxides posing excellent ferroelectric properties constitute important class of materials due to their tremendous use in various applications like sensor, actuators, transducers and micro-electro-mechanical devices etc. [1, 2]. However, formation of toxic PbO during synthesis has mostly restricted their commercial use in order to avoid harmful effects on environment [3, 4]. Sodium bismuth titanate (Na$_{0.5}$Bi$_{0.5}$TiO$_3$) based solid solutions having morphotropic phase boundary(MPB) analogous to Pb based materials (PZT) are recognised as most promising lead free ferroelectric materials and may replace Pb based materials up to some extent[5-7]. Moreover, pure Sodium Bismuth Titanate has some distinctive issues which are capturing much research attention recently such as ambiguity over its structure at room temperature, controversies on temperature dependent phase transitions and high leakage current problems [8, 9]. Earlier studies revealed that NBT system exhibits rhombohedral structure (R3c) at room temperature [10-15]. Also, recently Rao *et al*. [16] reported first principle study along with electric field dependent electron, neutron and XRD studies and suggested that global rhombohedral (R3C) phase is more stable for NBT system. While, some research groups reported monoclinic (Cc) order of NBT system at room temperature [17, 18]. Complexity of NBT structure depends on in-phase/out-of-phase octahedral tilting due to random distributions and different displacements of Bi/Na cations [5, 19, 20]. The A-site composition of (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$ system may be varied intentionally by taking non-stoichiometric proportion of Na/Bi volatiles or unintentionally due to high temperature loss of volatile elements during synthesis. The non-stoichiometric order at A site of perovskite structure having volatile elements has an effect on growth and densification of materials such as (Na,Bi) in NBT system analogues to Pb in Pb based materials [21]. It is reported earlier that A-site cations deficiency degrades the densification to some extent, in contrast, the A-site cation excess advances the sintering [22]. Either Bi excess or Na deficiency has been reported to induce same impact in Na$_{0.5}$ Bi$_{0.5}$TiO$_3$ matrix such as decrease in grain

size assist crystal densification which result in enhanced piezoelectric coefficient (d_{33}) and lower depolarization temperature (T_d)[23]. In most, Na and Bi non-stoichiometry have been independently studied in NBT based systems and accounted for improved dielectric, ferroelectric and piezoelectric properties [24, 25]. Hence keeping in view the crucial role of stoichiometry on properties of NBT based system; here we present the impact of both Na and Bi excess mol% on structural, dielectric, ferroelectric and piezoelectric properties of pure $Na_{0.5}Bi_{0.5}TiO_3$ lead free system.

II. EXPERIMENTAL DETAILS

Lead free $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics were prepared by sol gel method with different compositions having x=0, 0.02, 0.05 and 0.1which correspond to Na/Bi 0, 1, 2.5 and 5 excess mol%. The samples are hereafter named as NBT0, NBT1, NBT2.5 and NBT5 respectively. Pure powders (Analytical grade, Merck) of sodium nitrate ($NaNO_3$) and bismuth nitrate ($Bi(NO_3)_3.5H_2O$) were weighed according to designed chemical formula. These powders were dissolved in acetic acid with uniform stirring. Tetran-butyl titanate ($Ti(OC_4H_9)_4$) was mixed with acetyl acetone and 2-propanol in weight ratio of 1:3:5 to avoid its hydrolysis. The resulting stable solution of Ti was added drop wise to the solution of nitrates to get Na-Bi-Ti complex solution. The complex solution was stirred at 65°C temperature for 2 h and then mixed with the aqueous solution of citric acid taken in 1.2:1 weight ratios to nitrates. The resulting solution was dried at 80°C temperature to form gel which subsequently transformed into a powder. Heat treatment was given in steps, at 350°C for 0.5 h to remove hydrocarbons, pre-calcination at 650°C for 3 h and final calcination at 850°C for 2 h to achieve crystallisation. The calcined powders were uniformly mixed with 3% aqueous solution of PVA used as binder and pelletized in pellets of diameter 9mm and thickness ~0.8 to 1.2 mm using a hydraulic press and sintered at 1050°C for 2 h. Samples sintered at 1050°C were used for structural and electrical analysis. Silver (Ag) paste is coated on both sides of pellets and dried at 300°C temperature for 0.5 h to make ohmic contacts for electrical measurements.

Room temperature x-ray diffraction patterns of the samples were carried out by Panalytical's X'Pert Pro x-ray diffractometer using Cu$K\alpha$ radiation. Surface morphology and chemical element compositions of samples were determined using scanning electron microscopy (SEM) (Quanta 250, FEI make, Model No. D9393) equipped with an energy dispersive X-ray(EDS) detector. The Raman spectra of samples were carried out using iHR550 imaging Spectrometer(Make: JY HORIBA).The dielectric properties were measured by using an impedance analyzer (Wayne Kerr 6500B). The ferroelectric properties were studied by using P-E loop tracer(modified Sawyer–Tower circuit)of Marine India Ltd. at frequency of 50 Hz. For piezoelectric properties, pellets were poled electrically at 4 kV/mm in silicon oil bath at 85°C temperature for 2 h and piezoelectric coefficient (d_{33}) was measured by Piezo-Meter(Take Control, PM-35,UK).

III. RESULTS AND DISCUSSION

X-ray Diffraction
Fig. 1(a) shows x-ray diffraction patterns of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramic with different Na/Bi mol% excess compositions. It can be seen that all NBT ceramics exhibit typical diffraction peaks of ABO_3 perovskite structure and no other secondary phase is observed on increasing Na/Bi excess mol% up to 5 mol% at 1050°C sintering temperature.The XRD patterns of samples shown in Fig. 1 are in good agreement with previously reported structural analysis of non-stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$ ceramics [13, 26]. Rietveld refinement (FULLPROF software package-version 2000) of the room temperature X-ray diffraction data reveals rhombohedral hexagonal symmetry with the R3c space group for all samples as shown in Fig. 1(b). The lattice and refinement parameters obtained from Rietveld fitting are given in Table 1. No significant structural change has been observed in XRD patterns of NBT ceramics with varying excess mol% of Na and Bi. However, the close view of (024) diffraction peak over 2θ range of 46.5° to 47.5° as shown in inset of Fig. 1(a) depicts that the (024) peak first shifts towards the lower 2θ side for 1 mol% excess of Na and Bi (NBT1) followed by gradual shifting of the peak towards the higher peak 2θ value for NBT ceramic with 2.5 mol% excess of Na and Bi (NBT2.5). With further increasing of Na and Bi excess mol% to 5mol% (NBT5) the peak slightly shifts towards the lower 2θ value with significant reduction in the peak intensity. Usually a systematic

