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High temperature stress-induced “double loop-like” phase transitions in Bi-based perovskites

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Polycrystalline $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – 0.06BaTiO_3 samples were tested under uniaxial mechanical compression at various temperatures in the vicinity of the polar tetragonal to nonpolar tetragonal phase boundary. They are shown to display double loop-like stress-strain behavior, marked by a closed ferroelastic hysteresis loop. Thus, it forms a mechanical analog to the polarization-electric field hysteresis behavior of barium titanate above the Curie temperature. As temperature is increased there is an apparent loss of macroscopically observable ferroelasticity, despite the persistence of tetragonality. Macroscopic experimental results are discussed in conjunction with temperature-dependent and stress-dependent high-energy x-ray diffraction data. This reveals a phase transition below the Curie temperature, marked by a discontinuous change in lattice parameters and octahedral tilting during compressive mechanical loading. © 2010 American Institute of Physics. [doi:10.1063/1.3428373]

I. INTRODUCTION

Ferroelectrics (FEs) are a technologically important class of materials utilized in numerous engineered structures and systems. Historically, due to the excellent material properties and an acceptable Curie temperature, lead zirconate titanate (PZT) has been the material of choice. However, increasing government regulations, which limit the use of toxic substances such as lead, have increased pressure to find an environmentally safe alternative.¹ $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ (BNT), originally discovered by Smolenskii and co-workers² nearly 50 years ago, is an appealing lead-free FE alternative because of its large remanent polarization.³ However, BNT suffers from a large coercive field ($E_C=73 \text{ kV cm}^{-1}$)⁴ at room temperature as well as a rhombohedral to tetragonal phase transition below the Curie point,⁵ both of which limit its usefulness in the transducer industry.

Solid solutions of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ (BNT–100xBT) near the morphotropic phase boundary ($0.06 \leq x \leq 0.07$) have shown a reduced coercive field (30 kV cm^{-1}),³ in addition to a large remanent polarization at room temperature^{3,6} and the appearance of large unipolar strains at elevated temperatures.⁶ Initial investigations of BNT–100xBT claimed that there was a high temperature ($150 \leq T \leq 200 \text{ °C}$) FE to anti-FE (AFE) phase transition for compositions that contained less than approximately 10BT,⁴ in disagreement with more recent neutron powder diffraction measurements that show a rhombohedral ($R3c$) to tetragonal ($P4bm$) phase transition in BNT below the Curie temperature.⁷ In the work by Takenaka *et al.*,⁴ the appearance of a pinched polarization-electric field hysteresis loop observed in polycrystalline BNT–5BT at elevated temperatures was taken to be the result of a FE–AFE transformation. However, considering that the pinching in polarization hys-

teresis can be caused by many different mechanisms such as relaxor to FE transition,⁸ AFE to FE transition,⁹ or severe aging in FEs,¹⁰ the identity of the high temperature phase in the BNT–100xBT system remains unclear.

Despite their interesting and complex phase structures, to date there has been very few studies of the mechanical behavior of solid solutions of BNT–BT.¹¹ Such studies are vital for their implementation into devices. The following study presents macroscopic ferroelastic hysteresis curves for polycrystalline BNT–6BT at various temperatures from 25 to 300 °C. A unique stress-induced high temperature phase transition behavior not previously observed in polycrystalline FEs is presented and rationalized through an *in situ* high-energy x-ray diffraction (XRD) analysis done under compressive stresses at elevated temperature.

II. EXPERIMENTAL DETAILS

Solid solutions of BNT–6BT were prepared using the solid oxide processing method. The oxide precursors were reagent-grade oxide and carbonate powders: Bi_2O_3 (Alfa Aesar, 99.975%), TiO_2 (Alfa Aesar, 99.9%), Na_2CO_3 (Alfa Aesar, 99.5%), and BaCO_3 (Alfa Aesar, 99.8%). Each was weighed according to the stoichiometric formula and ball-milled for 24 h in an ethanol suspension followed by drying at 110 °C. Calcination of the powder was performed at 900 °C for 3 h. After calcination, the batch was again ball-milled, dried, and ground to ensure a fine, uniform powder. Pressed cylindrical disks of 20 mm in diameter and about 8.5 mm in thickness were then cold isostatically pressed in a silicone oil bath under a pressure of 350 MPa and sintered at 1150 °C for 3 h in an air atmosphere. Following sintering, the disks were ground to the final thickness, which was not identical for the XRD and mechanical experimentation.

