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Engineering the nature of polarization dynamics in lead-free relaxors based on (Bi_{1/2}Na_{1/2})TiO₃ **p**

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ABSTRACT

(Bi_{1/2}Na_{1/2})TiO₃ (BNT) is a lead-free ferroelectric material, which has shown promising electromechanical properties and energy storage capacities. These attractive functionalities and property performances are attributed to the relaxor behavior of BNT. However, the nature of the dielectric relaxation is not well understood in these materials, and the physical meaning of some important parameters associated with the permittivity is still under debate. In this Letter, we focus on the dielectric "shoulder," T_s , that is readily seen in the ε' -T curve of every BNT-based relaxor. It is found that the T_s is controlled by not only the typical compositional engineering but also by the thermal, electrical, or mechanical history. From a moderate temperature (≤ 250 °C), a sample can be rapidly cooled to room temperature or slowly cooled under an electrical bias or a mechanical bias in the form of a compressive stress. All three treatments lead to a nearly identical effect, which is to alter the T_s with respect to rest of the ε' -T curve that remains unperturbed. Therefore, the internal stress is identified to be a general perturbance to the polarization dynamics. Finally, the "breathing" model is revisited to interpret the physical meaning of T_s for these BNT materials under these metastable conditions.

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The most extensively studied relaxor ferroelectric material is the perovskite complex system often based on Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN). For 30 years or more, various experimental tools have been employed, ranging from the dielectric characterizations to very recently the highend microscopy observations,¹⁻⁴ for numerous studies that progressively converged on the fundamental nature of the dielectric relaxation in PMN. Compared to PMN, the understanding of the relaxor behaviors in lead-free (Bi_{1/2}Na_{1/2})TiO₃ (BNT) is still immature in spite of the current surge of publications on the high energy storage density achieved in BNT with sophisticated compositional modifications.⁵ The "design strategy" claimed in these reports, typically, considers minimizing the size of polar nanoregions (PNRs) and polar spatial correlations to make the polarization-electric field (P-E) loop slimmer. Unfortunately, the critical issues are seldom discussed, e.g., the impact of dopants on the microstructure of PNRs (linearity) and the dynamics of PNRs in response to the high field (nonlinearity). Addressing these questions demands systematic experimental and theoretical studies that should be more extensive and more awareness of thermal, electrical, and mechanical histories that can perturb these polarization dynamics. In this Letter, we will try to discuss the nature of relaxation (quasi-linear regime) through accessing the permittivity in BNT-based

relaxors with model compositions, 93% (Bi_{1/2}Na_{1/2}) TiO₃-7%BaTiO₃ (BNT-7%BT) and identify critical experimental parameters that can impact and rewrite the relaxation behavior.

BNT exhibits the characteristic behaviors for relaxor ferroelectrics, including the logarithm dependence of permittivity on the frequency, the aging/memory effects, etc.7.8 However, some features distinguish themselves in BNT from PMN relaxors (Table I). The most obvious difference is that the frequency dispersion in BNT vanishes at a temperature below $T_{\rm m}$; therefore, a shoulder at $T_{\rm s}$ is seen. A shoulder like feature could also be observed in PMN in the vicinity of the aging temperature but will disappear after re-annealing.⁹ Another critical difference is that, at the depolarization temperature T_{d} , poled BNT undergoes the ferroelectric to relaxor phase transition accompanied by the transformation of the crystal structure from R3c or P4mm (depending on the composition in relative to the morphotropic phase boundary) to P4bm.^{10,11} Therefore, T_d is not necessarily equal to a freezing temperature $(T_{\rm f})$ that is supposedly correlated with the $T_{\rm s}$, assuming T_s in BNT is equivalent to the T_{max} in PMN, via the Vogel-Fulcher relation.¹² Recently, multiple methods were demonstrated to increase the T_d in BNT to improve the thermal stability of the piezoelectric performance, which have helped the understanding of the

TABLE I. Contrasting the relaxor characteristics in BNT and PMN.

| | T _s T _m BNT | PMN reproduced from ref. 9 |
|----------------|---|--|
| $T_{\rm m}$ | independent of frequency | $\omega = \omega_0 \exp[-E/(T_{max} - T_f)]$ |
| T _s | history dependent (rapid/biased/compressed cooling) | in the vicinity of aging temperature |
| T_f | structural phase transition | $\omega = \omega_0 \exp[-E/(T_{max} - T_f)]$ |

phase transition behavior.^{13,14} Considering that T_d is a parameter that can be revealed only under high field, e.g., decay of remanant polarization with temperature, if we are discussing the low field response/relaxation, we should focus on T_s and seek for any method to control it.

