Terahertz Probing Irreversible Phase Transitions Related to Polar Clusters in Bi$_{0.5}$Na$_{0.5}$TiO$_3$-Based Ferroelectric

Jiyue Wu, Wenfeng Sun, Nan Meng, Hangfeng Zhang, Vladimir Koval, Yan Zhang, Robert Donnan, Bin Yang,* Dou Zhang,* and Haixue Yan*

Electric-field-induced phase transitions in Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based relaxor ferroelectrics are essential to the control of their electrical properties and consequently in revolutionizing their dielectric and piezoelectric applications. However, fundamental understanding of these transitions is a long-standing challenge due to their complex crystal structures. Given the structural inhomogeneity at the nanoscale or sub-nanoscale in these materials, dielectric response characterization based on terahertz (THz) electromagnetic-probe beam fields is intrinsically coordinated to lattice dynamics during DC-biased poling cycles. The complex permittivity reveals the field-induced phase transitions to be irreversible. This profoundly counters the claim of reversibility, the conventional support for which is based upon the peak that is manifest in each of four quadrants of the current–field curves. The mechanism of this irreversibility is solely attributed to polar clusters in the transformed lattices. These represent an extrinsic factor, which is quiescent in the THz spectral domain.

Terahertz (THz) radiation (100 GHz to 10 THz) is intrinsically able to probe low-energy lattice phonons$^{[1]}$ and other more complex normal (or collective), modes of solid-phase atomic or ionic assemblies$^{[2]}$ making it an ideal tool for elucidating fundamental structural and dynamical variations in dielectric materials.$^{[3]}$ In particular, THz techniques are useful to probe ferroelectric materials, which are comprised of non-centrosymmetric unit cells, each possessing a switchable polarization of their electric dipole moment. Of the class of ferroelectric materials, perovskite-structured Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT)-based compounds have attracted worldwide research interest in recent years with the development of lead-free forms$^{[4]}$ which have been deployed in a range of technological applications, including piezoelectric actuators, sensors, and dielectric capacitors. Each of these areas of utility is respectively attributed to their large electric field-induced strain,$^{[5]}$ high piezoelectric constant, and high specific energy. While earlier studies of the crystal structure and phase transitions of BNT have answered many questions, there still remain some key points that are controversial due to the complexity of Na–O and Bi–O bonds, and the octahedral tilt in the unit cell.$^{[6]}$ Due to these unique structural properties, phase transitions in BNT, and its derivatives, can be induced by applied electric fields of 10s of kV cm$^{-1}$ which, in most cases, are indirectly represented by the electrical field-dependent bipolar current, polarization, or strain loops

Dr. J. Wu, Dr. N. Meng, Dr. H. Zhang, Dr. H. Yan
School of Engineering and Materials Science
Queen Mary University of London
Mile End Road, London E1 4NS, UK
E-mail: h.x.yan@qmul.ac.uk

Dr. W. Sun, Prof. Y. Zhang, Dr. B. Yang
Department of Physics
Beijing Key Lab of Metamaterials and Devices
and Key Laboratory of Terahertz Optoelectronics
Ministry of Education
Beijing Advanced Innovation Center for Imaging Technology
Capital Normal University
Beijing 100048, P. R. China
E-mail: b.yang@chester.ac.uk

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aelm.201901373.
© 2020 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
The copyright line for this article was changed on 26 February 2020 after original online publication.

DOI: 10.1002/aelm.201901373
(I–E, P–E, or S–E, respectively). It is now well established that, such phase transitions can be directly observed using a variety of in situ methods, such as X-ray diffraction (XRD),[10] neutron diffraction,[11] and transmission electron microscopy (TEM). However, the local structural changes (below the nanometer scale), including chemical and displacement disorder, are normally too small for diffraction methods to detect. Consequently, dielectric measurement can be employed as a probe to sense electric field-induced phase transition.[8] In view of the complexity wrapped up in the dispersive polarizability, there is yet no detailed study of phase transition behavior of BNT from the intrinsic, atomic-level, dielectric property point of view. This makes THz dielectric spectroscopy a desirable method for probing polar materials, such as relaxor ferroelectrics. Hence the need for dielectrometry at THz energies.