High energy XRD experiments were carried out at beamline ID15A of the European Synchrotron Radiation Fa-

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FIG. 1. (Color online) Schematic diagram of the XRD setup.

cility. A beam energy of 68.02 keV was selected using a double Laue monochromator and beam size set to $0.3 \times 0.3 \text{ mm}^2$ using a set of tungsten slits. A sample of dimensions $1 \times 1 \times 1.6 \text{ mm}^3$ was placed under compression using a BOSE electroforce test bench. The sample temperature was controlled to a thermocouple in contact with the sample surface using a double hot air gun blowing on opposite sides of the sample. XRD patterns were recorded using a Pixium 4700 flat panel detector¹² at a distance of 882.2 mm from the sample. A schematic diagram of this setup is shown in Fig. 1. Using this geometry diffraction patterns with scattering vectors aligned both parallel and perpendicular to the loading direction can be isolated.¹³ Temperature dependent XRD measurements were done separately with the same equipment from room temperature to 208 °C.

For the determination of the exact wavelength and instrumental parameters, LaB_6 profile was recorded and refined using the software package FULLPROF.¹⁴ The Bragg peaks were modeled with the built-in Thompson–Cox–Hastings pseudo-Voigt function and the background was fit with a linear interpolation among selected points. The zero angular shift, scale factor, lattice parameters, and atomic parameters were refined. The refinements were carried out sequentially from low to high temperature data so that quick and reliable convergence was achieved. Since the noncubic distortion of the low temperature $P4bm$ phase was already too small to be distinguished from cubic symmetry in a straightforward manner, changes in the intensity ratio of the pseudocubic (200) to (110) and (111) were traced to detect the phase transition. The choice of the space group for the detected new phase was made based on group-subgroup relations.

Cylindrical samples used for macroscopic stress-strain measurements, with a final diameter of 5.9 mm and height of 6 mm, were core-drilled from the sintered, ground disk. Before testing, each specimen was annealed at 400 °C for 1 h and cooled with a rate lower than 1°C min^{-1} to room temperature to remove potential residual stresses. This annealing step was also preformed between mechanical compression tests to relieve residual stresses and depole the previously tested samples. The macroscopic ferroelastic behavior of unpoled BNT–6BT samples was characterized on a 10 kN screw-type load frame (Zwick, Z010). The longitudinal strain of a sample located inside of a heating chamber (accuracy of $\pm 0.1^\circ\text{C}$) was measured by a linear variable differential transducer (LVDT) capable of resolving displacements of approximately 10 nm. The LVDT was situated out-

FIG. 2. (Color online) Changes in the lattice parameters, the averaged linear expansion, and c/a of the tetragonal structure for polycrystalline BNT–6BT as a function of temperature. A discontinuous change in all the parameters presented is clearly discerned at about 195 °C, which is analyzed to be due to a $P4mm$ to $P4/mmm$ phase transition. (The size of symbols used approximately reflects 95% confidence interval for each fitted peak.)

side of the heated region. A detailed description of the experimental setup can be found elsewhere.¹⁵ During testing short-circuited specimens were compressively loaded to a maximum uniaxial stress of -385 MPa with a linear loading/unloading rate of -3.7 MPa s^{-1} .

III. RESULTS AND DISCUSSION

A. Temperature-dependent structure

A temperature dependent high-energy XRD study in conjunction with permittivity measurements was performed on BNT–6BT ceramics. In agreement with previous diffraction studies by Jones and Thomas⁷ on pure BNT and the permittivity measurements by Hiruma *et al.*¹⁶ on BNT-based systems, it was observed, based on temperature-dependent permittivity measurements, that the room temperature $R3m$ rhombohedral phase¹⁷ evolved into a $P4mm$ tetragonal phase at the depolarization temperature of 87 °C. In contrast to the previous studies,^{7,16} however, a further investigation above the depolarization temperature up to 208 °C revealed that there is another structural transition before the structure evolves into the cubic $Pm\bar{3}m$. Interestingly, this transition takes place at the temperature where the frequency dispersion in the permittivity vanishes. Combined with the group theory, this high temperature phase was determined to be $P4/mmm$, whose point group is $4/mmm$, which is no longer ferroelectrically active. In fact, this type of transition from FE to noncubic paraelectric was also reported in pure BNT through transmission electron microscopy.^{18,19} It was suggested that the nature of the transition be a second order whose microscopic state changes from FE–ferroelastic to paraelectric–ferroelastic, which will be one of the major points to be discussed in depth within this paper.

