Anomalous phase transitions of lead-free piezoelectric $xNa_{0.5}Bi_{0.5}TiO_3$ - $(1-x)BaTiO_3$ solid solutions with enhanced phase transition temperatures

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Temperature-dependent structural phase transitions and dielectric properties for a series of $xNa_{0.5}Bi_{0.5}TiO_3$ - $(1-x)BaTiO_3$ (NBT-BT) samples where x ranges from 0.05 to 0.30 have been investigated. Non-ambient x-ray diffraction together with dielectric data as a function of temperature have demonstrated an enhancement in the ferroelectric to paraelectric phase transition temperature with the increase in NBT content, including inhibition of two well-known low-temperature polymorphic phase transitions of BaTiO₃. Anomalous dielectric response has been observed for samples with $x \ge 0.20$ suggesting a crossover from a first-order to a second-order phase transition. The critical point lies between x=0.15 and x=0.20. Deviation from the classical Curie-Weiss law has been seen for samples having $x \ge 0.10$. A modified Curie-Weiss law was employed to model the dielectric response in the paraelectric phase and the maximum value of the critical exponent γ was found to be 1.45 for x=0.30. It is suggested that the dielectric properties are heavily influenced by the induced strain upon doping rather than chemical inhomogeneities and structural disorder, which are common occurrences in doped ferroelectrics.

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I. INTRODUCTION

The room-temperature phase diagram of the binary system of $xNa_{0.5}Bi_{0.5}TiO_{3}-(1-x)BaTiO_{3}$ (NBT-BT) is not intricate and the only structural phase transition from tetragonal (P4mm) to rhombohedral (R3c) has so far been reported at around x=0.94.¹ This is also known as a morphotropic phase boundary between the tetragonal and rhombohedral crystal structures where this material has demonstrated enhanced physical properties.¹⁻³ However, there are only a few reports available^{4,5} on the BaTiO₃ end of the phase diagram. The structure and the dielectric properties of the well-known ferroelectric material BT and numerous BT-based compounds is constantly being investigated in order to tailor the properties of this important lead-free material according to applications. Commonly, it has been seen that the solid solutions developed from BT upon doping, such as $Ba(Ti_xZr_{1-x})O_3,^6$ $Ba(Ti_rCe_{1-r})O_3,^7$ (Na_{0.5}K_{0.5})NbO₃-BaTiO₃,⁸ and BaTiO₃-BiAlO₃ (Ref. 9) demonstrate frequency-dependent diffuse phase transitions along with a decrease in ferroelectric to paraelectric phase transition. However, we have recently studied¹⁰ the structure of the xNBT-(1-x)BT system in the BT-rich end of the phase diagram ($x \le 0.40$) and a rare enhancement of the tetragonality along with an increase in the ferroelectric to paraelectric transition temperature upon doping was observed. Continuing that investigation in this paper, we discuss the consequences of doping on both the temperature-dependent structural phase transitions and the dielectric properties of BT.

II. EXPERIMENTAL DETAILS

Ceramics of NBT-BT were synthesized following a standard solid-state synthesis route. Starting materials (BaCO₃, TiO₂, Bi₂O₃, and Na₂CO₃) with purity greater than 99.9% were mixed by wet ball milling in ethanol media for about 24 h before the mixtures were calcined at 1000 °C for 4 h. The calcined powders were then sintered at 1200 °C for 4 h.

Room-temperature x-ray powder-diffraction patterns of the sintered ceramics were collected using a PANalytical X'pert Pro MPD (multipurpose diffractometer) in the 2θ range of $20^{\circ}-90^{\circ}$ in Bragg-Brentano geometry. Hightemperature diffraction patterns were recorded in the temperature range from 25 to 350 °C using an Anton Paar furnace (HTK1200N). Low-temperature diffraction was performed in the temperature range from 25 °C down to -253 °C on a Bruker D5005 diffractometer, which is equipped with a Phenix cryostat (Oxford Cryosystems). Both high- and low-temperature scans were recorded with an interval of 10 °C in temperature.

For dielectric measurements, disk-shaped pellets of approximately 13 mm in diameter and 1–2 mm in thickness were prepared using a uniaxial isostatic press. Silver paste was applied on the polished surfaces of the disks to form the electrodes and dried for several hours. High-temperature dielectric measurements were carried out using a custom-built furnace and a low frequency (LF) impedance analyzer (HP4192A) with computerized control and data acquisition through a LabVIEW interface. Temperature-dependent capacitance and conductance data were measured in the frequency range 50–150 KHz with a heating rate of 1 °C/min in the range from 25 to 450 °C.

