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On the phase identity and its thermal evolution of lead free (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-6 mol% BaTiO$_3$

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Temperature-dependent dielectric permittivity of 0.94(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-0.06BaTiO$_3$ (BNT-6BT) lead-free piezoceramics was studied to disentangle the existing unclear issues over the crystallographic aspects and phase stability of the system. Application of existing phenomenological relaxor models enabled the relaxor contribution to the entire dielectric permittivity spectra to be deconvoluted. The deconvoluted data in comparison with the temperature-dependent dielectric permittivity of a classical perovskite relaxor, La-modified lead zirconate titanate, clearly suggest that BNT-6BT belongs to the same relaxor category, which was also confirmed by a comparative study on the temperature- dependent polarization hysteresis loops of both materials. Based on these results, we propose that the low-temperature dielectric anomaly does not involve any phase transition such as ferroelectric- to-antiferroelectric. Supported by transmission electron microscopy and X-ray diffraction experiments at ambient temperature, we propose that the commonly observed two dielectric anomalies are attributed to thermal evolution of ferroelectric polar nanoregions of $R3c$ and $P4bm$ symmetry, which coexist nearly throughout the entire temperature range and reversibly transform into each other with tempera-ture. © *2011 American Institute of Physics*. [doi:10.1063/1.3645054]

I. INTRODUCTION

Lead-free piezoelectric ceramics have been studied extensively over the last decade in response to legislative enforcements, representatively the European RoHS/WEEE regulations.[1] Among the studied materials, solid solutions between a rhombohedral (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ (BNT) and a tetragonal BaTiO$_3$ (BT) reported firstly by Takenaka *et al.*[2] have been of particular interest largely because of two scientifically intriguing but unclear issues: (1) A morphotropic phase boundary (MPB) exists at 6–7 mol% BT, whose nature appears similar to that of the market dominating Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) piezoceramics. (2) A range of compositions (0-15 mol% BT) undergo a ferroelectric (FE)-to-antiferroelectric (AFE) phase transition above a temperature commonly denoted as depolarization temperature (T_d) in extension to the previously known polymorphism of pure BNT.[3,4]

The unclarity over the first issue arises from the fact that the MPB proposed based on dielectric and electromechanical properties has been continuously questioned by unsupporting structural evidences, *e.g.*, a range of compositions around the alleged MPB (6–10 mol% BT) show little distinction from a cubic symmetry.[5–7] A Raman spectroscopy study combined with X–ray diffraction experiments[8] proposed that a structural change happens somewhere between 5 and 6 mol% BT content. Later, it was shown that this boundary turned out to be nearly temperature-independent from ∼10 K to ∼470 K and shifts to somewhere between 6 and 7 mol% BT on electrical poling.[9] Recently, it was shown by an *in situ* X-ray

diffraction study[10] that two phase boundaries exist for unpoled BNT-100xBT ceramics ($0 \leq x \leq 0.15$), one at somewhere between 5 and 6 mol% BT and the other at 11 mol% BT. It was proposed that the former involves an oxygen octahedral tilt transition and the latter signifies a rhombohedral-to-tetragonal transition. It was further shown that the tilt boundary shifts to somewhere between 6 and 7 mol% BT and a structural MPB existing initially at BNT-11BT extends to a broad range of compositions, *e.g.*, 6–11 mol% BT when the materials are electrically poled, though an MPB-induced property enhancement takes place only at 6–7 mol% BT.

The onset of the second issue dates back to 1974 when Sakata and Masuda[3] showed that a typical ferroelectric polarization hysteresis loop of Sr-modified BNT evolved into a double hysteresis loop, which is one of the characteristics of antiferroelectricity above a temperature where the dielectric permittivity shows a so-called "hump" (will be referred to as a "shoulder" throughout the context, hereafter). The motivation for their work was given, when Smolenskii *et al.*[11] suggested a possible presence of two phase transitions in BNT, one at the temperature where the shoulder develops (will be referred to as T_s) and the other at the temperature where the dielectric maximum occurs. However, the nature of the former was not identified, while the latter was designated as a Curie temperature. Though the experimental work by Sakata and Masuda[3] has been accepted as a concrete evidence for the presence of FE-to-AFE transition in the material at T_s, again no supporting evidence has followed, yet. For example, no thermal arrest indicating a phase transition was detected at T_s by differential thermal calorimetry and no change was observed even in the domain structure around T_s.[12] Moreover, the structural investigations in the literature

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unanimously state that no structural change is obvious below 255 °C, converging to a conclusion that neither any trace of antiferroelectricity nor any apparent phase transition is evident at T_s.[9,13–16] An interesting feature to be noted in the structural works is that the rhombohedral and tetragonal symmetries coexist over an exceptionally large range of temperatures, *i.e.*, ~ 150 °C, which is unique among the known phase transitions.[15,16] This peculiar phenomenon was rationalized by a "relaxor" model assuming a two-phase mixture that consists of polar $R3c$ rhombohedral clusters dispersed in a "weakly polar" or "ferrielectric" $P4bm$ tetragonal matrix.[13,15]

On the other hand, Dorcet *et al.*[17,18] recently cast a new perspective over the structural aspect of pure BNT. Based on their observation of $1/2\{oee\}$ superlattice reflections suddenly appearing at ~ 200 °C and persisting up to ~ 300 °C during their *in situ* TEM experiments, they proposed that the conventionally designated two-phase coexisting region be actually a structurally modulated intermediate phase, where blocks of the low-temperature ferroelectric $R3c$ phases are aligned antiparallelly with $Pnma$ orthorhombic sheets in-between. They saw the origin of this structural modulation as two incompatible order parameters, one from ferroelectric/ferroelastic $R3c$ and the other from paraelectric/ferroelastic $P4/mbm$, and hence the commonly accepted $P4bm$ phase is discarded in their phase diagram. Assuming that the modulated phase is dynamical enough to respond to external electrical excitations, they proposed a "relaxor antiferroelectric" concept. Apart from the validity of the model, however, this model still needs further clarification. Firstly, although the model assumes that the ferroelectric $R3c$ evolves into a relaxor with the appearance of $Pnma$ symmetry, the dielectric permittivity strongly implies that pure BNT is a relaxor even at room temperature as long as it is not poled.[3] In addition, their key finding, the presence of $1/2\{oee\}$ superlattice reflection, on which the entire discussion is based, has not been verified elsewhere so far.