shift in XRD reflection lines has been reported for either excess of Bi or deficiency of Na in NBT ceramics [23, 27].
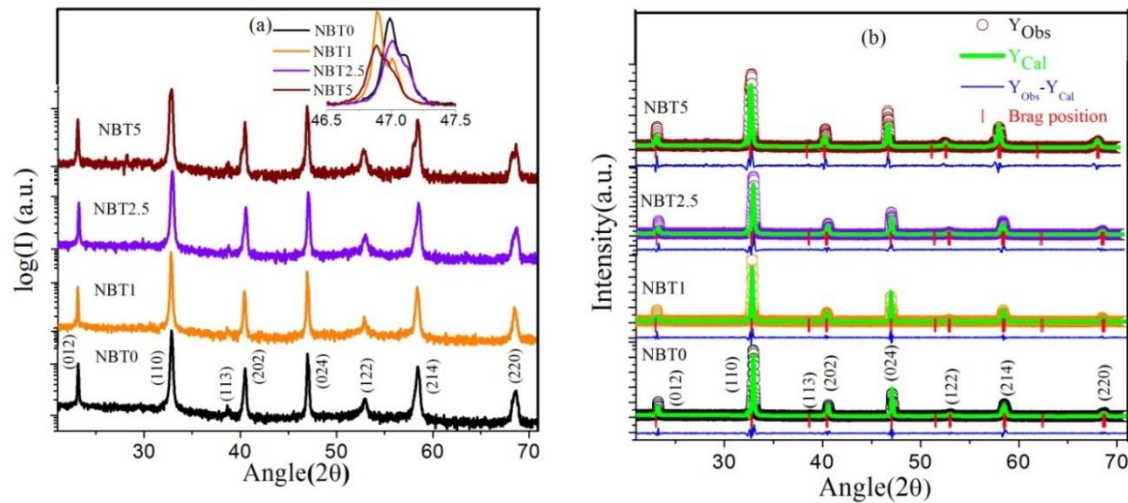

Fig. 1. (a)XRD patterns (b) Rietveld analysis of XRD patterns for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Table1. Rietveld refinement results (lattice parameters, cell volume), relative density (ρ_r) and dc resistivity(ρ_{DC}) for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Parameters(units)	NBT0	NBT1	NBT2.5	NBT5
a=b (Å)	5.4711	5.4726	5.4698	5.4732
c (Å)	13.3720	13.3845	13.3639	13.3780
Cell volume (in $Å^3$)	346.6	347.2	346.3	347.1
R_p, R_{wp}, χ^2	11.1, 16.3, 3.75	10.8, 16.0, 2.94	13.1, 18.2, 3.81	13.9, 19, 4.08
ρ_r(%)	86	97	90	94
ρ_{DC}(ohm-cm)	4.6×10^{11}	4.9×10^{11}	3.8×10^{9}	1.2×10^{9}

However, we have not observed such behavior in our Na and Bi excess NBT samples which indicates that excess of both Na and Bi plays a complex role in NBT system. Comparative intense and sharp XRD peak of NBT1 sample reveals uniform and large crystallites attributing that 1mol% excess of Na/Bi compensates the evaporation of volatiles and leads to growth of stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$ crystals which is also supported by lattice parameters and relative density measurements, given in Table 1. However, Bi loss in NBT0 sample and extravagant Na/Bi excess mol% in NBT2.5-NBT5 samples may contribute to compositional fluctuations and lattice deformation leading to distort and small intense XRD peak. The detail of density measurements is given in our previous work reported elsewhere [28].The relative density (ρ_r) of NBT sample with 1 mol% excess of Na/Bi is observed significantly higher than other samples(Table 1) which may be attributed to the compact crystal growth.

Scanning Electron Microscopy
Surface morphology of the samples are studied by scanning electron microscope (SEM) and shown in Fig. 2. The SEM micrographs represent polycrystalline nature of all samples.The average grain sizes of NBT0, NBT1, NBT2.5 and NBT5 ceramics are estimated using ImageJ software and are ~1.13μm, ~1.26μm, ~1.18μm and ~1.15μm respectively. Average grain size increases up to NBT1(x=0.02) and small variation is observed for further addition of Na/Bi volatiles. It can be clearly seen in SEM micrographs that NBT1 sample having 1 mol% excess of Na/Bi exhibits dense crystal growth with better grain connectivity as compared to other samples that is in good agreement with density evaluation under Rietveld refinement of XRD patterns discussed previously.
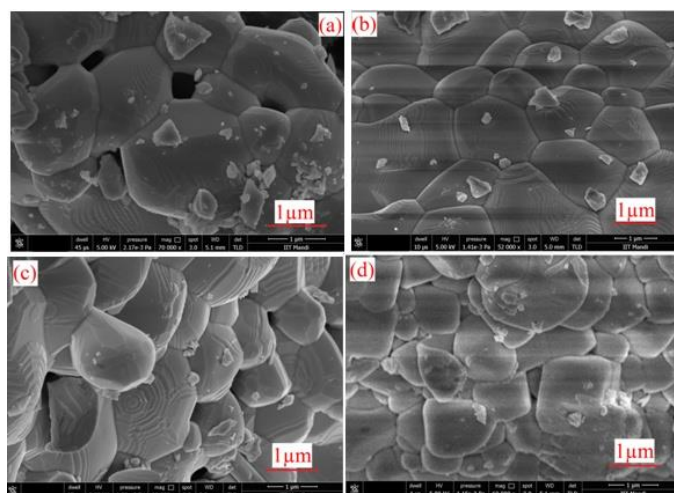
Fig. 2. SEM images of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics where (a) NBT0, (b) NBT1, (c) NBT2.5 and (d) NBT5