III. RESULTS AND DISCUSSIONS

A. Dielectric properties

The temperature and frequency dependence of the dielectric permittivity were investigated for six different composi-



FIG. 1. (Color online) Temperature-dependent dielectric constant of NBT-BT ceramics for different composition at frequencies 50, 100, and 150 kHz.

tions of NBT-BT ceramics between x=0.05 to 0.30. The real and the imaginary part of the dielectric permittivity ($\varepsilon = \varepsilon'$ $+i\varepsilon''$) were calculated from the capacitance (*C*) and the conductance (*G*) data, respectively, employing the following formulas assuming a parallel-plate capacitor model:

$$\varepsilon' = Cd/\varepsilon_0 D,\tag{1}$$

$$\varepsilon'' = Gd/\omega\varepsilon_0 D, \qquad (2)$$

where C=capacitance, G=conductance, d=sample thickness, D=area of the electrode, $\omega = 2\pi \times$ frequency in hertz, and ε_0 is the free-space permittivity. Figure 1 shows the temperature-dependent ε' and ε'' for the NBT-BT ceramics having different amounts of doping concentration at three different frequencies 50 100, and 150 kHz. The central peak observed for each composition defines the ferroelectric (noncentrosymmetric space group: P4mm) to paraelectric phase (centrosymmetric space group: $Pm\overline{3}m$) transition. It is evident that the doping has primarily resulted in shifting the peak temperatures (T_m) to higher temperature and second in broadening the ε' -T peaks with the increase in the doping content. Enhancement of transition temperatures is an unusual event in substitutional-type BT-based solid solutions and the only exception exist where Ba was partially substituted by Pb.¹¹ However, apart from Pb, there is a situation where Ca⁺² substitutes Ba⁺² in BT, the Curie temperature remains fairly constant (approximately 130-137 °C) till 20% of Ca concentration.¹²

The physical properties of PbTiO₃ differ from those of BaTiO₃ as a consequence of the covalent nature of the Pb-O bonding¹³ whereas Ba-O bonding is primarily ionic.¹⁴ From theoretical studies¹⁵ it was predicted the Bi should mimic Pb because of the presence of its stereochemically active lonepair electrons. Therefore, it is likely that the Bi-O bonding induces a different component of polarization in the structure because of its possible covalent nature, which could push the ferroelectric transition temperatures to higher values. Doping of different ions having different sizes also causes local distortion and strain in the structure and therefore, the broadening of the ε' -T could be explained as a consequence of the strain-induced relaxation of the polarization near the transition temperature.

It is further interesting to see that there was no frequency dispersion observed in the frequency range of 50-150 kHz for the samples where x is between 0.10 and 0.30. The data points for these ceramics at the three different frequencies are exactly on the top of each other and this makes NBT-BT ceramics distinguishable from typical compositionally disordered systems such as relaxors¹⁶⁻¹⁸ and doped quantum paraelectrics^{19–21} which demonstrate strong frequency dispersion in the dielectric constant in the frequency range from 0.1 kHz to 1 MHz. However, the sample with composition x=0.05 show relaxation before the ferroelectric phase transition along with large values of ε'' , which is linearly proportional to dielectric loss, in comparison with other compositions. This could be an effect of the conduction due to the presence of mobile charge carriers, which essentially reduce the resistivity of the bulk ceramics. The effect of dc conduction at high temperatures is also evident for the samples at x=0.15, where a huge increase in the ε' is seen for temperatures >350 °C.

The fall of the dielectric constant after the transition temperature in a ferroelectric material generally follows the Curie-Weiss law,



FIG. 2. (Color online) $1/\epsilon'$ vs temperature plot showing the deviation from the classical Curie-Weiss behavior with increasing *x*.



FIG. 3. (Color online) The variation in $(T_m - T_{CW})$ as a function of *x*. The crossover from positive difference to negative difference occurs between x=0.15 and x=0.20.

$$\varepsilon' = C/(T - T_{CW}),\tag{3}$$

where C is the Curie-Weiss constant and T_{CW} is called the Curie-Weiss temperature and generally refers to the ferroelectric transition temperature. To demonstrate the behavior of NBT-BT ceramics, the reciprocal of ε' as a function of temperature at a constant frequency of 150 kHz has been plotted in Fig. 2 for different compositions. A relatively high frequency was chosen to eliminate any parasitic contribution such as interfacial capacitance to the dielectric constant, which normally occurs at low frequencies. The linear relationship between $1/\varepsilon'$ and temperature is valid for x=0.0and 0.05; however, deviation from the Curie-Weiss law is evident for rest of the samples where $0.10 \le x \le 0.30$. The data where $T > T_m$ were fitted with a straight line and the Curie-Weiss temperature (T_{CW}) was estimated from the extrapolation of the fitted line. T_B refers approximately to the temperature below which $1/\epsilon$ does not follow the temperature linearly. For relaxor ferroelectrics such as $PbMn_{1/3}Nb_{2/3}O_3$, T_B is commonly known as the Burns temperature and it is regarded as a signature of the crossover between soft-mode and order-disorder dynamics.²² T_m is the temperature where the dielectric maximum occurs and ΔT_m , defined as $T_m - T_B$, is a measure of the extent of the devia-