The situation is more or less the same in the Ba-modified BNT system. Just like in pure BNT, no supporting evidence in terms of structural and thermal analyses has been presented, yet. The existence of AFE phase above T_s was proposed based only on the observation of a double hysteresis in the polarization hysteresis loop of BNT-5BT, which was again reported by Sakata and his co-workers.[2] Nevertheless, the presence of AFE order in BNT-based systems has been largely accepted in the community. Interestingly, the temperature for FE-to-AFE transition has been assigned to T_d instead of T_s in the later publications.[19–22] In fact, the use of T_d for FE-to-AFE transition is conceptually more logical than that of T_s in that the FE-to-AFE transition in this type of materials is supposed to be a first- order transition[12] and consequently should be frequency-independent with a sharp peak in the corresponding dielectric responses. It is, however, noted that T_d is always lower than T_s,[23] which makes the deviation from the structural data in the literature even larger. Nevertheless, the AFE issue drew greater attention when an exceptionally large strain was achieved in $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-modified BNT-6BT ceramics.[6] In analogy with the previous report in a single crystal

BNT-BT,[24] the appearance of the large strain was attributed to the birth of AFE phase with chemical modifications. Follow-up studies on composition[25] and temperature dependence[26] of polarization and strain hysteresis further revealed that field-induced strain is largest at a boundary where FE feature changes into "AFE" that is related to a high-temperature polymorph. The large strain was, indeed, confirmed to be related to a high temperature polymorph that transforms into a long-range ferroelectric phase reversibly under electric field, though this polymorph was proposed not AFE but a certain near "non-polar" phase[27] similar to the "low-temperature non-polar phase" proposed by Bakhrushev *et al.* in 1985 to dispute the AFE phase claimed by Sakata and Masuda[3] in 1974. The proposed near non-polar phase was identified as $P4bm$ that transforms into $R3c$ under electric field by an *in situ* neutron diffraction,[28] and the $P4bm$ phase was proposed being responsible for the relaxor properties of the system by an *in situ* TEM study.[29] The near non-polar phase was further supported by comparative studies of a series of BNT-BT-KNN ceramics, *i.e.*, one with FE order, another with intermediate feature, and the other with non-polar feature, on electrical fatigue experiments, which demonstrated that the FE phase fatigued significantly with cycling, while (near) non-polar phase was extremely stable against fatigue due to the absence of domain structure.[30,31] Later, it was shown that this near non-polar $P4bm$ phase is favored when Na^+ ions are replaced by bigger isovalent ions such as K^+ (Ref. [32]) or when A-site vacancy is created,[33–37] while unfavored with acceptor dopants generating oxygen vacancies.[33,37]

In the meantime, Ma *et al.*[23] proposed another "relaxor antiferroelectric" model with the terminology being the same with the model of Dorcet *et al.*[17] but with the underlying physics being completely different. Instead of seeing $R3c$ phase as polar nano-entity, they assumed that the $P4bm$ "ferrielectric" nanodomains give rise to the relaxor features. Given the assumption, they concluded that the $P4bm$ "relaxor AFE" phase of a short-range order should evolve into the $P4bm$ AFE of a long-range order at a temperature, where the dispersion in dielectric permittivity vanishes. A drawback is that this model requires a counterintuitive assumption that random fields that inhibit the formation of a long-range order should decrease with increasing temperature. Soon after, Ma and Tan[38] modified the initially proposed phase diagram in a way that the aforementioned controversial picture of the phase evolution is avoided by removing the region where the AFE phase of a long-range order is stable. Instead, they proposed a gradual decrease of the $P4bm$ nanodomains in size until they are progressively replaced by $Pm\bar{3}m$ cubic phase above the maximum dielectric permittivity temperature. In this revised phase diagram, however, the compositions designated with $P4bm$ symmetry are shown not to have the T_d, where the P(E) hysteresis loops of the compositions designated with $P4bm$ evolve from a well-defined to a constricted one (see, for example, Ref. [39]) and the origin of two anomalies is not resolved.

The first step to clarify all the issues regarding the phase relations and stability of the BNT-100xBT system should identify the true origin of the depolarization temperature and

the shoulder appearing in the dielectric permittivity. This should definitely be followed by understanding the true identity of the phases at room temperature and their thermal evolution. In this regard, we first explored the relaxor characteristics of BNT-6BT using dielectric permittivity data. The analyzed data were interpreted in comparison with the dielectric permittivity of a classical perovskite relaxor, PLZT ceramic, as well as with structural evidences.

II. EXPERIMENTAL PROCEDURE

Ceramic samples of $0.94(Bi_{1/2}Na_{1/2})TiO_3$-$0.06BaTiO_3$ (BNT-6BT) were prepared through a solid oxide route using reagent-grade elemental oxides and carbonates. The details of the processing conditions can be found elsewhere.[10] It is noted that a possible non-stoichiometry due to the volatility of Bi and Na is effectively avoided by the adopted processing route as demonstrated by inductively coupled plasma-mass spectroscopy (ICP- MS) and electron paramagnetic resonance (EPR) spectroscopy in our previous report.[33] As a reference for the current study, hot-pressed relaxor PLZT 8/65/35 ceramics were purchased from a commercial vendor (Boston Applied Technology).