Conventional dielectroscopy is typically deployed over a frequency domain spanning from 1 to 100 MHz. In this case, the dielectric response comprises of both the intrinsic (including lattice transformations), and extrinsic sources (including domain walls, grain boundaries, and point defects).[12] Extrinsic factors contribute less to net dielectric response at the higher GHz to THz frequencies due to their long relaxation times, thereby allowing the contribution from intrinsic processes to be isolated and characterized. Furthermore, coherent THz spectroscopy enables simultaneous determination of the real (in-phase) and the complex (quadrature-response manifest as energy-loss by heat), polarization-response to the probe electric field. Understanding the individual contributions from microscopic intrinsic and extrinsic dielectric factors will enable an engineered and therefore accelerated development, and optimization of the aforementioned macroscopic advantages of these important materials.

In this work, BNT-based ceramics are biased by a DC electric field while being simultaneously probed with a coherent THz beam field. A new experimental methodology is therefore introduced for the study of phase transitions in ferroelectrics to reveal their intrinsic dielectric response. For the first time, the difference in the THz dielectric behavior of BNT-derived ferroelectrics, before and after the application of a DC electric field, has been observed using THz time-domain spectroscopy (THz-TDS). THz-TDS revealed that the applied DC electric field-induced change in the phase transitions of BNT-based ceramics is irreversible and can be ascribed to the crystal chemistry at the sub-nanometer scale.

The ferroelectric properties of Bi$_{0.35}$Na$_{0.335}$Li$_{0.015}$Sr$_{0.3}$TiO$_3$ (BNLST) were characterized at different maximum amplitudes of an external DC electric field in order to determine its polarization state and switching dynamics. Relaxor-like slim P–E loops with a large field-induced polarization and a negligible remnant polarization are observed (Figure 1a); additionally, four current peaks can be observed in the I–E curves (Figure 1b, show that the largest volume of polar switching and phase transitions takes place inside of the material. Such behavior is different from that of other classic relaxors and resembles more the features of antiferroelectrics (AFE).[13] From the literature, it appears that the original state of BNLST is more like a non-polar or weak-polar arrangement of electric dipoles.[8] There is no evidence for an AFE ordering in the BNLST ceramics, such as reported in other BNT systems.[14] In addition, the electric field-induced strain dependence (Figure 1c) indicates an electrostrictive-like behavior (linearity of the strain (S) versus square of the polarization ($P^2$) dependence,[15]), which is macroscopically coincident with the nonpolar symmetry. In this case, the strain, related to

![Figure 1. a) P–E, b) I–E, and c) S–E loops of BNLST ceramics measured at different electric fields (up to 80 kV cm$^{-1}$) at room temperature and 1 Hz. The insert of (c) shows the linear relationship between S and $P^2$.](image-url)
the field-induced transitions, cannot be determined from the measured $S$–$E$ loops. The existence of the four current-peaks in the $I$–$E$ curves can be explained using field-induced phase transition theory:[8] the weak-polar state is transformed to the polar state at certain applied strengths of DC electric field (the peaks in the first and third quadrants), and then this polar state will relax to its original state upon removal of the coercive field (the peaks in the second and fourth quadrants). For this condition, it is generally accepted that the phase transitions in relaxors are reversible and the relaxor is in the “ergodic” state. However, to-date, there are no studies reporting whether the polar state goes “completely” or “partially” back to a weak-polar state after the applied electric field is switched off. The enclosed area of the ferroelectric hysteresis loops cannot be directly linked with the irreversibility of the phase transitions, but it can be related to the loss from friction due to the dipole rotations.