The qualitative and quantitative compositional analyses of the elements present in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$, x = 0, 0.02, 0.05 and 0.1 samples sintered at 1050°C temperature have been studied by Energy Dispersive X-ray spectrometer (EDS) attached to the SEM instrument and the corresponding EDS spectra are shown in Fig. 3. The results indicate that constituent elements are present in the samples in expected weight and atomic percentages. It is clear that the synthesized samples do not exhibit any other impurities apart from the constitutional elements of the $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ system. The EDS spectra have been measured 2 to 3 times by changing selective area of each sample to carry out a reliable quantitative analysis. The most probable trend of atomic and weight compositions in various NBT ceramics is given in Table 2. The values observed for these samples indicate that NBT1ceramic with 1 mol% excess of Na/Bi volatiles seems more stoichiometric as the observed atomic% of all elements is close to theoretical atomic% of $Na_{0.5}Bi_{0.5}TiO_3$ and Bi/Na ratio approaches to ~1 (i.e. 0.988) while comparing with other remaining samples having Na and Bi 0, 2.5 and 5mol% excess corresponding to x=0, 0.05 and 0.1. It is observed that Bi loss is more pronounced in $Na_{0.5}Bi_{0.5}TiO_3$ sample without Na/Bi excess, whereas excess of alkali metal (Na) concentration can be seen in NBT ceramics with 2.5 and 5mol% excess of Na and Bi elements.
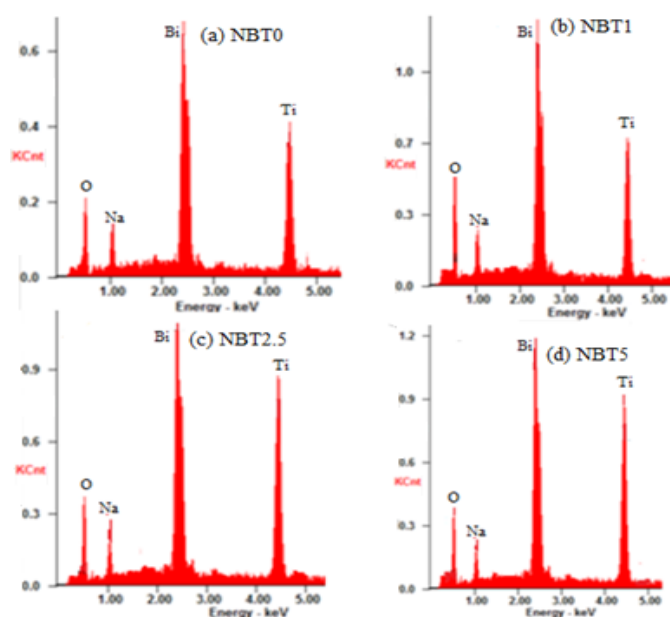

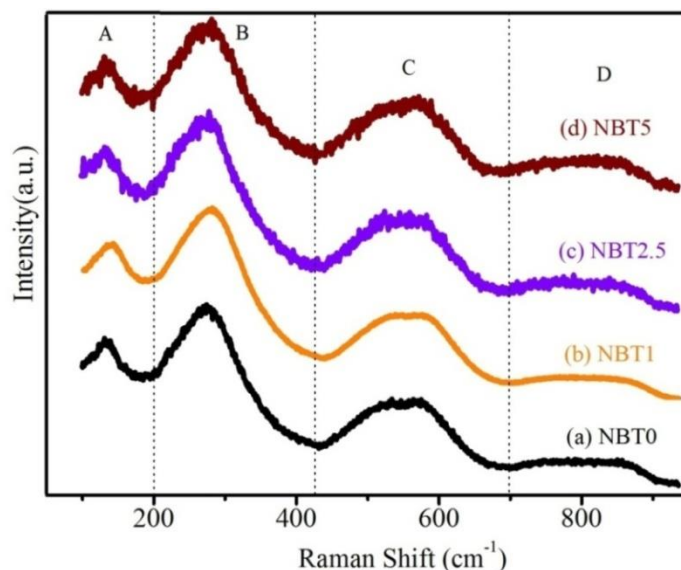**Fig. 3.** EDS spectra of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics with (a) 0, (b) 1, (c) 2.5 and (d) 5 mol% excess of Na and Bi

Table 2. Atomic% and weight% deduced from EDS measurements for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics sintered at 1050°C for 2 h

Elements	Atomic%				Weight%			
	NBT0	NBT1	NBT2.5	NBT5	NBT0	NBT1	NBT2.5	NBT5
Bi	9.26	10.08	10.59	11.08	48.12	49.82	49.78	50.04
Na	10.19	10.20	12.11	14.15	5.86	5.98	6.42	6.94
Ti	20.61	19.99	19.80	20.13	24.96	23.26	22.35	23.02
O	59.94	59.73	57.50	54.64	21.02	20.94	21.45	20
Bi/Na	0.909	0.988	0.874	0.783	8.21	8.33	7.75	7.21

Hirumaet al.[29] reported that small deviation in A-site cations (Na/Bi) stoichiometry drastically change the room temperature DC resistivity of NBT system by 3 orders of magnitude and influence the dielectric, ferroelectric and piezoelectric properties. In particular, Bi excess or Na deficiency in the starting $Na_{0.5}Bi_{0.5}TiO_3$ composition enhance the DC resistivity and piezoelectric coefficient (d_{33}) but lowers the depolarization temperature (T_d). In contrast, DC resistivity and d_{33} decrease and T_d enhances with Na excess or Bi deficient in $Na_{0.5}Bi_{0.5}TiO_3$ ceramic[23, 27, 30, 31]. In present work, room temperature DC resistivity of samples has been measured by using two probe method and values are given in Table1. An abrupt decrease in order from 10^{11} to 10^9 Ω-cm is observed as Na/Bi excess mol% raises from 1mol% (NBT1) to 5mol% (NBT5) signifying the presence of highly conductive alkali (Na) ions at A-site which further support the EDS analysis. Also, the large value of DC resistivity of NBT1 (ρ_{DC}= 4.9x10^{11} ohm-cm) confirms that 1mol% excess of Na/Bi volatiles leads to formation of stoichiometric composition with comparative small defects or vacancies.

Compositional Dependent Raman Spectroscopy
The short length scale ordering of perovskite structural phase of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ samples have been analysed using Raman spectra in the range of 100-900 cm^{-1} measured at room temperature and are shown in Fig. 4.