The structural information around the transition temperature obtained by Rietveld refinements is summarized in Fig. 2. It is seen that a drastic change in all the parameters occurs at the transition temperature of 195 °C. Below this boundary both the c and a lattice parameters are increasing. However, at the phase transition temperature c sharply decreases while a sharply increases, resulting in a discontinuous increase in the unit cell volume represented by the changes in the volume averaged pseudocubic lattice parameter of $P4mm$ ($3.1 \times 10^{-5} \text{ Å}^3/^\circ\text{C}$) and $P4/mmm$ ($1.5 \times 10^{-5} \text{ Å}^3/^\circ\text{C}$). The most

FIG. 3. (Color online) Surface plot (a) showing the evolution of selected XRD peaks for BNT-6BT perpendicular to the applied uniaxial stress. Due to the relatively weak intensity of the $(211)_{tet}$ superlattice reflection, a magnified view of the peak is presented (b) illustrating the changes in the position and FWHM of $(200)_{pc}$ reflection as a function of stress.

distinctive difference between $P4mm$ and $P4/mmm$ in the currently investigated system exists in their c/a ratios, which are larger and smaller than 1, respectively. Note that the $P4/mmm$ phase is supposed to be paraelectric-ferroelastic in terms of the point group but develops a negative spontaneous strain during the transition from $Pm\bar{3}m$ to $P4/mmm$. This is not common for most ferroelastics whose c/a ratio is larger than 1.

B. Stress-dependent structure

To elucidate the effect of uniaxial stress on phase stability and structural changes, *in situ* high-energy XRD was performed at 200 °C, slightly higher than the phase transition temperature (195 °C) of the stress-free specimen. It was assumed during analysis that the macroscopic and microscopic stress states were equivalent. In polycrystalline materials, however, grain-to-grain interactions and inhomogeneities can create fluctuations in the stress field between various grains. Figure 3(a) shows a surface plot of a selected 2θ region. At approximately -150 MPa the $(211)_{tet}$ superlattice reflection, which is characteristic of the presence of oxygen octahedral tilting, appears and its intensity increases continuously with stress. The fact that the stress easily converts $P4/mmm$ into $P4mbm$ and at higher stress levels into $P4bm$ indicates that there should be a phase boundary separating the systems with and without oxygen octahedral tilting at $x < 0.06$, since the compositions with a lower BT content are known to exhibit oxygen octahedral tilting.¹⁷ More importantly, the continuous change in the intensity clearly implies continuous tilting of the oxygen octahedra, which is expected to be rep-

resented by a change in the stress-strain curve around the stress level of -150 MPa. A further increasing stress level up to about -250 MPa is seen to induce a nonpolar-polar phase transition, which is apparent from a discontinuous change in the intensity ratio between $(111)_{pc}$ and $(200)_{pc}$ as well as a development of an anisotropic $(200)_{pc}$.

To better identify the stress-induced structural changes the peak fitting module in the commercial software ORIGIN was employed for single peak profile fitting of the $(200)_{pc}$ reflection from the diffraction patterns collected along the direction perpendicular to the applied stress direction. Due to the very small tetragonal distortion of the given system, all the $(200)_{pc}$ peaks were assumed to be a single peak, and the 2θ position and full-width-at-half-maximum (FWHM) value were determined using a pseudo-Voigt function. The results of this analysis are shown in Fig. 3(b). These two parameters were chosen to reveal the effect of stress on the lattice distortion (2θ values) and tetragonality or lattice stress (FWHM) of the pseudocubic system. Three distinctive critical stress levels, where both parameters changed abruptly, were approximately: -190 MPa (CS1), -240 MPa (CS2), and -320 MPa (CS3). The rate of change in both parameters up to CS2 remained relatively constant, despite the discontinuity observed at CS1. The decrease in the peak position, which indicates an increase in the average volume, was accompanied by an increase in FWHM. This implies that a macroscopically detectable strain induced by the stress is primarily volumetric up to CS2. At CS2, a significant contraction in the unit cell volume and decrease in FWHM are noted, which strongly indicates a phase transition at this stress level. From the intensity ratio between $(111)_{pc}$ and $(200)_{pc}$ as well as the presence of the $(211)_{tet}$ superlattice reflection, the space group of the transformed phase can be assigned as $P4bm$. It is interesting to note that a volumetric change was not observed in the $P4bm$ phase due to an external uniaxial stress. This is evident from the constant 2θ and FWHM values measured between CS2 and CS3. At stresses above CS3 the system developed a strong texture and a sharp increase in tetragonality, indicated by the presence of a noticeable anisotropy in the $(200)_{pc}$ peak. At the maximum stress, approximately -340 MPa, the sample fractured. It was therefore not possible to measure the diffraction patterns during unloading.