FIG. 4. (Color online) The variation in $\delta \epsilon' / \delta T$ as a function of *T* for different compositions showing first-order behavior of BT is gradually changing upon doping.

tion. It is evident from Fig. 2 that ΔT_m is zero for x=0.0 and 0.05, confirming the validity of the Curie-Weiss law; however, ΔT_m is nonzero for $x \ge 0.10$ and increases with x. This suggests the appearance of a kind of relaxation near the phase transition temperature upon doping which is responsible for flattening out the ε' -T peaks and the departure from the classical Curie-Weiss behavior. It is also evident that, as a consequence of the peak broadening, T_{CW} becomes greater than T_m for samples at x=0.20, 0.25, and 0.30. For a typical first-order displacive phase transition, this is inexplicable. Theoretically for BT, T_{CW} is lower than T_m by about 8-10 °C.²³ Figure 3 demonstrates the variation in the difference between T_m and T_{CW} as a function of x. A crossover from a positive difference to a negative difference can be seen between compositions x=0.15 and 0.20, suggesting a crossover from a first-order to a second-order phase transition

Chemical substitution in the structure can also be considered as a chemical pressure and it can be expected that the



FIG. 5. (Color online) Fitting of the modified Curie-Weiss law in the paraelectric phase of the NBT-BT ceramics.



FIG. 6. (Color online) (a) Room-temperature x-ray diffraction patterns for NBT-BT ceramics as a function of x. (b) Increasing values of splitting between (002) and (200) is evident with the increase in NBT doping in BT.

phase transitions should be modified in the same fashion as hydrostatic pressure does. The dielectric properties of BT under high pressure were studied by Samara *et al.*²⁴ and Ishidate *et al.*²⁵ and both suggested the existence of a critical pressure between 4–8 GPa where the first-order-type phase transition transforms into a second-order one. In addition, an elastic anomaly in BT under high pressure was reported²⁶ near the ferroelectric phase transition temperature, also suggesting a crossover from a first-order to a second-order phase transition.

To find out more about the character of phase transition as a function of doping concentration, $\delta\epsilon'/\delta T$ against *T* has been plotted in Fig. 4 for different *x*. Since ϵ' is directly proportional to the order parameter polarization (*P*), the sudden inflection of ϵ' near $T=T_m$ provides a definitive signature of first-order behavior for x=0.0 and 0.05. However, as *x* increases, the sudden inflection becomes more gradual suggesting a change to second-order behavior.

To model the temperature dependence of the dielectric constant after the ferroelectric phase transition, a phenomenological modified Curie-Weiss law²⁷ was tested,

$$1/\varepsilon' - 1/\varepsilon'_m = (T - T_m)^{\gamma}/C, \qquad (4)$$

where, T_m is the temperature at dielectric maximum and ε'_m is the value of the ε' at T_m . γ is considered as a quantitative measure of the diffuseness of a ferroelectric phase transition and it lies between 1 and 2. γ is 1.0 for normal ferroelectrics whereas γ is equal to 2 for ideal relaxor materials. In Fig. 5, $\log(1/\varepsilon' - 1/\varepsilon'_m)$ versus $\log(T - T_m)$ has been plotted for dif-



FIG. 7. (Color online) Contour plots showing the transformation of the $\{200\}$ peaks as a function of temperature. The dotted lines represent approximately the phase transition temperatures.

ferent values of x. The data were fitted with a straight line and the values of γ and log(C) were obtained from the slope and the intercept of the line, respectively (Table I). For BT, γ was found to be as 1.0, as expected, and the maximum value of γ was noted as ~1.45 for x=0.30. The values of γ and log(C) obtained from the fit are found to be independent of the frequency, although they are sensitive to the range of the data chosen for the fitting. It should also be mentioned that for x=0.25 and 0.30, the linear fit is not satisfactory near the phase transition temperature which suggests that the mechanism responsible for the diffuse phase transition in typical relaxor materials may not explain the behavior of these NBT-BT ceramics.

