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Two-stage processes of electrically induced-ferroelectric to relaxor transition in 0.94(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-0.06BaTiO$_3$

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The stability of electrically induced long-range ferroelectric order in a relaxor 0.94(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-0.06BaTiO$_3$ ceramic material has been investigated by temperature-dependent X-ray diffraction and electrical property measurements. The depolarization and ferroelectric-to-relaxor transition are identified as separate and discrete processes. It is observed that the induced ferroelectric domains first lose their ferroelectric/ferroelastic texture coincident with a peak signal in the thermally induced depolarization current. With further increase in temperature, the detextured ferroelectric domains are dissociated into nanoscale entities. This fragmentation marks the ferroelectric-to-relaxor transition. It is suggested that the ferroelectric-to-relaxor transition has features of a second order phase transition. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4805360]

Relaxor ferroelectrics have been of great interest due to their unique functional properties, such as large dielectric permittivity over a broad range of temperatures[1,2] and good piezoelectric properties,[3,4] which are useful in many practical applications.[5] Further interest has been drawn owing to the recent discovery of exceptionally large electromechanical strains of ∼0.45% in (Bi$_{1/2}$Na$_{1/2}$)TiO (BNT)-based lead-free relaxor ceramics suitable for actuator applications.[6] For the relaxor ferroelectrics to be qualified for useful electromechanical applications, temperature-dependent phase stability should be well-understood. The temperature of common interest is the depolarization temperature (T_d) that defines an upper limit[7] for piezoelectric applications as well as a lower limit[6] for actuator applications with large electric-field-induced strains. Despite the significance, the origin and nature of T_d in BNT-based relaxor ferroelectrics are not clearly understood. In the canonical relaxor ferroelectrics such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)[8,9] and (Pb$_{1-y}$La$_y$)(Zr$_{1-x}$Ti$_x$)O$_3$ (PLZT),[6,10] T_d determined from the peak of thermally induced depolarization current (TSDC) is known to match observation from both a dielectric anomaly and temperature-dependent X-ray diffraction. In addition, T_d (also frequently referred to as T_t) was shown to involve an evident latent heat, implying that the transition is of first order nature.[11,12]

On the other hand, a series of experimental works on BNT-based relaxor ceramics have revealed that a deviation of ∼10 °C exists between the so-termed T_d's, determined by TSDC and the dielectric anomaly.[13,14] Given that the origin of the depolarization phenomenon has been considered to be the ferroelectric-to-relaxor transition in lead-based relaxor ferroelectrics, the departure of the temperature for the dielectric anomaly from that of the peak in TSDC implies that the depolarization process of BNT-based relaxor ferroelectrics has a different origin. To unravel the mechanism of the depolarization of relaxor ferroelectrics, the thermal evolution of

an electric-field-induced ferroelectric phase in 0.94(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-0.06BaTiO$_3$ (BNT-6BT) ceramic was investigated by temperature-dependent dielectric, ferroelectric, and piezoelectric characterizations in relation to temperature-dependent X-ray diffraction studies.

BNT-6BT ceramics were sintered at 1150 °C for 3 h. Samples for dielectric and TSDC measurements were electroded with a silver paste, and then poled by two successive 6 kV/mm unipolar cycles at 50 mHz at room temperature. Dielectric permittivity was measured over a wide range of frequencies from 0.1 Hz to 1 MHz using an impedance analyzer (HP 4284A) on a poled ceramic during heating and cooling for two successive thermal cycles at a constant temperature change of 2 °C/min. Vogel-Fulcher fitting was performed for the data recorded during the cooling cycle. TSDC, provided as $P_{r,TSDC}$ on a poled ceramic, was recorded during heating at 2 °C/min by a Keithley 6517B ampere meter. A Sawyer-Tower circuit equipped with a temperature controllable silicone oil bath was used for large signal polarization hysteresis loops as a function of temperature, and temperature-dependent piezoelectric coefficient was measured by a custom-designed apparatus equipped with laser vibrometer (Politec sensor head OFV-505 and front-end VDD-E-600) using a sinusoidal AC excitation voltage of ±10 V at 1 kHz.[15] *In situ* temperature dependent X-ray diffraction study was performed on a bar-type sample of 1 × 1 × 10 mm^3 in transmission mode at beamline ID15B of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The beam energy of 87.19 keV was selected using a Laue monochromater. High-energy X-ray scattering techniques such as this allow for diffraction patterns to be collected from the bulk of the specimens. The details of the sample preparation and X-ray diffraction setup can be found elsewhere.[16]