**Figure 2** shows the temperature-dependent dielectric permittivity and loss tangent of BNLST at six different frequencies (1, 10, 50, 100, and 500 kHz; and 1 MHz), as measured before and after poling. For the unpoled sample, the anomaly corresponding to the highest permittivity value (denoted as $T_m$), becomes more pronounced at lower frequencies and shifts to a higher temperature with increasing frequency (Figure 2a). The strong dispersion of the permittivity peak is generally accepted as a fingerprint of relaxor behavior, dominated by relaxation processes of the polar nano-regions (PNRs).[16] PNRs are nanometer-sized regions having a local polarization and existing in the vicinity of $T_m$. In order to investigate the effect of an external field on PNRs, dielectric measurements were carried out on the same sample after poling in a DC field at 6 kV mm$^{-1}$ for 15 min, as shown in Figure 2b. By comparing the dielectric spectra in Figure 2a,b, it showed that the ferroelectric relaxor underwent an irreversible transition upon the application of the external electric field. Below $T_m$, there is a significant increase in the values of the real part of the dielectric permittivity ($\varepsilon'$) and loss tangent (tan$\delta = \varepsilon''/\varepsilon'$) of the poled sample due to the contribution of PNRs to the overall electrical response. It should be noted that the behavior of PNRs, as discussed here and following, is related to the arrangement of PNRs above the static freezing temperature ($T_f$). Below $T_f$, the long-range polar order of these nanoregions is locked after poling. Here, the $T_f$ of PNRs in BNLST is below room temperature, as determined by the dielectric data fitted according to the Vogel–Fulcher law.[18] In addition, the dielectric dispersion completely vanished above $T_m$ after poling. Compared with tan$\delta$ before poling, the value of tan$\delta$ decreases sharply at high temperatures (especially above 300 °C) after poling. The decrease of tan$\delta$ can be a result of a permanent structure-change after the application of the bias DC electric field. As reported for pure BNT, the monoclinic (C$\bar{2}$) phase is suppressed after poling, which enables the rhombohedral (R3c) structure to be revealed on a global length scale.[19] Meanwhile, the dispersion of tan$\delta$ diminishes at high temperatures (over 300 °C) after poling, which is another evidence for the regulation of crystal structure with the help of an external DC electric field. However, no macroscopic phase transitions of BNLST can be directly detected from the dielectric spectrum. $T_m$ cannot be assigned as the critical phase transition point based on the XRD results of BNLST as shown in Figure S1, Supporting Information. On a detailed inspection, there is no change in cubic structure (space group Pm-3m), at room temperature.
Despite the difference in dielectric spectra before and after poling, it is still not possible to definitively claim that the field-induced phase transitions are irreversible at the lattice scale, mainly due to the multiple extrinsic contributions to dielectric behavior at sub-GHz frequencies. Since intrinsic, lattice-level processes are at the energetics of THz electromagnetic radiation, the phenomenon of reversible or irreversible field-induced phase transitions can be assessed using coherent THz spectroscopy. The BNLST sample has high permittivity and high dielectric losses in the THz spectral band, therefore, two tailored measurement methodologies were implemented: a reflection-based THz measurement configuration and coplane DC biasing. The schematical plot of the reflected THz-TDS set up is presented in Figure 3 and the technical details are presented in Experimental Section. A polished, plane-parallel wafer, with a diameter of 13 mm and a thickness of 500 µm, was measured by the THz-TDS systems. As shown in the inset of Figure 3, silver paste was applied on opposite edges of a given sample’s same surface and served as electrodes, leaving the middle-area of the sample with a 5 mm-wide gap upon which the THz beam field-spot could fall. The electrodes were connected to a high voltage DC power supply and the poling was taking effect across the middle of the sample surface, where the effective area THz beam can probe due to the limited penetration depth. Prior to the THz-TDS measurement, the DC electric field was applied for 2 min. The THz beam field was propagated at normal incidence up to the sample-face (the sample-face being supported parallel to the plane of the optical table). This configuration was adopted to ensure simple kinematic reference of the sample-reflection with respect to the reference-mirror reflection (each resting under its own weight over a supporting rim); that is, a common optical path length was imposed ensuring that post-processing derivation of complex permittivity was not compromised by phase (path) error, to which THz-TDS is sensitive to. The difference between the sample’s reflected signal before and after poling is used to derive the change in dielectric parameters, including permittivity and loss tangent, where the first differential of permittivity with respect to reflectance was implemented with respect to the following equation:

$$\varepsilon(\omega) = \varepsilon'\omega + i\varepsilon''\omega = \left(\frac{1 + \sqrt{R}}{1 - \sqrt{R}}\right)^2$$  \hspace{1cm} (1)

the reflectance, \(R\), carries both amplitude and phase information and it is the ratio between the measured sample spectrum and the reference mirror spectrum; \(\omega\) is angular frequency, \(\varepsilon'\) and \(\varepsilon''\) are the real and imaginary parts of the permittivity, respectively. The detailed procedure of extracting the changes of dielectric parameters is presented in the Supporting Information (Figure S2, Supporting Information).

The real and imaginary parts of the dielectric permittivity of BNLST, as obtained by THz-TDS at 0.4 THz, are shown in Figure 3. The voltage was applied in the following cycle: (0, 0.2, 0.8 kV, because the applied voltage is too low. When the voltage reached 1 kV, there is a distinct increase in both the real and imaginary parts of the relative dielectric permittivity. This can be explained by the field-induced transitions that take place at 1 kV, resulting in the enhanced \(\varepsilon'\) and \(\varepsilon''\) due to the intrinsically induced polarization. When the voltage returns to zero, \(\varepsilon'\) and \(\varepsilon''\) increase again because the dipoles are no longer locked by the bias field (freezing effect) and respond easily to the AC THz beam field. After the application of the −1 kV voltage, the values of both \(\varepsilon'\) and \(\varepsilon''\) are slightly increased, when compared with those after poling at 1 kV. It is worth noting that \(\varepsilon'\) further increases after the removal of the applied DC bias field. This is direct evidence that the original polar state of BNLST was changed after the half-cycle of the applied voltage. In other words, the so-called “reversible” field-induced phase transition is not “completely” reversible. In addition, the drop of
The fluctuating atoms in PNRs can be treated as clusters of soft polarizations. Generally, there are four types of polarization processes contributing to the overall dielectric response. They can be sub-divided into two main categories: i) resonance processes and ii) relaxation processes. For resonance, electronic and atomic (ionic) polarizations are involved, whereas the dipolar (orientation) and interfacial (space charge) polarizations contribute to the relaxation.[31] Considering the resonance regime, electron and atomic polarizations, respectively, result from the oscillatory displacement of the electron cloud and atoms (ions) in response to the probe AC field. The system is considered to be composed of PNRs (circle with an arrow representing the direction of polarization) and non-polar regions (circle with shadow). One representative PNR is magnified before, during and after poling, corresponding to the position O, A, B, and C marked in the dielectric diagram, respectively. Each PNR is composed of polar clusters (red arrows representing the direction of spontaneous polarization of each polar cluster and black arrows representing the permanent change of the direction of spontaneous polarization after poling).

$\varepsilon''$ implies that less heat was dissipated due to the reduced friction among the external field-aligned dipoles.

Figure 4. The real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of dielectric permittivity of BNLST ceramics measured at 0.4 THz with the variation of applied voltage from $-1 \text{ kV}$ to $1 \text{ kV}$. The sequence of voltage is $0 \text{ V, 0.2 kV, 0 V, -0.2 kV, 0 V, ..., 1 kV, 0 V, -1 kV, 0 V}$. The schematic drawing illustrates the evolution of the structure at the lattice-level during the whole cycle. The system is considered to be composed of PNRs (circle with an arrow representing the direction of polarization) and non-polar regions (circle with shadow). One representative PNR is magnified before, during and after poling, corresponding to the position O, A, B, and C marked in the dielectric diagram, respectively. Each PNR is composed of polar clusters (red arrows representing the direction of spontaneous polarization of each polar cluster and black arrows representing the permanent change of the direction of spontaneous polarization after poling).