Fig. 4. Raman spectra of non-stoichiometric $(Na_{0.5}Bi_{0.5})_{1+x}$ TiO_3 ceramics with (a) 0, (b) 1, (c) 2.5 and (d) 5 mol% excess of Na and Bi

It was reported that in NBT ceramics having R3c crystal symmetry, the A-site disorder affects optically active modes by reducing from 18 (9A1+9E) to 13 (4A1+9E) optical modes [32], where A_1 and E are both Raman/IR active modes. In Fig. 4, the spectra can be grouped into four frequency regions: (A) 100–200 cm^{-1},(B) 200–450 cm^{-1},(C) 450–700 cm^{-1} and (D) 700–900 cm^{-1}. According to Kreisel *et al.*[33], the vibration mode in region A is associated with Bi/Na-O vibrations, the broad and highly intense band in region B is assigned to Ti-O vibrations, the modes in region C are associated with TiO$_6$ octahedral vibrations and finally region D in the high frequency range is mainly due to the

vibrations involving oxygen displacements. It can be seen from Raman spectra that all the major bands which are characteristics of vibrational modes in pure NBT system exist in all samples and observed Raman spectrum for NBT0 is in agreement with the previously reported results [34]. The peak position of Raman active mode can be specified by fitting the measured spectra and decomposing the fitted curves into separate Lorentzian components. The individual deconvoluted curves and fitted spectra are shown in Fig. 5. The mode frequencies has been assigned according to irreducible representation 4A1+9E used to describe the Raman active modes of rhombohedral R3c NBT ceramic [35] and are summarized Table 3. The spectra provide 6 optical modes which is less than that predicted 13 optical modes. The reduced experimental modes could be due to merging of closely spaced modes, thermal broadening and degeneracy of certain modes. One can notice that at 5 mol% Na and Bi excess in NBT5 ceramic, the spectra broaden and the intensities are observed to reduce. In addition shift in the phonon modes are observed in NBT ceramics. The A, B and C modes are first shifted to the higher frequency for 1mol% Na and Bi excess NBT1 ceramic. However, for 2.5mol% Na and Bi excess sample, the modes shift to the lower frequency side. Further, with 5 mol% Na and Bi excess in NBT5 ceramics, shift in the phonon modes towards higher frequency is observed. In other words, no systematic variation in Raman mode shift with Na and Bi excess mol% is observed.
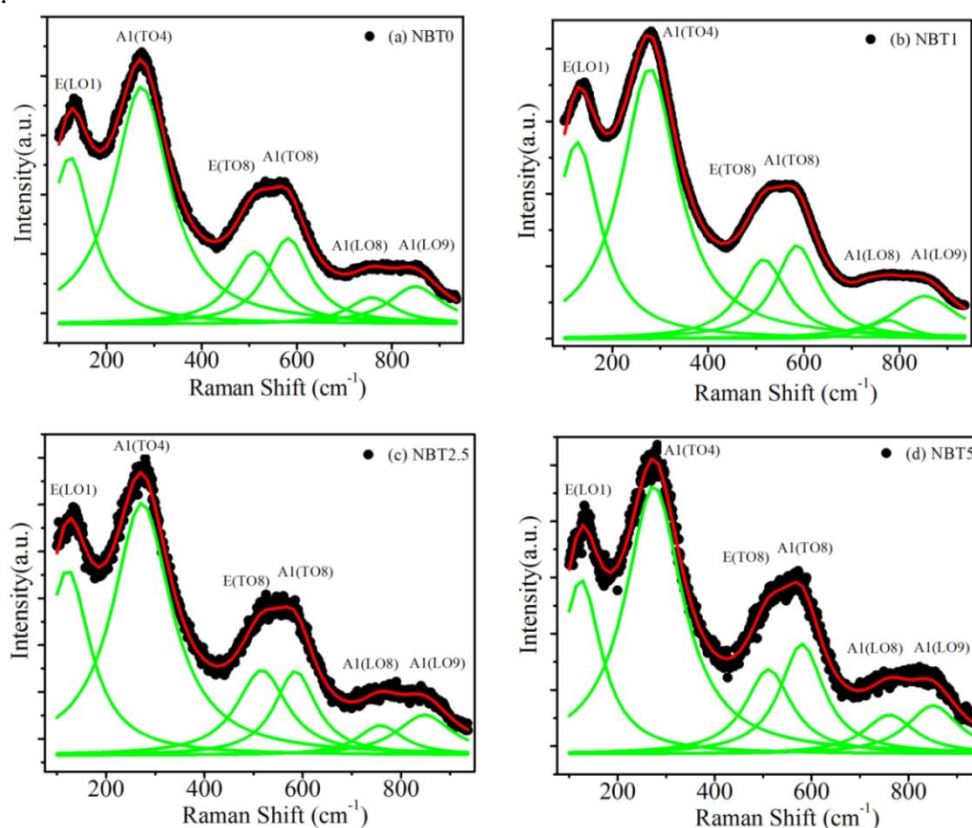

Fig. 5. Lorentz deconvoluted Raman spectra of non-stoichiometric $(Na_{0.5}Bi_{0.5})_{1+x}$ TiO_3 ceramics

Table 3. Raman bands for various $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Sample	Raman Band					
	E(LO1)	A1(TO4)	E(TO8)	A1(TO8)	A1(LO8)	A1(LO9)
NBT0	123	273	511	581	757	849
NBT1	126	278	515	586	755	849
NBT2.5	121	272	516	585	761	850
NBT5	124	274	511	580	760	850

Also, no significant shift in D modes is observed which suppresses the formation of oxygen vacancies. However, intensity variation and shifting of vibrational modes may correspond to disorderness introduced in crystal lattice with excess of Na/Bi mol%. The polycrystalline nature of the samples and random occupancy of cations of different masses at A-site (Na^{1+}, Bi^{3+}) may lead to broad Raman bands for all samples[36]. Similar Raman bands are observed for all samples which suggest Na/Bi excess mol% induces no structural phase change. Following Niranjan *et al.*[37], we observe three transverse modes which contribute to static dielectric tensor by providing large oscillator strength parallel: A_1 (TO4), A_1(TO8) and perpendicular: E(TO8) to polar axis. These transverse modes are seem to more intense and symmetric for $Na_{0.51}Bi_{0.51}TiO_3$(NBT1) sample than other samples. Moreover, comparatively low intensity of vibrational mode corresponding to O shifting A_1(TO8) at ~ 755 cm^{-1} signifies less oxygen vacancies for NBT1sample which further supports high value of relative density and DC resistivity for this sample.