Figure 1 shows temperature-dependent changes in a set of properties around the temperature of the electric-field-induced ferroelectric-to-relaxor transition (T_{F-R}), represented by a frequency-independent anomaly in dielectric permittivity ($ε'$).[10,17,18] Three distinct features are noted. First, T_{F-R} of

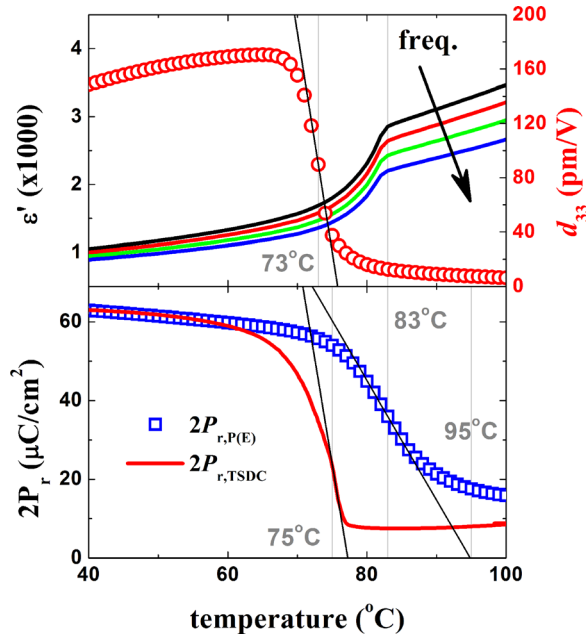a)Author to whom correspondence should be addressed. Electronic mail: jo@ceramics.tu-darmstadt.de

FIG. 1. Changes in ε' and *in situ* d_{33} in comparison with the switchable polarization, $2P_{r,P(E)}$ and $2P_{r,TSDC}$. The tangent lines are drawn at the inflection point of $2P_r$ and d_{33} curves.

83 °C is notably higher by ∼10 °C than the depolarization temperature (T_d) defined by the temperature where the maximum change (the peak of TSDC, i.e., inflection point) in the decreasing switchable polarization ($2P_{r,TSDC}$) from TSDC measurement[13–15] takes place. Second, the maximum change in the decreasing $2P_{r,TSDC}$ (75 °C) is fairly consistent with that in the decreasing piezoelectric coefficient d_{33} (73 °C). This implies that the change in $2P_{r,TSDC}$, indeed, reflects the depolarization phenomenon that causes the loss of poling-induced piezoelectricity.[13,14] Finally, the maximum decrease in $2P_{r,P(E)}(T)$, which is derived from large signal bipolar polarization hysteresis measurements at 6 kV/mm as a function of temperature, occurs at a significantly higher temperature of 83 °C than T_d from $2P_{r,TSDC}(T)$, but coincides with T_{F-R}. The listed three features suggest that T_{F-R} is also related to a certain depolarization process that is distinctive from that at T_d. Other than T_d and T_{F-R}, the so-called freezing temperature (T_f), where a high temperature ergodic relaxor transforms into a low-temperature nonergodic relaxor during cooling is of interest with an extreme broadening of the dielectric relaxation time spectra.[18–21] Since the T_f is known to match T_{ZP} (the temperature for zero polarization given by the x-intercept of tangent lines drawn at the inflection point of $2P_r$), as shown phenomenologically by Viehland *et al.*,[20]

two T_f's are considered, i.e., $T_{ZP,TSDC}$ and $T_{ZP,P(E)}$. The tangent line drawn from the inflection point of $2P_{r,TSDC}(T)$ and $2P_{r,P(E)}(T)$ yields T_{ZP}, respectively, at 77 °C and 95 °C.