$\varepsilon''$ implies that less heat was dissipated due to the reduced friction among the external field-aligned dipoles.

In summary, the results from the THz-TDS measurements, in the THz spectral domain, show that the BNT-based system undergoes field-induced phase transitions which are reversible after the removal of the applied field. The origin of the dielectric response can be directly linked with the intrinsic transformation of polar clusters at the atomic level. It was demonstrated that the BNT-based system undergoes field-induced phase transitions which are irreversible after the removal of the applied field. The origin of the dielectric response can be directly linked with the intrinsic transformation of polar clusters at the atomic level. It was demonstrated that the BNT-based system undergoes field-induced phase transitions which are irreversible after the removal of the applied field.
of the field-induced phase transitions is thought to be intrinsic (at the lattice level), coming from polar clusters within PNRs. Considering the correlation length limit of diffraction methods, THz-TDS spectroscopy is demonstrated to be a powerful probe for evaluation of phase transitions in ferroelectrics.

The irreversible, bias DC electric field-induced phase transitions were investigated in BNT-derived ceramics using THz-TDS. In contrast to THz dielectric spectroscopy, the conventional ferroelectric measurements of the $P$–$E$ (I–E) hysteresis loops indicated, unconvincingly, that the phase transitions induced by an external electric field are reversible. The differences in the THz dielectric properties of the unpoled and poled samples as well as of the samples subjected to the reverse-poling electric field, suggest the existence of a permanent field-induced lattice transformation, that is, local polar clusters. It is suggested that these polar clusters within the PNRs are responsible for the observed changes in the THz dielectric spectra. This work is essential in further understanding the intrinsic mechanisms underlying the phase transition behavior of the BNT-based materials. It provides an innovative approach of applying THz electromagnetic radiation to investigate the phase transition behavior in ferroelectric systems on the lattice scale.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors would like to thank the financial support of EPSRC (MASSIVE Project, EP/L017695/1; Teranet EP/M00306X/1), the Grant Agency of the Slovak Academy of Sciences (Grant No. 2/0038/20), China Scholarship Council (CSC, 201506630005), and the National Natural Science Foundation of China (Nos. U19A2087; S1672311), and the State Key Laboratory of Powder Metallurgy, Central South University, Changsha, China.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

dielectrics, phase transitions, polar clusters, relaxor ferroelectrics

---

**Experimental Section**

**Sample Synthesis:** The ceramic samples were prepared via the conventional solid-state method according to the chemical formula, Bi$_2$O$_3$Na$_{2/3}$Li$_{0.015}$Sr$_{0.3}$TiO$_3$. A stoichiometric batch of Bi$_2$O$_3$ (99.9% Sigma-Aldrich), Na$_2$CO$_3$ (99.5% Sigma-Aldrich), Li$_2$CO$_3$ (99.0% Alfa Aesar), SrCO$_3$ (99.5% Alfa Aesar), and TiO$_2$ (99.8% Sigma-Aldrich) powders were weighed after drying at 200 °C overnight. The ingredients were ball-milled for 4 h. Calcination of the mixture was carried out in two steps: at 800 °C for 2 h followed by 900 °C for 4 h. The calcined powders were ball-milled for another 4 h and then uniaxially cold-pressed into pellets at 70 MPa. These green discs were finally sintered at 1150 °C for 3 h. The density of all pellets was measured by the Archimedes method and it reached values above 95% theoretical density.