The most common way to manipulate the relaxor is doping. As one simple example, if we add only 1%–3% of Ta⁵⁺ as a donor dopant to BNT-7%BT (experimental details can be found elsewhere¹⁵) then dielectric property changes significantly [Fig. 1(a)], from which two effects are noteworthy. First, prior to T_s , the dielectric curves in different compositions are almost overlapping. Second, Ta⁵⁺ addition decreases the T_s , as well as the permittivity after T_s . Apart from the dielectric measurement, the P–E loop measured under low field should be able to reveal T_s too.¹⁶ Here, we use undoped BNT-7%BT as an example. Figure 1(b) shows the loops under 10 kV/cm at series of temperatures. The maximum polarization increases with temperature until ~140 °C, which coincides with the T_s in the dielectric curve. Same assessments are carried out in the doped cases under consistent conditions. It is seen that the maximum point indeed shifts to lower temperature [Fig. 1(c)].

Let us consider alternatives to the compositional modification to manipulate $T_{\rm s}$. In electroceramic materials, quenching is often used to avoid the super-oxidation process and changes the charge compensation mechanisms that would occur under typical furnace cooling.¹⁷ In BNT-x%BT relaxors, quenching from ~1000 °C was found effective in increasing the $T_{\rm d}$ by as much as 40 °C.¹⁴ Here, we also do air quenching but from \leq 250 °C; therefore, we call this treatment rapid cooling. Figure 2(a) compares the dielectric curves measured from BNT-7%BT-3%Ta in the untreated state and rapid cooled from different temperatures. As opposed to doping Ta⁵⁺ (Fig. 1), rapid cooling defers $T_{\rm s}$. When samples are rapidly cooled from 250 °C, the permittivity at $T_{\rm s}$ even exceeds that at the $T_{\rm m}$ ${\sim}278\,^{\circ}{\rm C}$, which is made possible by the fact that rapid cooling does not influence the temperature range below the original T_s or above T_m . The P-E loops are measured under 10 kV/cm in the sample rapid cooled from 250 $^\circ$ C. The maximum polarization as a function of temperature is shown in Fig. 2(b), from which the maximum point is found to correlate with the shift of $T_{\rm s}$. At 105 °C, the permittivity (100 Hz) increases by ~1.4 times by the rapid cooling [Fig. 2(a)]. The maximum polarization is also increased by ~ 1.4 times [Fig. 2(c)], suggesting that 10 kV/cm still belongs to the quasi-linear regime for BNT-7%BT-3%Ta. However, if the loop is measured under 70 kV/cm, the treatment seems to make little difference [Fig. 2(d)]. In contrast to the quasi-linear loop under low field, a high field loop shows notable hysteresis and some double loop feature. It indicates that the rapid cooling affects the linear response only rather than the nonlinear response. Therefore, T_d in undoped BNT-7%BT (poled at room temperature after rapid cooled) maintains despite that the T_s has been increased by rapid cooling [Fig. 2(e)], confirming T_d and T_s unnecessarily correlated.

Although the nature of T_s in BNT-based relaxors is not completely understood, it has been known that the ergodicity



FIG. 1. (a) Temperature dependent dielectric constant in undoped and Ta⁵⁺ doped BNT-7%BT, T_s marked by the arrows. (b) Low field P–E loops measured in undoped BNT-7%BT at various temperatures. (c) Maximum polarization under low field as a function of temperature in different compositions.



FIG. 2. Impacts of rapid cooling on dielectric relaxation. (a) BNT-7%BT-3%Ta rapid cooled from different temperatures. (b) Maximum polarization under low field as a function of temperature measured in BNT-7%BT-3%Ta rapid cooled from 250 °C. (c) Low field P–E loop measured at 105 °C in BNT-7%BT-3%Ta rapid cooled from 250 °C. (d) High field P–E loop measured at 105 °C in BNT-7%BT-3%Ta rapid cooled from 250 °C. (e) T_d in undoped BNT-7%BT rapid cooled from 250 °C.

dominates at T_s . So, electrical poling presumably is ineffective because of the reversibility of the nonlinear response [Fig. 2(e)].¹⁸ However, if we apply an electric bias at an elevated temperature and slowly cool it with furnace under that field (biased cooled), we observe the same phenomena as the rapid cooling. The increase in T_s is more significant when biased cooled from higher temperature or under larger field [Figs. 3(a) and 3(b)]. Note that the delay of T_s is the result of biased cooling rather than the poling. In a Mn-doped PMN single crystal, Luo *et al.* proposed that space charges are driven to migrate until trapping at the boundary of the polar nanoregions (PNRs) during elevated temperature poling. After the state being preserved by field cooling, the pinned PNRs show suppressed low field and high field kinetics.¹⁹ A more dramatic phenomenon is observed Ce-doped Sr_{0.61}Ba_{0.39} Nb₂O₆ (SBN), a tungsten bronze structured relaxor. The biased cooled samples are first depoled by heated up to above T_{max} . Upon subsequent zero field cooling through T_{max} , it can spontaneously develop a