It is generally agreed that T_f of relaxor ferroelectrics is assessed by the Vogel-Fulcher relation for the temperature of the maximum dielectric permittivity (T_{max}) as a function of measurement frequencies.[19–21] In the case of BNT-6BT, however, T_{max} values are not unambiguously found due to a convolution of different processes that deviate from the overall dielectric signals of well-understood (especially near T_{max}'s) low-temperature dielectric relaxations.[22] Nevertheless, the imaginary part of the dielectric permittivity (ε'') for the dielectric relaxation part is so pronounced that we could use it to estimate these temperatures, based on the fact that the T_{max} in ε' matches that of the inflection point in ε''.[23] It is worth pointing out that the position of T_{max}'s showed no hysteresis during cooling and heating within the experimental tolerance, which implies that the ergodic-to-nonergodic relaxor transition could be a second order phase transition.

As shown in Fig. 2(a), the thermal evolution of T_{max} is well-described by the Vogel-Fulcher relation, given as

$$\omega = \omega_0 \exp\left[-\frac{E_A}{k(T_{max} - T_f)}\right], \quad (1)$$

where ω, ω_0, E_A, and k denote measurement frequency ($2\pi f = 1/\tau_{max}$), preexponential factor defining the theoretical maximum frequency for the vibration of polar nanoregions (PNRs), activation energy, and Boltzmann constant, respectively.[21] A best fit yields T_f of 74 °C, which is consistent with the estimation from both $2P_{r,TSDC}$ and d_{33}. A comparison of ω_0 of 2.53×10^{11} Hz and E_A of 0.104 eV with the corresponding values of 1.03×10^{12} Hz and 0.0407 eV in PMN[20] suggests that the PNRs in BNT-6BT could be bigger in size and thus less dynamic. The implication of the presence of T_f is best-seen from the reciprocal permittivity. As presented in Fig. 2(b), T_f coincides with the onset temperature for the reciprocal permittivity to deviate from linearity, i.e., the onset of a significant increase in ε'. On the other hand, the tangent line drawn from the inflection point in $1/\varepsilon'$ becomes zero at 94 °C that is equal to T_{ZP} estimated from $2P_{r,P(E)}$.

Figure 3(a) presents a part of the temperature-dependent X-ray diffraction patterns covering $\{311\}_{pc}$, $\{222\}_{pc}$, and $\{320\}_{pc}$ reflections for selected temperatures. An apparent non-cubic distortion is seen to evolve out of a pseudocubic phase only after an electrical poling treatment, previously
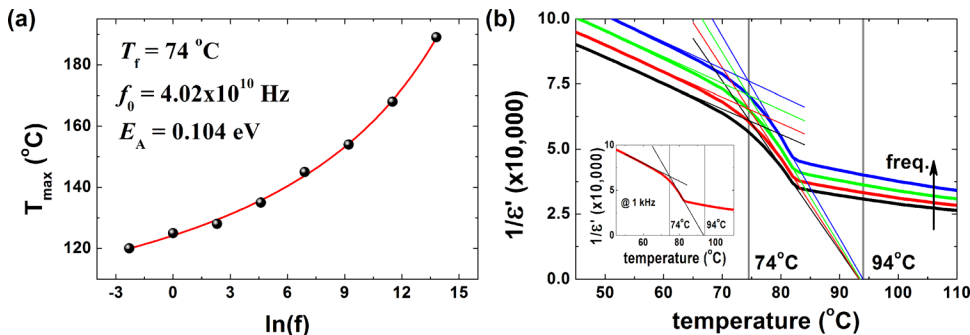