B. Structural investigation

Room-temperature x-ray diffraction patterns of NBT-BT ceramics as a function of composition are shown in Fig. 6, which confirms the formation of a single perovskite phase for each composition with a tetragonal structure (space group: P4mm). However a distinct change in the lattice parameters was seen and as a consequence, enhancement of the tetragonality (c/a ratio of the tetragonal unit cell) was noted as a function of x as explained previously in detail.¹⁰

To complement the dielectric results and follow the structural phase transition as a function of temperature, hightemperature x-ray diffraction patterns were collected. Figure 7 shows the contour plots of the high-temperature x-ray diffraction data for $\{200\}$ reflections for the samples from x

TABLE I. Parameters obtained for the NBT-BT ceramics from the Figs. 2, 5, and 7.

Composition	<i>x</i> =0.0	x=0.05	<i>x</i> =0.10	<i>x</i> =0.15	x=0.20	<i>x</i> =0.25	<i>x</i> =0.30
T_m (°C)	136.1	173.9	194.1	194.7	212.0	210.4	214.0
T_{CW} (°C)	98.1	75.1	171.8	96.31	232.8	246.3	249.9
ΔT_m (°C)	0.0	0.0	60.8	17.3	160.8	194.0	188.6
$\log(C)$	4.54(1)	5.671(7)	5.02(2)	5.043(9)	5.82(1)	6.06(1)	6.47(1)
γ	1.001(7)	0.921(5)	1.10(1)	1.063(5)	1.277(4)	1.341(7)	1.448(6)
$T_{\rm PT}$ (from diffraction data)	124	167	180	185	194	193	205



FIG. 8. (Color online) The variation in the strain along $[100]_c$ and $[001]_c$ directions of the tetragonal unit cell as a function of composition.

=0.05 to 0.30. It is evident that the tetragonal doublet of the {200} is gradually collapsing to a single peak through a region of coexisting phases. The structural phase transitions from a polar phase to a nonpolar phase occur between 124 and 205 °C depending on the composition as listed in Table I $(T_{\rm PT})$. The high-temperature phase was modeled with a centrosymmetric cubic structure having space group Pm3m. From the lattice parameters obtained for the tetragonal phase at room temperature and the cubic phase at 325 °C, a quantitative strain can be defined along the $[001]_{c}$ and $[100]_{c}$ direction as $(c_t - c_c)/c_c$ and $(a_t - a_c)/a_c$, respectively. These two parameters have been plotted in Fig. 8 as a function of xand it is evident that the strain along the $[001]_c$ direction which is also the direction of the spontaneous polarization in the tetragonal unit cell, increases with the increase in the doping.

It is well known that in BT the direction of the spontaneous polarization changes to $[011]_c$ (space group: *Amm*2) at around 0–5 °C and to $[111]_c$ direction (space group: *R3m*) when it is cooled further down to around –90 °C. However, low-temperature diffraction patterns recorded for NBT-BT ceramics from room temperature down to –253 °C demonstrated no evidence of structural phase transitions even for the sample with *x*=0.05. Figure 9 shows the contour plot of the diffraction patterns in the temperature range between 25 and –253 °C. Each vertical line represents a different Bragg reflection {*hkl*} as a function of temperature and remains unaltered throughout the temperature range investigated. This suggests that the local strains generated by the doping are frozen and as a result, the two polymorphic phase transitions



FIG. 9. (Color online) Contour plot of the low-temperature x-ray diffraction patterns for the sample x=0.05.

observed for BT have been suppressed, as shown theoretically by Zhong *et al.*²⁸ in undoped BT.

C. Conclusions

xNBT-(1-x)BT ceramics where $x \le 0.30$ show dielectric properties and phase transition characteristics that are distinct from other more conventional BT-derived solid solutions. Non-ambient x-ray diffraction results have revealed that two out of three structural phase transitions as a function of temperature in BT are suppressed leaving only a single ferroelectric to paraelectric phase transition in all the doped samples. However, an increase in the ferroelectric transition temperature as a function of doping has been noted from both high-temperature diffraction and dielectric measurements. The temperature dependence of the dielectric constant has also demonstrated frequency-independent broad maxima near the transition temperatures, which suggests that the relaxation of the polarization is not the result of chemical inhomogeneities or polar nanoregions; rather it is strongly coupled with the strain induced by the doping. This has also caused the negative values of $T_m - T_{CW}$ for the samples with x > 0.20, which cannot be explained within the framework of Landau-Devonshire theory. The Curie constant (C) obtained from the fitting of the modified Curie-Weiss law was of the order of $10^5 - 10^6$, which indicates that the mechanism of the phase transition is not going toward the order-disorder type as a function of doping, as for order-disorder-type phase transitions C is typically $\sim 10^2 - 10^{3.29}$ It would further be interesting to investigate the ferroelectric properties along with the piezoelectric properties to establish the suitability of the materials in various applications.

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