C. Macroscopic experimental measurements

The macroscopic ferroelastic constitutive behavior for unpoled BNT-6BT at various temperatures up to 300 °C was characterized under uniaxial compressive stress. Representative hysteresis curves at 25, 190, 200, and 215 °C are presented in Fig. 4. At room temperature polycrystalline BNT-6BT displays typical ferroelastic behavior. During initial loading the sample response is linear to the applied compressive stress. However, at a critical stress level, defined here as the onset stress, σ_o , domains begin to ferroelastically reorient, marked by a nonlinear change in the tangent modulus. The onset stress is found by a tangent-intersection method shown explicitly in Fig. 4(a). The onset stress at room temperature for BNT-6BT was measured as approxi-

FIG. 4. (Color online) Stress-strain hysteresis curves for BNT-6BT polycrystalline specimens at various temperatures. The coercive stress (blue dot), onset stress (red triangle), remanent strain (green square), and initial compliance ($s_{33}=1/E$) are labeled on the ferroelastic hysteresis curve at 25 °C; the direction of loading is indicated by the inset arrows.

mately -212 MPa. As the compressive stress is increased the switching rate maximizes at the inflection point, defined as the coercive stress, σ_c . Upon unloading from the maximum stress the material behavior appears initially linear. This linear regime is followed by nonlinear material behavior principally caused by domains reorienting back to their original state due to local internal electrical and mechanical fields. This deviation from linearity is referred to as back-switching. When the compressive stress is removed a remanent strain, ϵ_R , remains due to domains that have remained in the ferroelastically reoriented directions.

High temperature compressive loading experiments of polycrystalline BNT-6BT above the phase transition temperature previously shown in Fig. 2, which separates the polar tetragonal $P4mm$ and the nonpolar tetragonal $P4/mmm$ phases, show closed loop stress-strain behavior [Fig. 4(b)]. It is assumed that a high temperature stress-induced phase transition between these two space groups, as shown to occur at 200 °C due to compressive mechanical loading in Fig. 3, was responsible for this closed hysteresis behavior, similar to the paraelectric-FE electric field-induced phase transition in BT above the Curie temperature.^{20,21} Please note for comparison to high temperature double loop behavior in BT that the independent variable (electric field) is located on the abscissa, while the polarization is on the ordinate. As temperature was increased from 25 °C the macroscopic remanent strain decreased to zero above approximately 200 °C. In the region between 200 to 220 °C the specimens exhibited a

FIG. 5. (Color online) Remanent and maximum strain as a function of temperature for polycrystalline BNT-6BT samples loaded under uniaxial compression to a maximum stress of -385 MPa.

closed (double loop) hysteresis. The term double hysteresis loop was originally used to describe the electric field induced cubic-tetragonal phase transformation in barium titanate above the Curie temperature.²¹ However, in the case of a stress-induced phase transition it is not possible to apply tensile stresses large enough to develop both lobes of the double loop. At stress levels above the phase transition stress the material behavior was linear. Due to the applied stress the domains transforming from $P4/mmm$ to $P4bm$ had a preference for crystallographic orientation 90° to the applied stress. This resulted in an automatic loss of domains available to be ferroelastically switched in the $P4bm$ phase upon completion of the stress-induced phase transition. Experiments at temperatures above 220 °C did not show closed loop behavior because the maximum compressive stress (-385 MPa) was no longer large enough to initiate a phase transformation. Experiments of BNT-6BT at 250 °C, well within the stress-free $P4/mmm$ region between the high temperature cubic phase ($Pm\bar{3}m$) and the lower temperature stress-free $P4mm$ phase, show a linear stress-strain behavior despite the ferroelasticity expected from the point group symmetry. For this reason $P4/mmm$ will be referred to as a potential ferroelastic.