Dielectric Studies
Figs. 6 (a) to (d) represent the temperature dependent dielectric properties at different frequencies 1 kHz to 1MHz measured for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics.

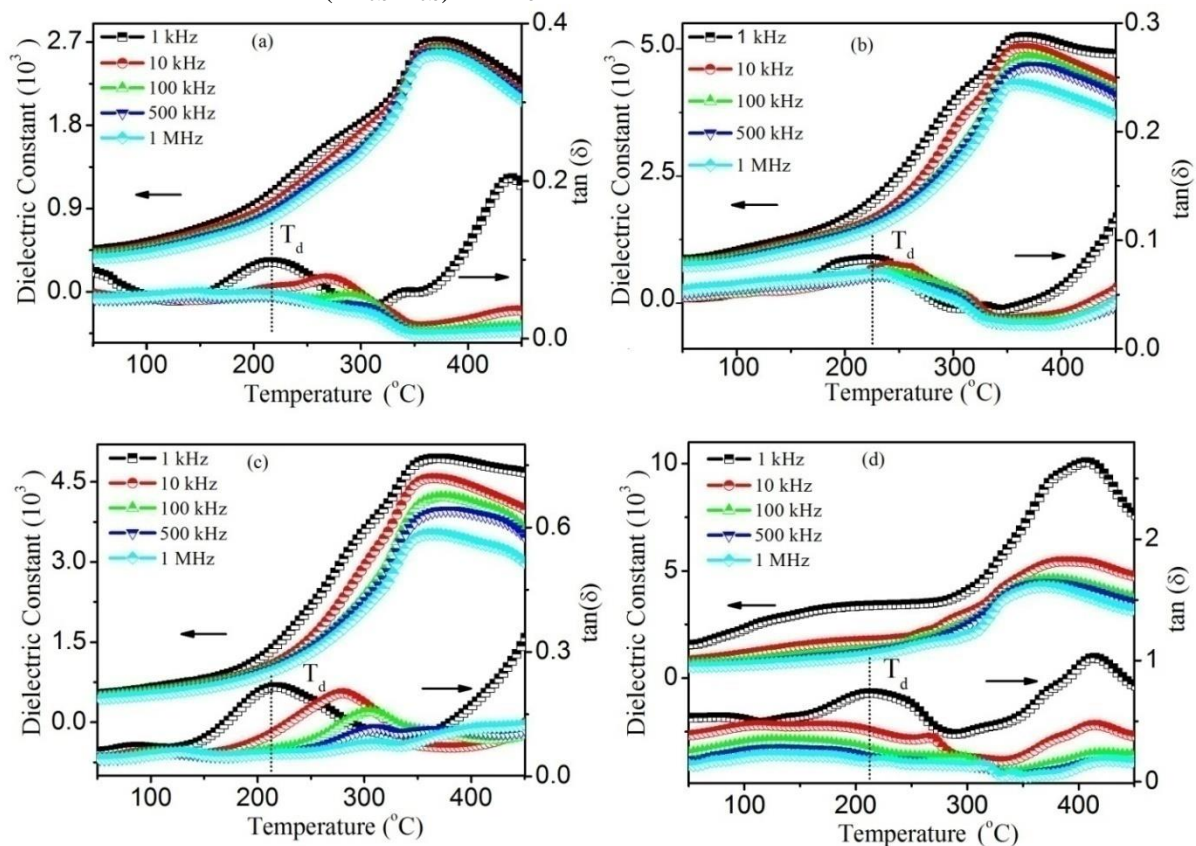**Fig. 6.** Variation of dielectric parameters with temperature at various frequencies of $(Na_{0.5}Bi_{0.5})_{1+x}$ TiO_3 ceramics with Na/Bi excess mol% (a) 0, (b) 1, (c) 2.5 and (d) 5

Table 4. Depolarization temperature (T_d) and maximum dielectric constant (ε_m) temperature (T_m) at different frequencies of $(Na_{0.5}Bi_{0.5})_{1+x}$ TiO_3 ceramics

Sample	1 kHz			10 kHz			100 kHz			500 kHz			1 MHz		
	T_m (ºC)	ε_m	T_d (ºC)	T_m (ºC)	ε_m	T_d (ºC)	T_m (ºC)	ε_m	T_d (ºC)	T_m (ºC)	ε_m	T_d (ºC)	T_m (ºC)	ε_m	T_d (ºC)
NBT0	371	2708	218	371	2645	257	371	2610	280	371	2600	296	371	2564	299
NBT1	369	5237	224	365	5018	240	373	4827	262	373	4670	266	360	4306	252
NBT2.5	368	4942	210	360	4570	271	376	4208	305	373	3970	310	364	3524	312
NBT5	406	10068	220	389	5442	265	373	4586	298	369	4436	315	369	4277	320

In general, NBT system exhibits two dielectric anomalies known as depolarization temperature(T_d) at which remnant polarization decays steeply and maximum temperature(T_m) at which dielectric constant attains maximum value [38]. The depolarization temperature (T_d) may involve phase transformation from field induced ferroelectric to relaxor phase or from one polar phase to another phase of different symmetry and is very crucial as it restricts high temperature piezoelectric application of NBT system. T_d is usually related to lattice distortion [39], cation vacancies[40] or oxygen vacancies [20] for NBT based ceramics. In previous reported papers, non-stoichiometry of Na or Bi in NBT system creates vacancies at A-site which produces defect field, breaks the long range ferroelectric order and results in decrease of T_d[7, 23, 27]. The values of T_d, T_m and maximum dielectric constant (ε'_m) at T_m of all the samples at different frequencies are summarized in Table 4. In present study, T_d is determined at a temperature when tan δ reaches the first peak as reported in earlier works[41, 42].The dielectric peaks at T_m for the NBT ceramics are broad suggesting that the phase transition at T_m is diffusive in nature. No variation in T_m is observed for NBT0 ceramic as a function of frequency. However, the tan δ peaks at T_d exhibit strong frequency dependence representing relaxor phase transition at T_d. It is observed that the T_m shifts slightly towards the lower temperatures with increasing frequencies for excess Na/Bi added NBT ceramics. Comparative high value of T_d (~224°C at 1 kHz) and small deviation on increasing frequency from 1kHz to 1MHz for NBT1 sample than other samples suggest stable ferroelectric order for this sample.