Dielectric permittivities were measured on ground and polished disk-shaped samples (the ratio between diameter and thickness > 10) with burned-in silver electrodes by an impedance analyzer (HP4284A) equipped with a temperature-controllable furnace. All specimens were thermally annealed above $400\,°C$ and furnace-cooled to remove any possible influence from the sample preparation. Two successive thermal cycles were applied to a poled sample for 4 different frequencies of $100\,Hz$, $1\,kHz$, $10\,kHz$, and $100\,kHz$ at the ramping rate of $120\,°C/h$ up to $500\,°C$ to obtain the dielectric permittivity data for both poled and unpoled conditions to ensure minimal artifacts. To measure the temperature-dependent polarization hysteresis loops, a Sawyer-Tower circuit with $15\,\mu F$ measurement capacitance was used, samples being placed in a thermal bath filled with a high-temperature insulating silicon oil. The frequency of $5\,Hz$ was applied to all the measurements to minimize artificial influences during the measurements possibly due to an increased conductivity especially at elevated temperatures.[40,41]

To reveal the local features in the symmetry, the specimen for transmission electron microscopy (TEM) was prepared by a conventional ceramographic technique, consisting of polishing, dimpling, and ion milling. Before ion-milling the sample was thermally annealed at $400\,°C$ to remove any residual strain induced during the sample preparation. TEM specimen was slightly carbon coated to prevent charging under the incident electron beam. The experiments were performed with FEI CM20 (FEI, Eindhoven, The Netherlands), operated at $200\,keV$.

III. RESULTS

Figure 1 provides the polarization hysteresis (P(E)) loops of (a) a commercial relaxor PLZT 8/65/35 in comparison with (b) those of BNT-6BT ceramics at various temperatures. It is noted that although a double-hysteresis loop-like P(E) curve has been frequently referred to as a concrete
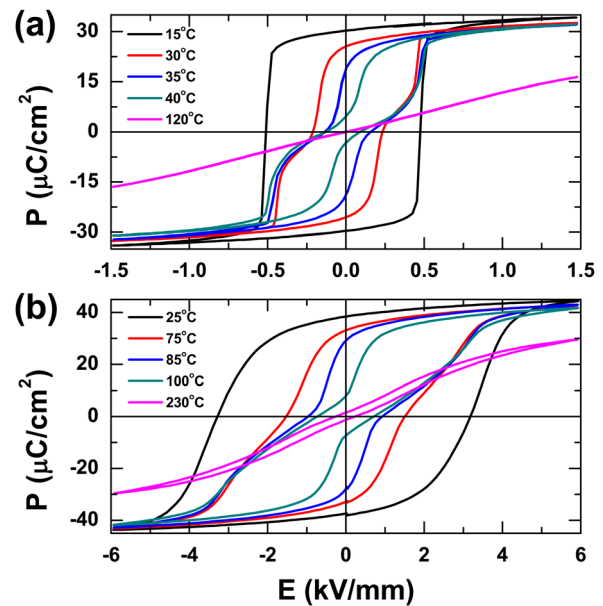

FIG. 1. (Color online) Temperature-dependent polarization hysteresis of (a) PLZT 8/65/35 and (b) BNT-6BT measured at 5 Hz.

evidence for the presence of an AFE order in BNT-based lead-free piezo-ceramics, a constricted P(E) loop is also clearly visible in the relaxor PLZT 8/65/35 that is one of the classical perovskite relaxor materials. In fact, a similar constricted P(E) loop was also observed in another classical perovskite relaxor single crystal, $Pb(Mg_{1/3}Nb_{2/3})O_3$- $0.1PbTiO_3$ (PMN-0.1PT).[42] Consequently, it is said that the constriction in the P(E) loop merely reflects the presence of a certain phase at zero electric field, which is a "non-polar" or "weakly polar" phase converting to a polar phase on the application of electric field.

In the case of PLZT 8/65/35, a significant constriction starts to appear at $\sim 30\,°C$, followed by a drastic drop in the remanent polarization (P_{rem}) at $\sim 40\,°C$. After the sudden drop, P_{rem} was observed to decrease gradually with temperature until the P(E) loop becomes linear with a negligible P_{rem} (see, for example, the presented P(E) loop at $120\,°C$). The thermal evolution of P(E) loop of the BNT-6BT is virtually the same as that of the PLZT 8/65/35 except for the fact that a non-negligible P_{rem} remains persistent even after a significant drop above $\sim 85\,°C$. It is noticed that the P(E) loop even at $230\,°C$ still exhibits a hysteretic behavior instead of being linear.

Figure 2 presents the real part (ϵ') and imaginary (ϵ'') part of the dielectric permittivity of both unpoled and poled PLZT 8/65/35. A strong frequency dispersion with frequency-dependent broad maxima is discerned in both ϵ' and ϵ'' for the unpoled specimen. Here, three points are to be noted: (1) Both ϵ' and ϵ'' exhibit a broad asymmetric peak shape. The broadness in the shape profile is much larger at higher temperature side and at lower temperature side of the local maximum in ϵ' and ϵ'', respectively. (2) The frequency dispersion is more pronounced before the signal culminates in ϵ', while it is after the culmination in ϵ''. (3) The temperature for the maximum in ϵ' (T_m') is always higher than that in ϵ'' (T_m''). All these observations point to the fact that the
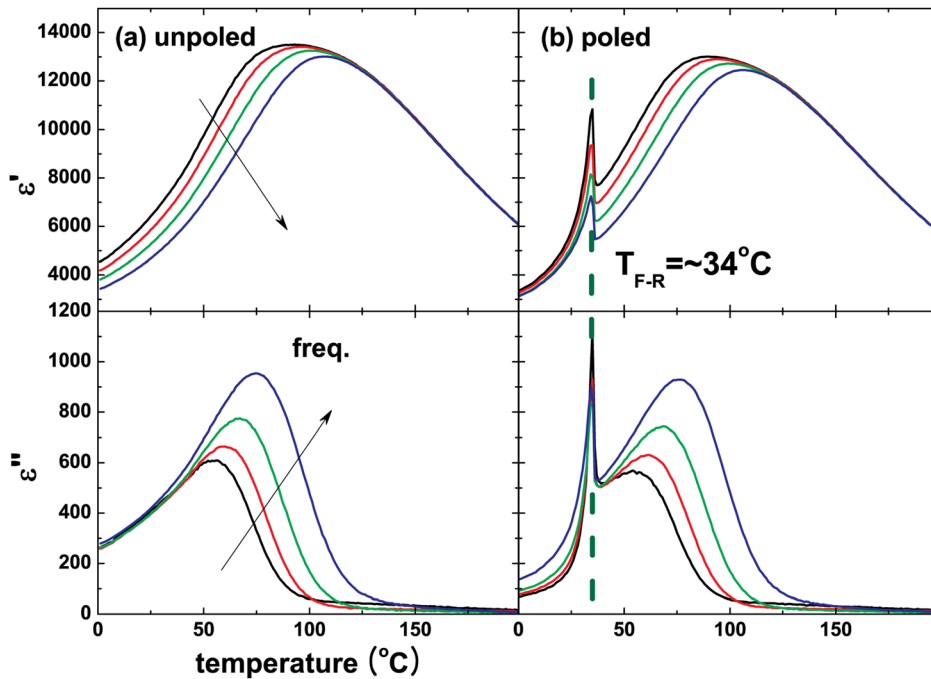
FIG. 2. (Color online) Temperature-dependent ϵ' and ϵ'' of (a) unpoled and (b) poled commercial PLZT 8/65/35 relaxor ceramics at four different frequencies, *i.e.,* 100 Hz, 1 kHz, 10 kHz, and 100 kHz. It is noted that the disruption of an electrically induced ferroelectric order involves a frequency-independent discontinuous change both in ϵ' and in ϵ''.