**Electrical Characterization:** Electrical measurements were performed on the pellets with silver paste fired on both major sides. The temperature dependence of the real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the dielectric permittivity was tested from room temperature up to 500 °C using an LCR meter (Agilent, 4284A, Hyogo, Japan) attached to a PC-controlled furnace. The I–E, P–E, and S–E loops were measured using a ferroelectric tester (NPL, Teddington, U.K.), at a frequency of 1 Hz and at room temperature.

**Reflection Based THz-TDS Set-Up:** A femtosecond Ti: sapphire amplifier system with a repetition rate of 1 kHz and a central wavelength of 800 nm was used as a light source. The optical beam was split into a pump beam and a probe beam by a polarizing beam splitter. The pump pulses passing through a chopper were used to generate THz radiation by a conventional electric–optic crystal of ZnTe. The THz beam was focused by a parabolic mirror and normally applied onto the broad face of the sample. Reflected THz pulses were then collected and steered by the parabolic mirrors, and focused onto a ZnTe crystal. The probe optical pulses passed through the same ZnTe detector crystal, a 1/4 wave plate, and a Wollaston prism, respectively. The elliptic polarization emerging from the 1/4 wave plate is analyzed by the prism into orthogonal component polarizations of electric vector that are angularly resolved and directed onto two balanced photodiodes, from which the magnitude and phase of the THz field is deduced.

**References**

[1] D. Giovanni, W. K. Chong, Y. F. Liu, H. A. Dewi, T. Yin, Y. Lekina, Z. X. Shen, N. Mathews, C. K. Gan, T. C. Sum, Adv. Sci. 2018, 5, 1800664.

[2] K. Y. Tian, B. Yang, Y. Yue, D. T. Bowron, J. Mayers, R. S. Donnan, C. Dobó-Nagy, J. W. Nicholson, D.-C. Fang, A. L. Greer, G. A. Chass, G. N. Greaves, Nat. Commun. 2015, 6, 8631.
[3] a) D. S. Rana, I. Kawayama, K. Mavani, K. Takahashi, H. Murakami, M. Tonouchi, Adv. Mater. 2009, 21, 2881; b) L. Li, P. Li, N. Lu, J. Dai, X. C. Zeng, Adv. Sci. 2015, 2, 1500290.

[4] a) C. Ma, H. Guo, S. P. Beckman, X. Tan, Phys. Rev. Lett. 2012, 109, 107602; b) X. Ren, N. Meng, H. Yan, E. Bilotti, M. J. Reece, Polymer 2019, 168, 246.

[5] X. Liu, X. Tan, Adv. Mater. 2009, 21, 2881; b) L. Li, P. Li, N. Lu, J. Dai, X. C. Zeng, Adv. Sci. 2015, 2, 1500290.

[6] a) C. Ma, H. Guo, S. P. Beckman, X. Tan, Phys. Rev. Lett. 2012, 109, 107602; b) X. Ren, N. Meng, H. Yan, E. Bilotti, M. J. Reece, Polymer 2019, 168, 246.

[7] a) G. Viola, R. McKinnon, V. Koval, A. Adomkevicius, S. Dunn, H. Yan, Phys. Rev. Lett. 2012, 109, 107602; b) X. Ren, N. Meng, H. Yan, E. Bilotti, M. J. Reece, Polymer 2019, 168, 246.

[8] J. Wu, A. Mahajan, L. Riekehr, H. Zhang, B. Yang, N. Meng, Z. Zhang, H. Yan, Nano Energy 2018, 50, 723.

[9] H. Yan, F. Inam, G. Viola, H. Ning, H. Zhang, Q. Jiang, T. Zeng, Z. Gao, M. J. Reece, J. Adv. Dielectr. 2011, 1, 107.

[10] J. E. Daniels, W. Jo, J. Rödel, J. L. Jones, Appl. Phys. Lett. 2009, 95, 032904.