The cationic (Na^{1+}, Bi^{3+}) disorder at A-site is responsible for diffusive transition behavior of NBT system [43]. Also, change in diffuseness is observed with increase in Na/Bi excess mol% addition. In normal ferroelectrics, the Curie Weiss law is followed and defined as

$$\frac{1}{\varepsilon'} = \frac{T - T_0}{C} \quad (T > T_0) \qquad (1.1)$$

Where, C is the Curie Weiss constant describing the behavior of ferroelectric transition and T_0 is the Curie Weiss temperature. In order to have detail understanding of phase transition in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics, inverse dielectric constant is plotted as a function of temperature using above Curie-Weiss eq. (1.1) at frequency 100 kHz. The Curie-Weiss plots between $\frac{1}{\varepsilon'}$ and temperature exhibited straight lines with slope 1/C and intercepts at x-axis taken as T_0 values and are shown in Fig. 7.
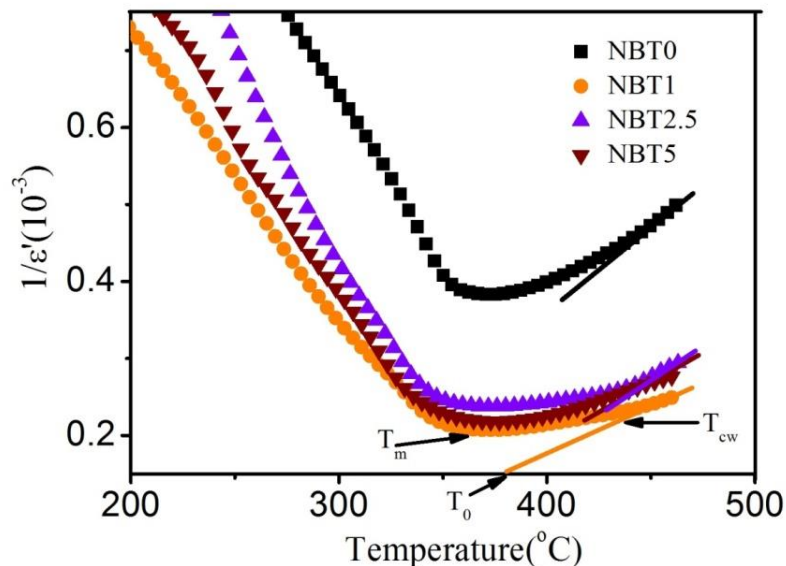

Fig. 7.   Inverse dielectric constant plots as a function of temperature at 100 kHz for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Table 5.   The Curie-Weiss temperature (T_0), the temperature at which ε' starts to follow Curie-Weiss law (T_{CW}), maximum dielectric constant temperature (T_m) and deviation temperature (ΔT_m) for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Sample	T_0 (°C)	T_{CW} (°C)	T_m (°C)	ΔT_m (°C)
NBT0	376	428	371	57
NBT1	381	435	373	62
NBT2.5	385	434	376	58
NBT5	380	441	373	68

The extracted parameters after fitting of eq. (1.1) are listed in Table 5. It is noticed that dielectric constant does not obey Curie-Weiss law above Curie temperature and the deviation defined by

$$\Delta T_m = T_{CW} - T_m \qquad (1.2)$$

Where, T_{CW} represents the temperature from which the inverse dielectric curve follows the Curie-Weiss law. T_m is the maximum dielectric constant temperature. According to Landau's theory of phase transition, a first order transition occurs when $T_C > T_0$ and a second order phase transition appears if $T_C = T_0$. In the present investigation T_C or T_m is observed close to T_0 rather T_0 appears slightly above T_m. Therefore, the transition is of second order. In order to quantify the diffuseness, modified form of Curie-Weiss equation suggested by Uchino and Nomura is used [44]

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C} \qquad 1 \le \gamma \le 2 \qquad (1.3)$$

Where, γ is the degree of diffuseness with limiting values 1 and 2 for the characterstics of normal and complex diffuse phase transition respectively. C is the Curie like constant and ε'_m is the maximumn value of dielectric constant.
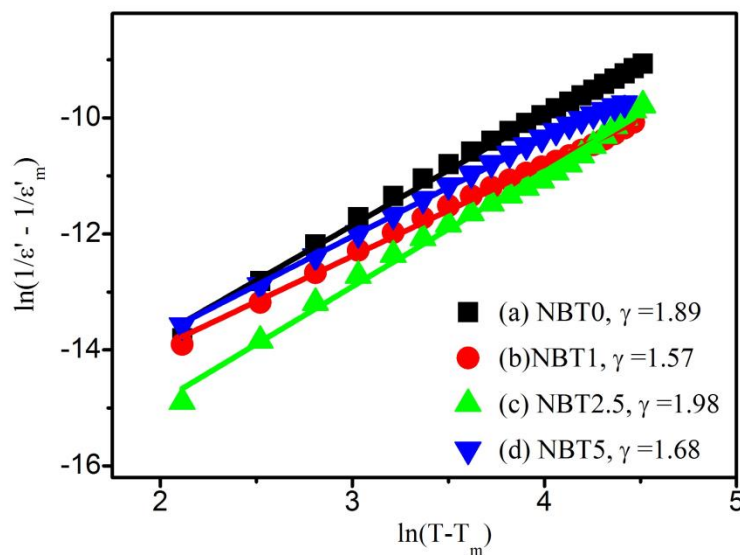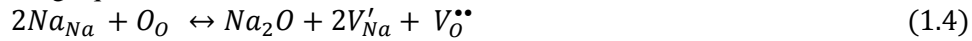

Fig. 8.   Variation of ln ($1/ \varepsilon'-1/\varepsilon'_m$) as a function of ln (T-T$_m$) for $(Na_{0.5}Bi_{0.5})_{1+x}$ TiO$_3$ ceramics with Na/Bi excess mol%; (a) 0, (b) 1, (c) 2.5 and (d) 5 sintered at 1050°C temperature

The diffuseness in phase transition can be evaluated by using modified Curie –Weiss relation from the ε' vs. temperature data at 100 kHz for $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics sintered at 1050°C, the curves between ln $(\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m})$ vs. ln(T-T$_m$) are plotted for all ceramics and shown in Fig. 8. The γ values observed from Curie-Weiss fitting are listed in Fig. 8. The γ values range from 1.57 to 1.98 suggesting diffusive behaviour and higher disorder in non-stoichiometric $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics.