appearance of T'_m is merely a consequence of a thermal evolution of relaxation time distribution or correlation length distribution of polar nanoregions (PNRs), which has nothing to do with any measurable structural transition.[42–45]

The application of an electric field that is strong enough to overcome the random fields exerted by PNRs induces a macroscopically discernable ferroelectric order.[46] This induced ferroelectric order can be either stable or unstable on the removal of the applied electric field depending on the position of a ferroelectric-to-relaxor transition temperature (T_{F-R}), where the field-induced ferroelectric order can no longer be stable without an external bias field.[47] This electric-field-induced ferroelectric order and its return to relaxor state are clearly grasped in the ϵ' and ϵ'' curves of a poled PLZT 8/65/35 sample as shown in Fig. 2(b). T_{F-R} is located at $\sim 34\,°C$, where both ϵ' and ϵ'' show a sharp peak at the same temperature regardless of the measurement frequency.

Figure 3(a) is the ϵ' and ϵ'' of unpoled BNT-6BT recorded during heating. It is seen that the ϵ' consists roughly of two parts, one with a frequency dispersion appearing at a lower temperature (the first anomaly, which will be denoted by a subscript "FA") and the other without it appearing at a higher temperature (the second anomaly, which will be denoted by a subscript "SA"). Although the ϵ' provides no further information of their origin, it can be said that at least the lower-temperature frequency dispersive part is due to the relaxor contribution, which is apparent also from ϵ''. With increasing temperature, another dielectric anomaly with a frequency dispersion in ϵ'' develops after ϵ''_{FA} vanishes. A couple of features distinctive from ϵ''_{FA} are discerned: (1) The magnitude of the peak value in ϵ''_{SA} decreases with frequency, which is opposite to that of ϵ''_{FA}. (2) Temperature dependence of the frequency dispersion in the peak positions is much larger in ϵ''_{SA} ($\Delta T \simeq 120°C$) than in ϵ''_{FA} ($\Delta T \simeq 40°C$). Here, it is noticed that ϵ'_{SA} indeed has a frequency dispersion, which is evident

from the anomalies indicated by arrows in the shape profile, and the $\Delta T \simeq 120°C$ is consistent with that in ϵ''_{SA}. Thus, it can be said that the ϵ'_{SA} is another process that is also related to PNRs. This means that the contribution of these two processes to the ϵ' can be deconvoluted qualitatively with the following two assumptions. (1) The mean relaxation time for the PNRs of a different symmetry contributing to the ϵ'_{FA} can be quantified collectively by an averaged single value, which enables the static dielectric permittivity (ϵ_S) to be uniquely determined. (2) The appearance of ϵ'_{FA} and ϵ''_{FA} can be attributed to independent processes.

As demonstrated by a series of earlier works,[44,48–50] logarithmic relaxation time cannot be explained by a single Debye-type relaxation but by a collective contribution of multiple Debye-type relaxations that can be described by a statistical distribution of relaxation time at a given temperature. It is known that this behavior can be simulated properly either by Gaussian[48,49] or by Lorentzian[50] distribution function. Since the integrated form of Gaussian and Lorentzian functions can be simulated by sigmoidal functions, the following simple sigmoidal function was used instead to reach convergence in a reasonable time scale:

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = \frac{1}{1 + e^{\log \omega \tau / \sigma}}, \qquad (1)$$