[11] Y. Liu, L. Norén, A. J. Studer, R. L. Withers, Y. Guo, Y. Li, H. Yang, J. Wang, Phys. Rev. B 2013, 88, 224103.

[12] a) J. Rödel, W. Jo, K. T. Seifert, E. M. Anton, T. Granzow, D. Damjanovic, J. Am. Ceram. Soc. 2009, 92, 1153; b) F. Yang, M. Li, L. Li, P. Wu, E. Pradal-Velázquez, D. C. Sinclair, J. Mater. Chem. A 2018, 6, 5243.

[13] S.-E. Park, M.-J. Pan, K. Markowski, S. Yoshikawa, L. E. Cross, J. Appl. Phys. 1997, 82, 1798.

[14] W. Jo, T. Granzow, E. Aulbach, J. Rödel, D. Damjanovic, J. Appl. Phys. 2009, 105, 094102.

[15] G. Viola, T. Saunders, X. Wei, K. B. Chong, H. Luo, M. J. Reece, H. Yan, J. Adv. Dielectr. 2013, 03, 1350007.

[16] L. E. Cross, Ferroelectrics 1987, 76, 241.

[17] G. Xu, Z. Zhong, Y. Bing, Z. G. Ye, G. Shirane, Nat. Mater. 2006, 5, 134.

[18] a) H. Vogel, Phys. Z. 1921, 22, 645; b) G. S. Fulcher, J. Am. Ceram. Soc. 1925, 8, 339.

[19] B. N. Rao, R. Datta, S. S. Chandrashekar, K. D. Mishra, V. Sathe, A. Senyshyn, R. Ranjan, Phys. Rev. B 2013, 88, 224103.

[20] a) B. Yang, R. J. Wyld, D. H. Martin, P. Goy, R. S. Donnan, S. Caroopen, IEEE Trans. Microwave Theory Tech. 2010, 58, 3587; b) C.-H. Lee, N. D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J. A. Mundy, L. F. Kourkoutis, Y. Nie, M. D. Biegalski, J. Zhang, M. Bernhagen, N. A. Benedek, Y. Kim, J. D. Brock, R. Uecker, X. X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D. A. Muller, I. Takeuchi, C. J. Booth, C. J. Fennie, D. G. Schlom, Nature 2013, 502, 532.

[21] a) Y. Tan, G. Viola, V. Koval, C. Yu, A. Mahajan, J. Zhang, H. Zhang, X. Zhou, N. V. Tarakina, H. Yan, Eur. Ceram. Soc. 2014, 34, 2064; b) Z. Yan, D. Zhang, X. Zhou, H. Qi, H. Luo, K. Zhou, I. Abrahams, H. Yan, J. Mater. Chem. A 2019, 7, 10702.

[22] L. Zhu, J. Phys. Chem. Lett. 2014, 5, 3677.

[23] L. Zhu, Q. Wang, Macromolecules 2012, 45, 2937.

[24] J. Petzelt, Ferroelectrics 2008, 375, 156.

[25] T. Tsurumi, J. Li, T. Hoshina, H. Kakemoto, M. Nakada, J. Akedo, Appl. Phys. Lett. 2007, 91, 182905.

[26] J. Li, H. Kakemoto, S. Wada, T. Tsurumi, H. Kawaji, J. Appl. Phys. 2006, 100, 024106.

[27] V. Dorcet, G. Trottier, P. Boullay, Chem. Mater. 2008, 20, 5061.

[28] V. A. Shuvaeva, D. Zekria, S. M. Weber, P. Bhattacharya, P. A. Thomas, Phys. Rev. B 2005, 71, 174114.

[29] I. Levin, I. M. Reaney, Adv. Funct. Mater. 2012, 22, 3445.

[30] V. Bovtun, S. Kamba, A. Pashkin, M. Savinov, P. Samoukhina, J. Petzelt, I. P. Bykov, M. D. Glinchuk, Ferroelectrics 2004, 298, 23.