FIG. 3. (a) BNT-7%BT = 3%Ta biased cooled under 20 kV/cm from different temperatures. (b) BNT-7%BT = 2%Ta biased cooled from 250 °C under different fields. (c) BNT-7%BT=1%Ta compressed cooled from 250 °C under 350 MPa.

polarization along the same direction. Such "repoling" behavior was also attributed to the redistribution of space changes (aging). As the space charge electromigration needs time, these two phenomena are conceivably more pronounced if the poling lasts longer.²⁰ However, the T_s in our case is found to be independent of the poling time. In Fig. 3, the cooling starts immediately after the electric bias is turned on. If the bias and the temperature are both hold, dc degradation will be taking place, during which the space charge migration leads to the conductivity rise by more than five orders of magnitude.¹⁵ Nevertheless, the T_s in the biased cooled degraded sample is identical to that measured from the undegraded biased cooled sample. Thus, the delay of T_s is the result of biased cooling, rather than the elevated temperature poling, nor is it directly due to the space charge redistribution.

Given that rapid cooling and biased cooling have nearly identical effects on the T_s , we can assume that the mechanisms are also similar. We have ruled out the space charge as the possible cause for biased cooling, then we say, it is not the case for rapid cooling either. Zang *et al.* investigated the "quenching" from \leq 500 °C in BNT-6%BT and noticed an enhancement of permittivity within an intermediate temperature window. The space charge was thought to be the reason as the quenching can circumvent the aging process accompanying the furnace cooling.²¹ In our case, we might explain the rapid cooling effect in an alternative way when examining it in combination with other equivalent treatments.

In general, the phase transition in ferroelectrics can be triggered by temperature, electric bias, or stress. Webber's group has some intriguing studies regarding the stress modulated phase transition in BNT-x%BT relaxors.^{22,23} Their study reveals that poling the BNT-6%BT by compressive stress at 150 °C (followed by the field cooling) leads to a noticeable change in permittivity around T_s aside from the primary impact around T_d .²⁴ Inspired by that interesting study, we implemented the "compressed cooling" in our BNT-7%BT-1%Ta but from an even higher temperature. The experimental procedures are as same as the biased cooling but only replacing the electric bias with compressive stress. Figure 3(c) shows that the compressed cooling features have nearly identical effect with rapid cooling and biased cooling. This draws a conclusion that in common is an internal stress and distributed stress gradients that facilitate the correlation of polar regions in all three treatments, namely, the compressed cooling applies the stress directly while the other two treatments induce this thermally and electrostatically.^{25,26} Recall that in Fig. 1 we doped Ta⁵⁺ to the B-site of BNT-7%BT so that T_d and T_s are both lowered. Previously it was thought that the aliovalent dopant enhances the randomness of the local field hence weakens the ferroelectric correlated dipole ordering.⁶ However, if we consider the doping effect in combination with the three other treatments, we might take an alternative interpretation into account, that is, the doping in the octahedral site creates a local strain in the unit cell (tailors the tolerance factor) such that the T_s is changed. This could explain why the Zr⁴⁺ and Sn⁴⁺ with the same charge but different sizes from Ti⁴⁺ can also achieve similar effects.²⁷

Previously, T_s was interpreted as a threshold between different dielectric relaxation processes.^{7,28} The frequency dispersion below $T_{\rm s}$ originates from the thermal evolution of two coexisting PNRs with, respectively, R3c and P4bm phases, while the frequency independent T_m represents the structural transition from R3c to P4bm. After revealing how T_s can be engineered, we will try to draw a picture of the polarization dynamics in BNT-based relaxors. One of the early models to describe relaxors is the "superparaelectric" model.²⁹ Assuming the introduction of the stress term into the free energy expression alters the energy landscape, it could lower the barrier between local minima (vibration of PNRs) while not changing the barrier between global minima (rotation of PNRs). However, the "superparaelectric" model may encounter difficulty to explain why only the permittivity around $T_{\rm s}$ is enhanced while the permittivity below that is not. There are also other weaknesses with the "superparaelectric" model, but it provided a very useful starting point to understand relaxor ferroelectric materials. An alternative model that was proposed 20 years ago by Glazounov and Tagantsev was the "breathing" model.³⁰ We now try to apply it to BNT-based relaxors. In the "breathing" model, one important dimension is the length of the boundary of PNRs, L. However, the boundaries are pinned by the random local field, which is determined in BNT by the Bi³⁺ and Na⁺ sharing the A-site. So, this provides another important dimension aspect that being the length between the pinning





Appl. Phys. Lett. **119**, 112904 (2021); doi: 10.1063/5.0064160 Published under an exclusive license by AIP Publishing sites, l_p [Fig. 4(a)]. In response to an electric field, the unpinned boundary segment is bent. Consequently, the volume of the PNR, therefore, the dipole moment, is changed. Summing up the contributions from all PNRs with the number density N gives us the permittivity

$$\varepsilon \propto N \cdot l_p^2.$$
 (1)