where τ, σ, and ϵ_∞ are the average relaxation time at a given temperature, its distribution, and the dielectric permittivity at a very high frequency, respectively. ω refers to the measurement frequency. ϵ' data for the frequencies from 100 Hz to 100 kHz at a logarithmic scale below 130 °C, where a possible interference from the second anomaly, *i.e.*, ϵ'_{SA}, is negligible, are selected for fitting. All the data were fit simultaneously with the ϵ_∞ being set to be a shared constant. The application of the scheme leads to a partial construction
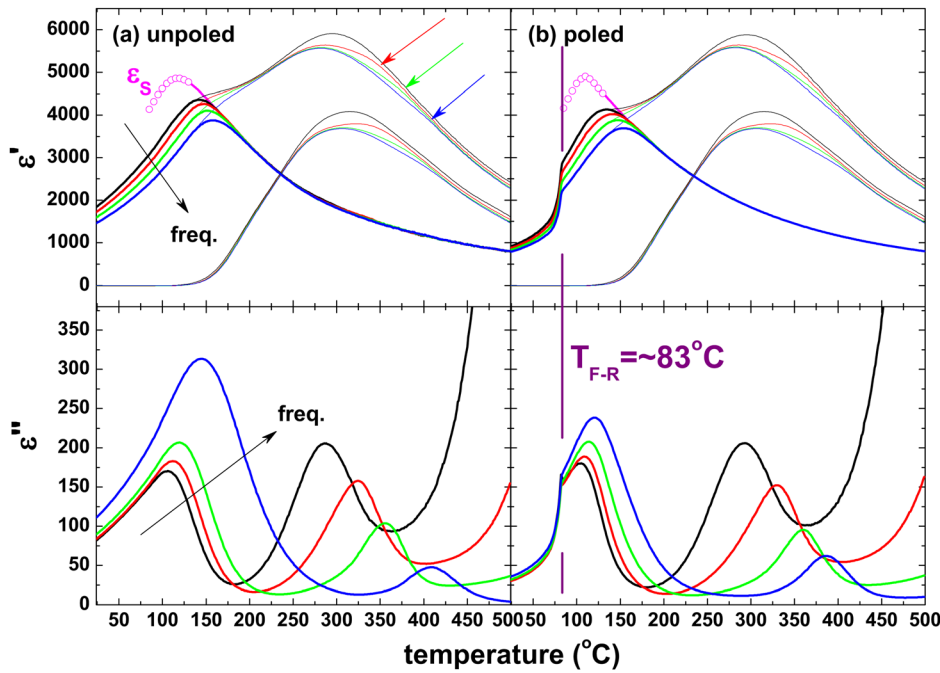
FIG. 3. (Color online) Temperature-dependent ϵ' and ϵ'' of (a) unpoled and (b) poled BNT-6BT ceramics. The relaxor contribution (ϵ'_{FA}) to ϵ' was deconvoluted using the static dielectric permittivity (ϵ_S) calculated from phenomenological models. The dielectric permittivity for the second anomaly (ϵ'_{SA}) was given merely by subtracting ϵ'_{FA} from ϵ'. Frequency dependence of ϵ'_{SA} is obvious both in ϵ'_{FA} and ϵ''_{FA}.

of ϵ_S of the system as shown in Fig. 3 with an open circular symbol. A further extension of ϵ_S to higher temperature regime is made based on the following phenomenological model for the ϵ_S data where the reciprocal ϵ_S has an obviously linear dependence on the temperature squared.[51,52]

$$\frac{1}{\epsilon' - \epsilon_\infty} \simeq \frac{1}{\epsilon'} = \frac{1}{\epsilon'_m} + \frac{(T - T_m)^2}{2\epsilon'_m \delta^2}, \qquad (2)$$

where δ is a diffuseness parameter. Given the estimated ϵ_S, the deconvolution of ϵ'_{FA} from the entire ϵ' is straightforward, since ϵ'_{FA} merges into ϵ_S when the differential ϵ'' becomes zero at each frequency. The missing part in ϵ'_{FA} for each frequency was estimated by using an asymmetric double sigmoidal function with an assumption that the degree of shift in T'_m as a function of frequency is the same with that in T''_m from ϵ''_{SA}.

ϵ'_{SA} is estimated merely by subtracting ϵ'_{FA} from ϵ', since neither the origin nor physical model for ϵ'_{SA} is known at the current stage. This estimated ϵ'_{SA} exhibits two intriguing features. Contrary to the aforementioned assumption that ϵ'_{SA} could also be due to a thermal evolution of PNRs based on the frequency dispersion in ϵ''_{SA}, virtually no frequency dispersion is observed for a range of temperatures, *e.g.,* from $\sim 130\,°C$ to $\sim 240\,°C$. In addition, the shape profile strongly indicates that ϵ'_{SA} could be a convolution of more than two independent processes.

ϵ' and ϵ'' for a poled BNT-6BT ceramic are shown in Fig. 3(b). A discontinuous change in ϵ' is observed at $\sim 83\,°C$, which corresponds to the temperature where a significant drop in P_{rem} is observed (Fig. 1(b)). ϵ'_{FA} for poled specimen is constructed by the application of exactly the same procedure on the ϵ' data above T_{F-R} but below $130\,°C$. Interestingly, little influence of electrical poling on ϵ'_{SA} and ϵ''_{SA} is denoted. From the phenomenological similarity with ϵ'

and ϵ'' of PLZT 8/65/35 (Fig. 2), the discontinuous change in ϵ' is T_{F-R} where the electric-field-induced ferroelectric order transforms back to relaxor.

To better understand the dielectric anomalies in ϵ'' in relation with the structural aspect, TEM analysis was performed on unpoled BNT-6BT specimen at room temperature. Bright field (BF) image revealed nothing but a "grainy" contrast with no evident trace of ferroelectric domains as shown in Fig. 4(a). It is noted that the square shaped regions visible in the BF image are defects.[53] Systematic tilting experiments revealed that these defects were most likely pores of 10 to 25 nm in size. Thereby, a slight translation between top and bottom layer can cause the stripe-like moiré pattern. The selected area electron diffraction (SAED) pattern taken along [130]$_{pc}$ (the subscript "pc" denotes pseudo-cubic index system) zone axis on the same region reveal that each grain has a trace of rhombohedral $R3c$ and tetragonal $P4bm$ symmetry, indicated by the presence of $1/2\{ooo\}$ and $1/2\{ooe\}$ ("o" and "e" refer to odd and even Miller indices) superlattice reflections, respectively.[54] The streaking in $1/2\{ooe\}$ superlattice reflection implies that the entity conceiving a tetragonal $P4bm$ symmetry is a few-nanometer-thick platelet. In spite of the evident presence of both rhombohedral and tetragonal symmetries, no obvious non-cubic distortion in the Bragg reflections is detected. A possibility that this observation may be due to heating of the specimen by electron-beam[55] was discarded, since the contrast remained very stable throughout the experiment. In fact, the observation is fairly consistent with the previous X-ray diffraction studies.[10]