FIG. 2. (a) Vogel-Fulcher fitting of the temperature of the maximum dielectric permittivity as a function of measurement frequency. (b) Inverse dielectric permittivity for selected frequencies of 0.1, 1, 10, and 100 kHz as a function of temperature. The tangent lines were drawn at the inflection points and the region, where the dielectric permittivity decreases linearly. The inset in (b) illustrates the relation between the tangent lines and the reciprocal permittivity.
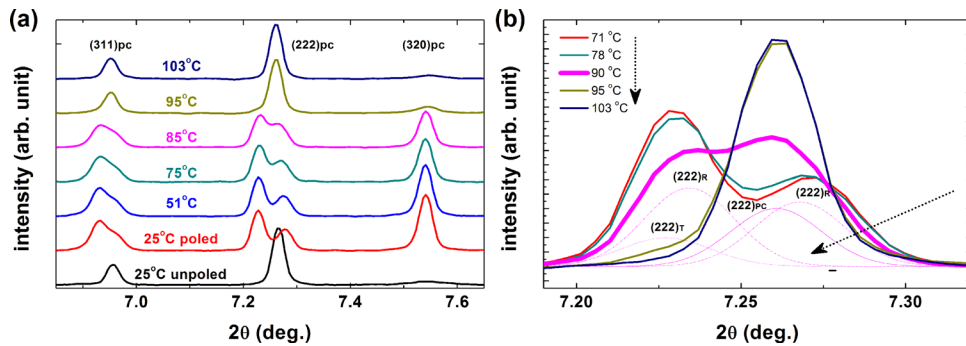
FIG. 3. (a) Three reflections in the XRD patterns for selected temperatures ($\lambda = 0.0143$ nm) with the scattering vector, q, parallel to E, and (b) expanded view of $\{222\}_{pc}$ for selected temperatures with the deconvoluted peak components of the $\{222\}_{pc}$ at 90 °C. The position of each component was estimated by Rietveld analysis using FULLPROF,[28] and the deconvolution was done using Gaussian profiles.

suggested as an electric-field-induced phase transition.[16,22] In contrast to the canonical relaxors such as PLZT, where the application of electric field merely extends the coherency length of polar entities within the given symmetry, the electric-field-induced change in BNT-6BT was shown to involve a clear change in symmetry.[24,25] The diffraction pattern of a poled ceramic was analyzed to consist of a mixture of about 80% rhombohedral and 20% tetragonal phase.[16] With increasing temperature, the most drastic change is seen to happen at ∼95 °C, where almost all the poling-induced non-cubic distortions disappear. An expanded view of $\{222\}_{pc}$ for selected temperatures is given in Fig. 3(b). The degree of poling represented by the ratio of $(222)_R$ to the total intensity of rhombohedral phase starts to decrease in the temperature range of 71–78 °C, to which T_f, determined both from the Vogel-Fulcher analysis and from the TSDC measurements, belongs. In the temperature range between 78 and 90 °C where the dielectric anomaly and the inflection point in $2P_{r,P(E)}$ occurs, not only the degree of poling but also the total intensity of both rhombohedral and tetragonal phases decrease with the pseudocubic phase starting to appear. A full transition to the pseudocubic phase, the nature of which is identical with that of the unpoled state, is observed to be completed in the temperature range of 95–103 °C that includes T_{ZP} of $2P_{r,P(E)}$.

The difference between T_{ZP} determined by TSDC and dynamic $P(E)$ measurements strongly suggests that the transition from the electric-field-induced ferroelectric order to relaxor state follows two steps, i.e., a detexturization of poled macroscopic ferroelectric domains, followed by a miniaturization of the ferroelectric macrodomains. In fact, $2P_{r,P(E)}$ induced by large signal bipolar hysteresis measurements above $T_{ZP,TSDC}$ was seen to decay significantly with time converging to the corresponding $2P_{r,TSDC}$, implying that the phase existing between $T_{ZP,TSDC}$ and $T_{ZP,P(E)}$ is a ferroelectric without sustainable remanent polarization. Given that the nonergodic relaxor state is a consequence of frozen random fields at and below T_f,[17] it is reasonable to assume that the loss of macroscopically induced long-range ferroelectric order is closely related to defrozen random fields reinforcing the depolarization field. It follows that the transition from nonergodic relaxor to a ferroelectric state by the application of an electric field can also be assumed to take place in two steps. The application of an electric field first aligns randomly oriented polar nanoregions or nanodomains along the external field direction. This is followed by the formation of long-range ferroelectric domains with a further increase in the electric-field strength. This interpretation is