Ferroelectric and Piezoelectric Properties

The room temperature Polarization vs electric field (P-E) hysteresis loops of all samples are shown in Fig.9. All the samples exhibit typical ferroelectric loops at room temperature. It can be seen that the variation of Na/Bi stoichiometry affects the ferroelectric properties of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics. P-E hysteresis loop observed for NBT0 sample without excess of Na/Bi mol% exhibits high coercive field. This may be elaborated on basis of Schottky defects resulted from Na/Bi non-stoichiometry given by following equations[45,46]:

$$2Na_{Na} + O_O \leftrightarrow Na_2O + 2V'_{Na} + V_O^{\bullet\bullet} \tag{1.4}$$

And,

$$3Bi_{Bi} + 2O_O \leftrightarrow Bi_2O_3 + 2V'''_{Bi} + 3V_O^{\bullet\bullet} \tag{1.5}$$

Therefore, oxygen vacancies ($V_O^{\bullet\bullet}$) are created from Bi or/and Na loss which are highly mobile and interact with domain walls to hinder their movement, resulting in increased coercive field (E_c ~25.7 kV/cm) [47].
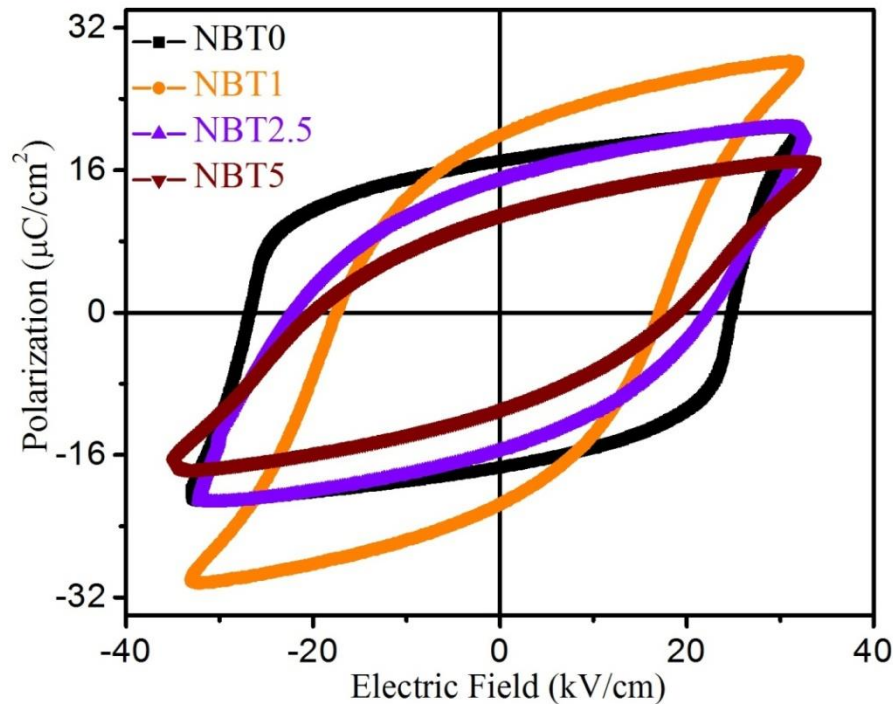

Fig. 9. The combined plots of room temperature polarization vs. electric field (P-E) hysteresis curves for non-stoichiometric $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

A typical slim and saturated P-E hysteresis loop observed for NBT1 may arise due to the growth of stoichiometric composition without any Na/Bi loss or generation of negligible amount of oxygen vacancies in the sample. P-E hysteresis loops become more slanted for 2.5 mol% and 5mol% excess of Na/Bi which may signify that large deviation of Bi/Na stoichiometry results in weakening of long ferroelectric order in samples[45].

Fig.10. shows variation of remnant polarization (P_r), coercive field (E_c) and piezoelectric coefficient (d_{33}) of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramic as function of concentration of Na/Bi excess addition.

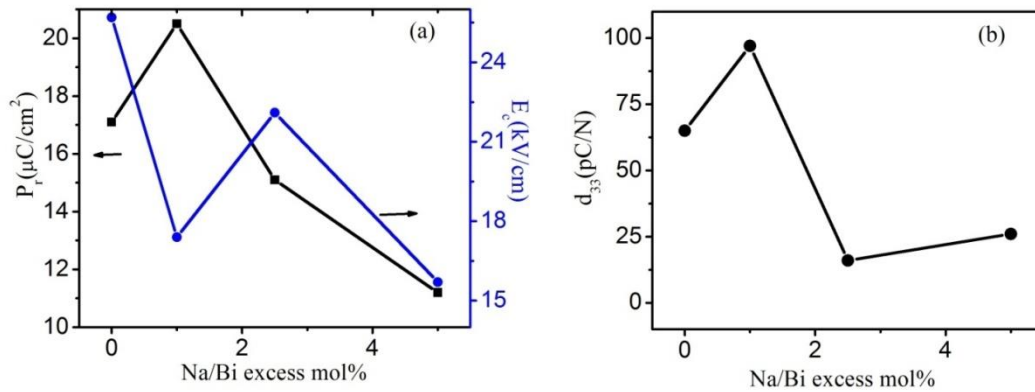**Fig. 10.**   Variation of (a) Ferroelectric parameters (P_r, E_c), and (b) Piezoelectric coefficient (d_{33}) of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics as a function of Na/Bi excess mol% addition

Table 6. Ferroelectric parameters and piezoelectric coefficient for various $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics

Sample	P_{max} ($\mu C/cm^2$)	P_r ($\mu C/cm^2$)	E_c (kV/cm)	d_{33}
NBT0	20.8	17.1	25.7	65
NBT1	29.2	20.5	17.4	97
NBT2.5	20.8	15.1	22.1	16
NBT5	17.1	11.2	15.7	26

It can be seen that maximum values of P_r ~ 20.5 $\mu C/cm^2$, d_{33} ~ 97 pC/N and minimum value of E_c ~ 17.4 kV/cm is achieved for NBT1 ceramics with 1mol% of Na/Bi excess addition, whereas P_r and d_{33} values decrease with further increase of Na/Bi excess addition. The values of P_r, E_c and d_{33} for all samples are given in Table 6. The enhancement of ferroelectric and piezoelectric properties of NBT1 may be attributed to compensation of Bi loss, compact crystal growth with uniform grains connectivity which leads to easier movement of domains and comparatively long range ferroelectric order. However, decrement of ferroelectric as well as piezoelectric properties at higher Na/Bi excess concentration i.e. at x = 0.05(NBT2.5) & x = 0.1(NBT5) may correspond to the segregation of Na^+ and Bi^{3+} ions at grain boundaries which come into play due to incorporation of excess Na/Bi in crystal structure. In general, the stability of ferroelectric domains in ABO_3 type perovskites depends on the coupling between TiO_6 octahedra with A-site cations. The segregation of Na^+ and Bi^{3+} ions hinders the coupling of TiO_6 octahedra which result in reduction of ferroelectric domains stability [27, 48, 49].