IV. DISCUSSION

The long-standing controversies over the structurally uncertain polymorphism including the AFE issue in
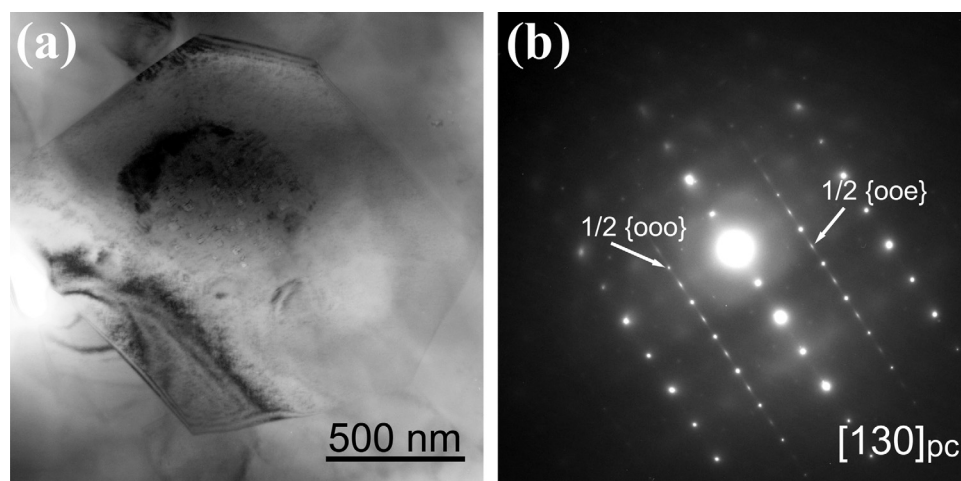
FIG. 4. (a) TEM bright field (BF) image of BNT-6BT taken at ambient temperature, showing a grainy contrast, which is representative for the whole sample (b) the corresponding selected area electron diffraction pattern along $[130]_{pc}$ pseudo-cubic zone axis exhibits both types of superlattice reflections (marked with arrows), respectively $1/2\{ooo\}$ and $1/2\{ooe\}$.

BNT-based materials are well represented by the fact that at least five different versions of phase diagrams have been proposed for the BNT-100xBT system alone.[9,39,40,56,57] In addition, the phase identity and stability even at room temperature, which have been considered less controversial, were shown to be much more complicated than the previously thought.[58] Therefore, it seems that the resolution of the existing controversies should require questioning and reconsidering no matter what has been accepted in the community. In this regard, we reviewed and re-interpreted the key experimental facts having shaped the current views such as the unusual shape of the temperature-dependent dielectric permittivity spectra, the development of constricted P(E) hysteresis loops above T_d, and the complexity in the structures.

A. Dielectric permittivity

As noted, the relaxor nature of BNT-based materials is widely accepted in the community. However, when the dielectric permittivity spectrum of pure BNT was first reported by Smolenskii *et al.*,[11] the apparent presence of the relaxor features was completely overlooked. More precisely speaking, they were not able to think of relaxor as a possible identity of the pure BNT, because it was right then that the dispersion in dielectric permittivity of complex perovskite-structured materials such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) under different ac frequencies was first discovered and even the archetypal relaxor PMN was strongly believed to be a normal ferroelectric with the phase transition to a paraelectric being diffused.[59,60] The normal ferroelectricity of PMN was claimed based on their observation of well-defined P(E) hysteresis loops induced at temperatures sufficiently lower than T'_m. Note that until early 1990 s when two discrete relaxor states, *i.e.,* ergodic and non-ergodic, were identified,[43,61–66] PMN had been consistently considered to be a normal ferroelectric with a diffuse phase transition.

Similarly, pure BNT was designated as a normal ferroelectric, because of its well-defined P(E) hysteresis loop at room temperature. The maximum dielectric constant temperature and the shoulder appearing at $\sim 200\,^\circ C$ were assigned

to the Curie point and an indicator for a phase transition, respectively. This assumption was justified by discontinuously changing thermal expansion coefficient near T_s, even though the validity of the estimated thermal expansion coefficient from the given dilatometry data is highly questionable. All the claims were later accepted by Sakata and Masuda[3] for their investigation without being questioned, even though the dielectric permittivity data of pure BNT as well as of Sr-modified compositions at different frequencies clearly demonstrate the relaxor feature at all temperatures below T_s. It is highly possible that if the relaxor nature of pure BNT was grasped without the "crudely" estimated thermal expansion coefficient data, the dielectric permittivity profile could be interpreted in relation to the aging phenomena commonly known in relaxors. In fact, it was later shown in the two representative relaxors, PLZT (Ref. 67) and PMN-0.1 mol%PbTiO$_3$,[68] that aging could make the typical dielectric permittivity profile of relaxor materials almost identical with that observed in BNT-based materials, *i.e.,* two successive dielectric anomalies, frequency-dispersive one at a lower temperature and frequency-independent at a higher temperature.

B. Constriction in P(E) hysteresis loop

The appearance of constricted P(E) hysteresis loops around T_d (Refs. 2, 3) is the most controversial among the listed. Although it has been considered a concrete evidence for the presence of FE-to-AFE transition in BNT-related materials, it is noted that the constricted P(E) loops in perovskite-structured materials are induced in many different occasions. It is, of course, observed when an AFE phase transforms into an FE under electric field as demonstrated in the archetypal AFE ceramics, PbZrO$_3$ (Ref. 69) and AgNbO$_3$.[70] It also appears when a sufficient amount of electric field is applied to a paraelectric (PE) phase slightly above FE- to-PE transition temperature as clearly shown in BaTiO$_3$,[71] as well as when non-ergodic relaxor near non-ergodic to ergodic transition temperature or ergodic relaxor evolves into an FE phase with electric field.[43,72] Or, a constriction develops even when an FE is severely aged such as in acceptor-doped "hard" PZT

ceramics.[41,73] It means that the constriction in P(E) hysteresis loops alone cannot be taken as a phase-identifier, because it is commonly expected in the materials showing an electric-field-induced phase transition where the polarization is the order parameter or where strongly aligned dipoles form an internal bias field in the absence of electric field.