strongly supported by the fact that *in situ* electric-field-dependent X-ray diffraction experiments showed that the non-cubic phase appearing during poling was already highly textured and the degree of texture did not increase noticeably regardless of a further increase in the applied electric-field level.[16] Also, though no structural change was evidenced by high-resolution neutron diffraction, a noteworthy electromechanical strain of more than 0.3% at 6 kV/mm was observed in the Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-modified relaxor BNT-(Bi$_{1/2}$K$_{1/2}$)TiO$_3$ system.[26] Therefore, it can be said that the transition between relaxor and ferroelectric phase is hysteretic; the relaxor-to-ferroelectric transition involves a percolation of aligned PNRs, and the reverse transition involves a dissociation of randomly oriented macroscopic ferroelectric domains. This leads to a conclusion that the free energy of the induced ferroelectric state is competitive with that of the unpoled relaxor state and the energy barrier between the two states is large enough to result in a hysteretic behavior between the forward and backward transition. It is further concluded that the random fields, responsible for the formation of PNRs, should also be the reason for the loss of macroscopically induced poling state of nonergodic relaxors.

On the other hand, the present investigation leaves the identity of ferroelectric-to-relaxor transition to be controversial in that the order parameter P vanishes earlier than this transition. The rationale for a first-order phase transition in the previous studies[8,9,11,12] was given by the fact that the transition happens discontinuously with an endothermic signal, where both the $2P_{r,TSDC}$ and the dielectric signal exhibits frequency-independent anomaly during heating. There are at least three points that suggest the designation of a first-order transition to the ferroelectric-to-relaxor transition in the case of BNT-6BT may be incorrect.

i.   This transition, induced under zero-field heating after a poling treatment, cannot be induced reversibly during cooling without the aid of an external electric field, which is also the case for the canonical relaxor ferroelectrics.

ii. The ferroelectric-to-relaxor transition is rather continuous over a range of temperature of ∼10 °C starting from 83 °C to 95 °C, although a clarification of this observation could only be possible with good quality single crystals.

iii. A significant relaxation decays a switchable polarization, induced temporarily by an external field to a certain remanent value that vanishes with complete disappearance of the trace of non-cubic distortion.

Taking the phase transition temperature as the one where the non-cubic distortion completely vanishes, this transition is accompanied by divergence of dielectric permittivity as shown in Fig. 2(b). Within the context of the Landau-Ginzburg-Devonshire phenomenological theory,[27] therefore, the ferroelectric-to-relaxor transition in BNT-6BT can be classified as a second order phase transition. The lack of reverse transition during cooling is due to a large kinetic barrier from the relaxor to the ferroelectric state, which requires an external electric-field input as an activation energy.

Thermal depolarization of a ferroelectric phase, induced out of a nonergodic relaxor BNT-6BT by electric field application, was investigated by dielectric, ferroelectric, and *in situ* structural characterizations. It was demonstrated that the freezing temperature is the true depolarization temperature where the field-induced piezoelectricity disappears with detexturization of macroscopic ferroelectric domains. A complete recovery of the initial relaxor state was observed to be made at a temperature higher than the depolarization temperature. The onset of this recovery was reflected in the dielectric permittivity as a frequency-independent anomaly but the completion of this transition took place at a much higher temperature where the reciprocal permittivity, extrapolated linearly from the inflection point of the dielectric anomaly, vanishes. It is proposed that ferroelectric-to-relaxor transition be a second order phase transition.

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