Note that l_p is dependent upon temperature and frequency. At higher temperatures, the depinning becomes easier, hence, l_p increases. Under lower frequencies, larger segments featuring longer relaxation time for depinning have more time to respond, hence, l_p increases. However, the upper limit for the increase in l_p is *L*. Therefore, the frequency dispersion vanishes once that limit is reached via changing either frequency or temperature, then

$$\varepsilon \propto N \cdot L^2.$$
 (2)

The critical temperature for $l_p = L$ is the T_{max} in PMN and the T_s in BNT, which should vary with frequency as well. In PMN, the PNRs reduce the size and number density after T_{max} , resulting in the drop of permittivity, untill they cease to exist at the Burns temperature. In BNT, on the contrary, the permittivity is increasing from T_s to T_m , suggesting that the PNRs are growing in size and number density within this temperature window. The real "freezing" takes place at the frequency independent T_m, beyond which BNT behaves similarly to PMN. Thus, our experimental treatments introduce internal stress to the system to disturb the spontaneous thermodynamic evolution of the PNRs, when their sizes L tend to decrease with the cooling. Very likely, the disturbance does not result in anisotropy in ε_{ii} , despite that the stress gradient profiles induced by different treatments are not necessarily identical, otherwise we might have observed opposite effects after compressed cooling and biased cooling. Eventually, the size of PNRs, L, in the cooled state is larger than those in the untreated sample. In the meantime, the random local field stays the same as it is determined only by the composition, hence, l_p is unchanged. Therefore, the permittivity below the original T_s is unaffected as it complies to Eq. (1). In the treated sample, T_s must be deferred to achieve $l_p = L$, while the permittivity at T_s is enhanced as it is calculated in Eq. (2). It is important to note that our treatments may only intervene in the temperature dependence of L but not the number density N. This gives rise to the possibility that there is space for L to grow when cooling from $T_{\rm m}$ when N is decreasing undisturbedly. Note that such "space" is supposedly the nonpolar regions, in which the PNRs are embedded. Both "superparaelectric" and "breathing" models assume the existence of nonpolar volume in relaxors, although the very recent "polar slush" model describes the domain structure in PMN as tiny domains separated by low angle interfaces without any nonpolar phase.^{4,31} In the BNT case, the traditional relaxor descriptions to the nature of the polarization dynamics could bare consideration through the "breathing" model. Indirect evidence could be found from the conductivity behavior in BNT. In our latest paper,¹⁵ we noticed that the relaxor phase possesses an ionic conductivity greater than that of the ferroelectric phase by orders of magnitude in the same BNT ceramic. Additionally, the activation energy for oxygen vacancy migration is about 0.2 eV lower in the relaxor phase than in the ferroelectric phase. This suggests that nonpolar space could exert smaller scattering probability against the electromigration of oxygen

vacancies. Furthermore, the fact that $T_{\rm m}$ and the corresponding permittivity are not adjusted by our treatments implies that $N_{\rm m}$ and $L_{\rm m}$ could be determined only by the composition if the freezing at $T_{\rm m}$ is related to a structural transition; therefore, Ta⁵⁺ doping can change it. Very likely, each grain is not completely filled with PNRs even at $T_{\rm m}$, otherwise the permittivity at $T_{\rm m} (\propto N_m \cdot L_m^2)$ would have reached the full potential of a certain composition. However, this is not case. As a consequence of intense treatments, the permittivity magnitude at the new $T_{\rm s}$ can exceed that at $T_{\rm m}$, suggesting the growth of L during cooling can be "faster" than the reduction of N such that $N_s \cdot L_s^2$ $> N_m \cdot L_m^2$. The hypothetical process described above is illustrated in Fig. 4(b).

In conclusion, we identified three independent treatments, rapid cooling, biased cooling, and compressed cooling, to have nearly identical impacts on the dielectric property in BNT-based relaxors by deferring the $T_{\rm s}$ while maintaining the other parameters like $T_{\rm d}$ and $T_{\rm m}$. Therefore, we postulated that the internal stress or the stress gradient plays a critical role in the dielectric relaxation in BNT. In the context of the "breathing" model, we hypothesized that T_s is controlled by the size of PNRs. Via introducing perturbations to the cooling process, the metastable size of PNRs can be engineered, giving rise to the observed phenomenon. Our work could raise awareness of the history dependence of dielectric relaxation and bring insight into the nature of polarization dynamics in BNT. We hope that these metastable states will be investigated in more detail and with diffraction and transmission microscopy methods to test for the nature of the PNRs and applicability of the "breathing" model mechanism to account for the T_s and relaxations.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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