C. Polymorphism

The peculiarity of polymorphism in BNT was first pointed out by Pronin *et al.*[12] They reported that only two distinctive phase transitions were detected by birefringence and calorimetry study on single crystal BNT, one at $\sim 295\,^\circ$C and the other at $\sim 540\,^\circ$C, neither of which matched with any of the dielectric anomalies nor indicated the presence of AFE. This was strongly supported by neutron diffraction studies[13,16] that there were indeed only two visible phase transitions existing but these transitions were highly diffused, *i.e.*, one from $\sim 255\,^\circ$C to $\sim 420\,^\circ$C involving a rhombohedral $R3c$ to a tetragonal $P4bm$ transition and the other from $\sim 520\,^\circ$C to $\sim 540\,^\circ$C involving the tetragonal $P4bm$ to a cubic $Pm\bar{3}m$ transition. Here, it is noted that again no trace of AFE phase was detected and the non-cubic distortion was so insignificant that the designation of symmetry was made from the superlattice reflections.

Assuming that the superlattice reflections are invisible to neutron/X-ray diffraction techniques, one may say that no phase transition can be depicted over a wide range of temperatures, *e.g.*, from room temperature at least up to $\sim 550\,^\circ$C. This is indeed the case as demonstrated in BNT-based solid-solutions with a relatively high amount of other compounds such as BNT-BT-KNN (Ref. 74) and BNT-$(Bi_{1/2}K_{1/2})TiO_3$ (BKT)-$Bi(Zn_{1/2}Ti_{1/2})O_3$ (BZT) (Ref. 75) systems. Neutron diffraction studies revealed neither superlattice reflections nor obvious non-cubic distortions in both systems throughout the temperature regime of interest, though the unique shape profile of the dielectric permittivity spectra of BNT was still maintained. Note that the absence of obvious phase transition is one of the representative features of relaxor materials.[76] In fact, the relaxor nature of BNT-based materials from the microscopic point of view was recently demonstrated extensively in a comparative study of PMN and BNT (Ref. 77) as well as in piezoresponse force microscopy and diffuse-scattering study of BNT- BT single crystals.[57,78] This is consistent with the recent hot-stage

TEM investigations showing that the coexistence of $R3c$ and $P4bm$ symmetries are detected at all temperatures from room temperature to as high as $\sim 700\,^\circ$C.[17,79] As well, Schmitt *et al.*[54] reported the coexistence of $R3c$ and $P4bm$ phase was evident in BNT-related ternary systems, again leading to a conclusion that both $R3c$ and $P4bm$ phases are present at a nano-scale level. Therefore, a reasonable assumption for the polymorphism in BNT-based materials is that $R3c$ and $P4bm$ symmetries coexist as nano-scale entities throughout the temperature regime of a common interest on a long-range $Pm\bar{3}m$ symmetry as a matrix.

D. BNT-6BT as a relaxor

Given the premise that BNT-6BT is nothing but a relaxor, the peculiarity in the shape profile of its dielectric permittivity can be interpreted either by an aging effect or by the currently proposed model. Between the two, it is highly likely that the aging effect is ruled out from the following reasons. The temperature for the T_s, which is highly sensitive to the aging temperature,[67,68] does not vary from study to study, though the processing condition for each study cannot be the same. Also, even after a thermal annealing at sufficiently high temperature (see, for example, Fig. 3(a) that is recorded directly after the first measurement on poled BNT-6BT.), the shape remains the same. Hence, the currently observed dielectric permittivity spectra can be assumed to be due to the coexisting $R3c$ and $P4bm$ PNRs. Here, it can be said that the free energy between the coexisting rhombohedral $R3c$ and tetragonal $P4bm$ PNRs at room temperature is so small that interconversion between the symmetries is relatively easy. As noted, the assumption is well supported by a recent neutron diffraction study on BNT-6BT showing that the intensity ratio of $1/2\{ooo\}$ to $1/2\{ooe\}$ increases with electric field and by TEM and diffuse scattering studies showing that a wide range of BNT-100xBT ($x = 0$, 0.03, 0.04, 0.08) compositions exhibit the coexistence of both $R3c$ and $P4bm$ over a large range of temperatures.[17,78,79] This implies that the $R3c$ PNRs would easily transform into $P4bm$ PNRs with increased temperatures. In fact, this assumption is well supported by the fact that the structure of BNT-6BT probed by X-ray diffraction technique is nothing but cubic, and significant rhombohedral and tetragonal distortions are only visible with the application of electric field above a
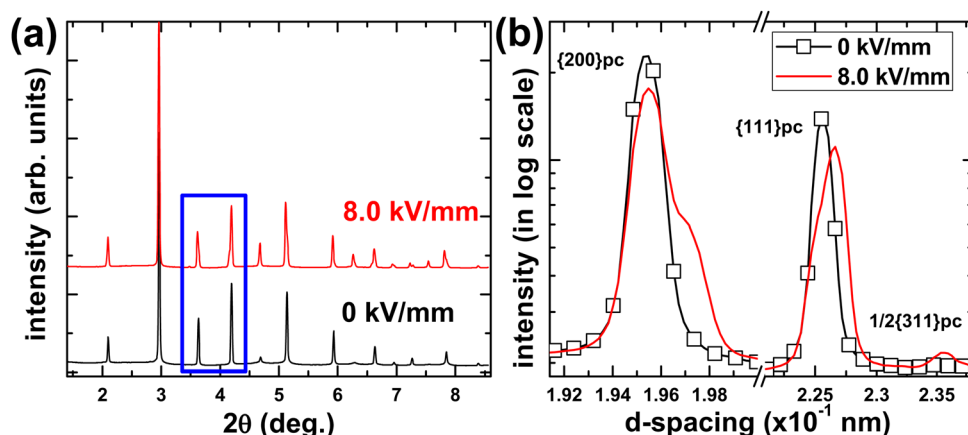