The thermal effect on the macroscopic strain was quantified at numerous temperatures, as shown in Fig. 5. At temperatures below approximately 185 °C there was an apparent linear decrease in remanent strain with increasing temperature. However, at temperatures above 185 °C the decrease in remanent strain became nonlinear until approximately 200 °C, where the remanent strain vanished. This temperature corresponds well to the $P4/mmm$ - $P4mm$ stress-free phase transition temperature determined by XRD (Fig. 2). It appears from the macroscopic ferroelastic measurements that the reduction in remanent strain was continuous. In contrast, previous high temperature ferroelastic measurements of PZT displayed a linear decrease in remanent strain to the depolarization temperature ($T_D=250$ °C) where it remained zero up to the Curie temperature ($T_C=300$ °C).¹⁵ Experimental measurements between the Curie temperature and the $P4mm$ - $P4/mmm$ phase transition temperature (e.g., 250 and 300 °C) did not display a remanent strain. There are two possible explanations for this behavior. First, the critical stress required to ferroelastically reorient domains is outside

of the applied stress regions used during experimentation, either less than -3.7 MPa or greater than -385 MPa. Previous studies on lanthanum-doped bismuth ferrite–lead titanate ($\text{BiFeO}_3\text{-PbTiO}_3$)²² have shown an increase in switchability with decreasing c/a ratio, indicating that the critical stress in the $P4/mmm$ phase may be lower than the applied preload (-3.7 MPa). Second, that $P4/mmm$ is in fact paraelectric–paraelastic. However, permittivity measurements clearly show an additional dielectric anomaly at around 278 °C. Such an anomaly is known to be related to the transition to the paraelectric–paraelastic cubic $Pm\bar{3}m$, indicating that $P4/mmm$ should be ferroelastic.

The maximum strain, obtained at the maximum stress of -385 MPa, does not show the same nonlinear decreasing trend with temperature increasing through the $P4mm$ – $P4/mmm$ phase transition. Maximum strain values, instead, show an apparent linear decrease up to the maximum temperature of 300 °C. As temperature is increased the energy threshold for ferroelastic switching decreases potentially increasing the number of domains that can be mechanically reoriented. The lower energy barrier for switching, however, is offset by a simultaneous decrease in the spontaneous strain of the unit cell, which has been shown to decrease the macroscopic remanent and maximum strains during uniaxial compressive loading. In BNT–6BT, as previously observed in PZT,¹⁵ there was a linear decrease in maximum strain throughout the temperature range examined. Interestingly, this same trend in maximum strain is observed in BNT–6BT despite the high temperature phase transition at the $P4mm$ – $P4/mmm$ boundary around 195 °C. It appears that the decreasing tetragonality was offset by the additional strain increase during the stress-induced $P4mmm$ – $P4bm$ phase transition, keeping the maximum strain values stable. It is also important to note that the reference strain used to determine the remanent and maximum strain values was at the temperature under consideration with a preload of -3.7 MPa. It is likely that if the decrease in strain during the heating cycle were considered the maximum strain would show an anomaly at the phase transition temperature.

The stability of the mechanical properties of BNT–6BT was measured as a function of temperature in terms of the effective compliance and characteristic stresses, as shown in Fig. 6. In the lower temperature $P4mm$ phase the compliance was found to increase nonlinearly with increasing temperature, where a maximum was measured at 185 °C corresponding well to the beginning of the sharp continuous decrease in remanent strain (Fig. 5). This temperature is lower than the stress-free phase transformation temperature determined by x-ray and permittivity measurements. A decrease in the phase transition temperature due to uniaxial compressive stress perpendicular to the polarization direction, which is the case in mechanically compressed ferroelastic materials, was not expected. It has been shown using a Devonshire thermodynamic formalism that a two-dimensional compressive stress perpendicular to the polarization in a normal FE should increase the Curie temperature.^{23,24} Above this temperature there was a discontinuous decrease in compliance due to the initiation of a transition to the higher temperature $P4/mmm$ potentially ferroelastic phase. With increasing tem-

FIG. 6. (Color online) (a) Compliance and (b) characteristic stresses (onset and coercive stress) as a function of temperature for BNT–6BT. The curve fit lines are meant only to guide the eye.

perature there was a subsequent nonlinear decrease in compliance to values comparable to those at room temperature. Previous measurements of the compliance of single crystal BT as a function of temperature around the FE–paraelectric transformation temperature have shown similar results to that presented here.²⁵ Because of the measurement technique utilized, it was not possible to separate the intrinsic from the extrinsic reversible contributions, such as reversible domain wall motion. The compliance values presented here are therefore effective values, representing not only the composite intrinsic response of all the domains present but also the effects of nonlinear reversible behavior.