In order to investigate the temperature stability of ferroelectric behavior in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics, the temperature dependent P-E hysteresis loops have been measured in temperature range 30-200°C and are shown in Figs. 11 (a)-(d). The P-E hysteresis loop of NBT0 ceramic at a temperature of 30°C as in Fig 11(a) shows a typical ferroelectric shape. As the temperature is increased to 200°C, the shape of hysteresis loops appears narrow, but retains the characteristics of ferroelectric behavior. No deformation of P-E hysteresis loop is observed indicating the existence of ferroelectric character. As the temperature increases, the polarization values of NBT0 ceramics increases up to applied temperature of 200°C and coercive field decreases. The similar temperature dependent ferroelectric behavior can be noticed for NBT1, NBT2.5 and NBT5 ceramics as shown in Figs 11(b)-11(d).
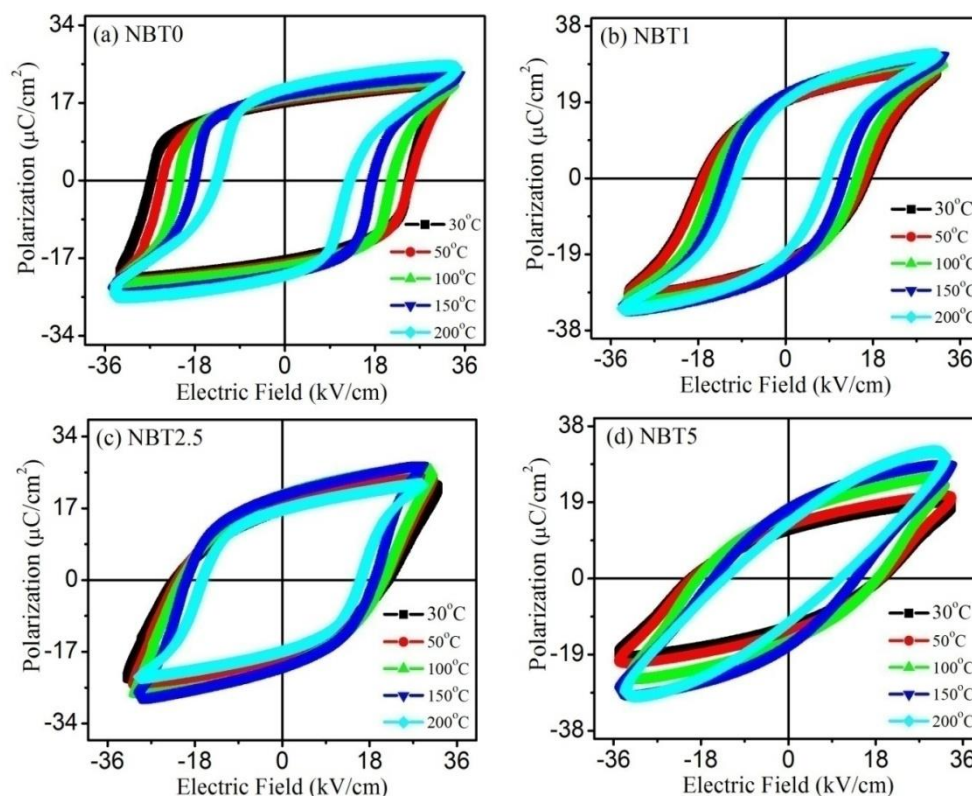
Fig. 11. The P-E hysteresis loops of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics at various temperatures with Na/Bi excess mol% (a) 0, (b) 1, (c) 2.5 and (d) 5

The area of hysteresis loop which is a measure of energy loss is influenced by concentration of Na/Bi excess addition in NBT ceramics. The area of P-E hysteresis loop decreases with the increasing Na/Bi excess addition in NBT ceramics and the loop becomes linear at 5mol% Na/Bi excess concentration. The observation of ferroelectric hysteresis loops for all NBT ceramics over measured temperature range up to 200ºC reveals the presence of ferroelectric order in these samples. The result is consistent with dielectric properties of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ceramics, where the observed depolarization temperature T_d lies well above 200ºC. The decrease in coercive field (E_c) with increase of temperature for all samples may be attributed to decrease in domain switching resistance. On the other hand remnant polarization (P_r) values for NBT0and NBT1samples prolong up to the temperature 200ºCwith typical ferroelectric hysteresis loop shape whereas the P_r values decrease significantly for NBT2.5 and NBT5 samples at 200ºC with the appearance of slightly distorted hysteresis loop.

IV. CONCLUSIONS

In summary, we have systematically studied the effect of Na/Bi excess mol% on structural, dielectric, ferroelectric and piezoelectric properties of $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics. A pure perovskite crystal structure is observed for 0 to 5 mol% excess of Na/Bi in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics based on x-ray diffraction and Raman spectra analysis. Elemental analysis by EDS reveals Bi loss in NBT0, surplus alkali(Na) in NBT2.5 and NBT5 and stoichiometric composition (Bi/Na ~1) in NBT1sample which is supported by surface morphology, relative density and DC resistivity measurements. Compositional fluctuations induced due to excess mol% of Na/Bi result in variation in dielectric as well as ferroelectric and piezoelectric properties. Complex impedance analysis is under progress for more clear understanding of electrical transport phenomenon in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics. Temperature dependent PE curves for NBT0 and NBT1 represents stable ferroelectric order up to 200ºC temperature which is in good agreement of depolarisation temperature (T_d) observed during dielectric measurements. Therefore, we can conclude that adequate control of Na/Bi excess mol% in $(Na_{0.5}Bi_{0.5})_{1+x}TiO_3$ ceramics lead to improvise the structural as well as electrical properties.

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