FIG. 5. (Color online) (a) *In situ* X-ray diffraction pattern of BNT-6BT at its virgin state in comparison with that at 8 kV/mm. (b) An expanded view of $\{200\}_{pc}$ and $\{111\}_{pc}$ reflections. To pronounce the $1/2\{311\}_{pc}$ superlattice reflection, the intensity of which is considerably weak compared to that of Bragg reflections, the intensity of reflections are plotted on a logarithmic scale. The diffraction data were obtained with a monochromatic beam of 87.19 keV at ID15 in the European Synchrotron Radiation Facility (ESRF). Details of analyses and a complete set of data are available in Ref. 10.
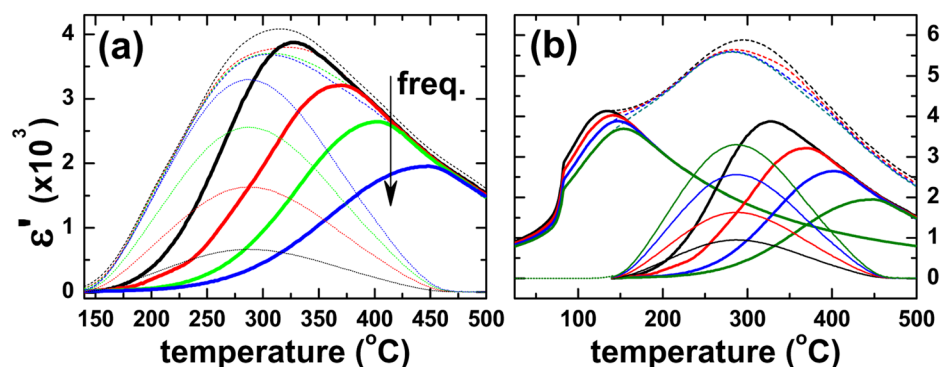
FIG. 6. (Color online) (a) A suggested deconvolution of ϵ'_{SA} based on an assumption that ϵ'_{SA} results from two independent processes, *i.e.,* a frequency-independent one coming from $R3c$-to-$P4bm$ transition and a frequency-dispersive one induced by $P4bm$ PNRs. (b) A summary of the deconvolution on ϵ' of poled BNT-6BT.

certain threshold field level.[10] In this regard, it is said that the previously proposed field-induced phase transition could be merely a consequence of a relaxor being transformed into a ferroelectric phase. In other words, the previously referred "pseudocubic"[7] or rhombohedral[10] phase should actually be a "cubic" or very slightly distorted "non-polar" phase "decorated" with two PNRs of a different symmetry. This argument is best illustrated in Fig. 5.[10] Though the $1/2\{311\}_{pc}$ superlattice reflection seems to develop due to electric field application, it is already present, as shown in Fig. 4(b), even before an electrical poling treatment. It follows that the coherence length of the entities with an $R3c$ symmetry in unpoled state is too small to be visible in X-ray diffraction, *i.e.,* PNRs.

Given this assumption, three consecutive events are expected to happen during heating. The initially existing mixture of $R3c$ and $P4bm$ PNRs undergoes a thermal evolution resulting in a broad dielectric maximum, followed by a transition of $R3c$ to $P4bm$ PNRs, and then finally all the $P4bm$ symmetries undergo a thermal evolution giving rise to another frequency-dispersive dielectric maximum. As already shown in Fig. 3, the first event is easy to be grasped from the deconvoluted ϵ'_{FA}. However, the other two events are not readily seen from the subtracted ϵ'_{SA}. Since a part of ϵ'_{SA} should show frequency dispersive broad dielectric maximum, which is apparent from the clear frequency dispersion in ϵ''_{SA}, another deconvolution on ϵ'_{SA} is warranted. Assumption was made that ϵ'_{SA} consists of a signal related to $R3c$-to-$P4bm$ transition and that related to thermal evolution of $P4bm$ PNRs and the two processes are independent. Since the $R3c$-to$P4bm$ transition should be based on a thermodynamic origin, the corresponding dielectric signal is expected to peak unanimously at a certain temperature regardless of measurement frequencies. Based on the assumed constraints with the apparent presence of a shoulder at high temperature side, a fit was performed and presented in Fig. 6(a). The underlying mechanisms, constituting the entire dielectric permittivity spectra discussed so far, are summarized in Fig. 6(b). Since the current interpretation of ϵ'_{SA} of BNT-6BT is constructed with the assumptions that are not rigorously correct, the presented deconvolution cannot be accepted with full precision. Nevertheless, it is still reasonable to say that all the peculiarities and controversies in the polymorphism in BNT-BT system can be rationalized by categorizing the system as a relaxor with coexisting PNRs of different symmetries.

V. CONCLUSIONS

The origin of several unclear issues in BNT-6BT, such as the constriction in the polarization hysteresis loops, the frequency dispersion and the unusual presence of two local maxima in the dielectric permittivity as well as the so-called depolarization temperature, was investigated. In comparison with the equivalent data sets obtained from one of the classical perovskite relaxors, PLZT, it was shown that the depolarization temperature is the temperature where an electric-field-induced long-range ferroelectric order reverts back to the initial relaxor state upon heating. Accordingly, the constriction occurring in the hysteresis loops, previously considered as a concrete proof of AFE, is merely a consequence of an electric-field-induced relaxor-to-ferroelectric transition. Based on the X-ray and electron diffraction techniques, it was proposed that BNT-6BT at room temperature has a cubic symmetry with rhombohedral $R3c$ and tetragonal $P4bm$ polar nanoregions, and the second local maximum in the temperature-dependent dielectric permittivity results from a mixed contribution from $R3c$-to-$P4bm$ transition and a thermal evolution of $P4bm$ polar nanoregions.

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