The measured onset and coercive stresses were found to both linearly decrease from room temperature up to 185 °C at a rate of $1.02 \text{ MPa } ^\circ\text{C}^{-1}$ and $1.48 \text{ MPa } ^\circ\text{C}^{-1}$, respectively. Additionally, the difference between these two characteristic stresses was also found to decrease with temperature, in part due to the increase in the initial effective compliance and the tangent modulus at the coercive stress. Between 185 and 190 °C there was a discontinuous increase in both stress parameters that coincided with the discontinuity measured in the effective compliance (shown as a dotted line in Fig. 6), which was followed by a linear increase in the characteristic stresses to 220 °C at a rate of $-3.64 \text{ MPa } ^\circ\text{C}^{-1}$ and $-5.30 \text{ MPa } ^\circ\text{C}^{-1}$, respectively. The difference between the characteristic stress parameters increased with temperatures above 185 °C. Above 220 °C the maximum applied stress, limited by the capabilities of the load frame, was no longer large enough to drive a nonlinear material response significant enough to determine the coercive stress. The increase in characteristic stresses above 200 °C corresponds to a decrease in the hysteresis within the closed loop. It is interesting to note that the XRD analysis (Fig. 3) of BNT–6BT at 200 °C under compressive loading, which showed the appearance of octahedral tilting and asymmetry at the lower angle side of the $(200)_{pc}$ peak beginning at -150 MPa, corresponds well with the coercive stress measured from macroscopic stress-strain curves. In addition, from Fig. 3(b) it is apparent that -210 MPa, where the satu-

ration of these effects in the XRD analysis was shown, is approximately where macroscopic measurements show a saturation of the strain response.

There exists a possibility that the observed high temperature closed loop hysteresis in BNT–6BT is due to antiferroelasticity, a concept first introduced in 1969 by Aizu to describe the theoretical stress-induced phase transition from point symmetry *mmm* to point symmetry *2/m* at temperature T_0 .²⁶ Potentially antiferroelastic single crystals of lithium cesium sulfate (LiCsSO_4) have been shown around the ferroelastic phase transition temperature (202 K) to display a double loop behavior as well as a typical ferroelastic behavior, depending on the crystal lattice orientation.^{27,28} This behavior, however, was only observed in response to shear stress. Further experimental results of LiCsSO_4 under uniaxial compression did not show an antiferroelastic-like behavior.²⁹ Antiferroelasticity is only possible if the cells are equally distorted in an opposite sense, alternately with a zero resultant,³⁰ which is a possibility in this material due to the *c/a* ratio in the higher temperature *P4/mmm* that is less than one. Just as AFEs can be changed to FEs by an electric field, it is expected that antiferroelastics can be changed to ferroelastics by an applied mechanical stress. The analog in the field of ferroelectricity, antiferroelectricity has been thoroughly studied in Pb-based perovskites, most notably in modifications of PZT close to the lead zirconate (PZ) end member.³¹ A characterizing parameter in antiferroelectricity is the critical electric field for induced ferroelectricity, which depends on composition,³² temperature,³³ and stress state.⁹ However, the electric field required for an AFE–FE phase transition in PZ increases with decreasing temperature leading to the classical double loop polarization-electric field loop only below the AFE–FE phase transition temperature, the opposite of that observed in BNT–6BT.

IV. CONCLUSIONS

Stress-free XRD analysis on polycrystalline BNT–6BT showed a phase transformation between polar tetragonal *P4mm* and nonpolar tetragonal *P4/mmm* at 195 °C, well below the Curie temperature. However, the application of a uniaxial compressive stress at 200 °C initiated a (211)_{tet} superlattice reflection, characteristic of oxygen octahedral tilting, representing a stress-induced *P4/mmm*–*P4/bm* phase transition at 200 °C. Additional macroscopic uniaxial compressive loading experiments on unpoled polycrystalline BNT–6BT specimens revealed closed loop hysteresis behavior in the vicinity of the stress-free *P4mm*–*P4/mmm* transition temperature. Macroscopic compressive measurements at higher temperatures, well away from both the lower tempera-

ture polar phase and the higher temperature cubic phase, have shown a lack of ferroelastic switching in the *P4/mmm* phase, despite the measured tetragonality.

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