Dynamic Behavior of Polar Nanoregions in Re-Entrant Relaxor 0.6Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$–0.4PbTiO$_3$

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The existence of polar nanoregions (PNRs) is the most important characteristic of ferroelectric relaxors; however, the size determination and the dynamic of PNRs remain uncertain. Herein, it is revealed that a re-entrant relaxor behavior and ferroelectric–paraelectric transition coexist in complex perovskite oxide 0.6Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$–0.4PbTiO$_3$. Two dielectric anomalies, 1) the low-temperature re-entrant relaxor transition and 2) the high-temperature diffuse phase transition (DPT), are described by the phenomenological statistical model. The sizes of the two kinds of PNRs corresponding to two ferroelectric states were obtained. The dynamics of PNRs are analyzed using isothermal electrical modulus, which shows three critical temperatures associated with the DPT, the formation, and freezing of PNRs, respectively. The temperature evolution of the PNRs evolution depends on the stoichiometry of bismuth. The results provide new insights into the dynamic behavior of PNRs and the modification way of re-entrant relaxor behavior.

1. Introduction

Re-entrant relaxors have long been attracting considerable attention in view of their unique physical properties.[1–3] The re-entrant relaxor behavior is characterized by a strong frequency dependence of the real part of permittivity, which is supplemented by a dielectric plateau for the temperatures higher than the maximum permittivity temperature ($T_m$). Moreover, further increasing the temperature leads to a diffuse phase transition (DPT) around the ferroelectric to paraelectric phase transition temperature.[4]

The term “re-entrant” was used to mean that upon cooling/heating, a highly ordered ferromagnetic/ferroelectric state emerges from a complex coexistence of relaxor and ferroelectric state with less order, which resembles cluster glass or spin glass phases.[5,6] The similarity between the re-entrant transition and the disordered state grown in macroscopic order phase has been studied for a long time.[2,4,5] It has been found that in many re-entrant relaxors, the relationship between the probing frequency and $T_m$ can be described by the Vogel–Fulcher law.[7] It is also interesting that the activation energy is very high (0.2–0.3) eV for re-entrant relaxor, compared to the activation energy of 0.01–0.05 eV for canonical dipole glass and 0.02–0.15 eV for ferroelectric relaxors. It suggests that the re-entrant relaxor behavior is a typical weakly coupled relaxor behavior and thermally activated process.[8,9] The re-entrant relaxor behavior has been reported in Pb/Bi perovskite oxides.[10,11] Chen, et al.[12]
deemed that the re-entrant relaxor of 0.65Bi(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}-0.35PbTiO\textsubscript{3} originates from the complex ionic substitution in the A and/or B sites, suggesting that clustering of B site ions promotes the polar nanoregion (PNRs) to enter a more disordered state, where the relaxor state of 0.65Bi(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}-0.35PbTiO\textsubscript{3} is attributed to the nucleation and growth of the PNRs. The size of PNRs is dominated by the clustering of the same-type ions and/or quenched random electric fields caused by heterovalent ions.\textsuperscript{[13]} However, determining or tuning the size of PNRs in either the paraelectric state or the relaxor state is very difficult.

Since PNRs appear in the polar phase in the re-entrant relaxors, their dynamics and evolution (e.g., the orientation of PNRs) with respect to temperature and stoichiometry are critical to understand the characteristic and origin of re-entrant phenomenon. In this paper, we investigated the re-entrant relaxor behavior of 0.6Bi(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}-0.4PbTiO\textsubscript{3} ceramics by using 1) the phenomenological statistical model as described in ref. [14], 2) the Vogel–Fulcher law, and 3) isothermal electrical modulus. Our analysis provides key parameters to reveal the different dynamics of PNRs in the re-entrant region and the DPT region. In particular, we are able to qualitatively determine the size of PNRs in the re-entrant dipole glass-like relaxor and the DPT.

### 2. Results and Discussion

All the major diffraction peaks in the X-ray diffraction (XRD) profile can be indexed by a perovskite structure according to the XRD pattern of the 0.6B\textsubscript{1-x}MT-0.4PT ceramics (Figure 1).

Unfortunately, there are impurities in the sample that give rise to some extra peaks. The reflection of the impurity Bi\textsubscript{2}Fe\textsubscript{12}TiO\textsubscript{19} (JCPDS#01-087-1897, tetragonal phase, space group: P42/mnm) increases with the bismuth addition, indicating more Bi\textsubscript{2}O\textsubscript{3} dissolving from the lattice.\textsuperscript{[4]} No superlattice reflection can be observed from the diffraction profiles, suggesting the absence of A/B sites ordering. The mixture phase model P4\textsubscript{mm} + Pm\textsubscript{3}m was employed to carry out the Rietveld refinement of the XRD pattern. The cell parameters of the sample were calculated, and the cell volume and the fraction of composition in the tetragonal phase and the cubic phase are listed in Table 1. The phase fractions of the tetragonal and cubic phases are near 60% and 40%, respectively. It is noteworthy that the Pm\textsubscript{3}m space group is an ideal perovskite structure in which all atoms are

| %Bi | a [Å] | c [Å] | V [Å\textsuperscript{3}] | Fraction of P4\textsubscript{mm} |
|-----|------|------|----------------|-----------------------------|
| 2%Bi | 3.95992(1) | 4.03189(9) | 63.25 | 57.59% |
| 0%Bi | 3.96101(6) | 4.03193(5) | 63.26 | 60.83% |
| 2%Bi | 3.98202(4) | 4.03189(9) | 63.14 | 41.08% |

**Table 1.** The refined cell parameters of the 0.6B\textsubscript{1-x}MT-0.4PT.
located on sites with a center of inversion.\textsuperscript{[15]} It is easy to form nanoscale entities throughout the temperature regime of common interest on a long-range pseudo-cubic symmetry as a matrix in ceramics of complex A/B site with electronic lone pair.\textsuperscript{[11,15]} As the value of $c/a$ of tetragonal ferroelectric phase is very low, 1.0178(9)–1.0200(0), it is extremely difficult for the samples to form a large polarization.

To characterize the microstructure, SEM micrographs of the 0.6B\textsubscript{(1-x)MT-0.4PT ceramics were obtained, which are shown in Figure 2. All the ceramics show dense, homogeneous grains without pores. With the increase of bismuth, there is no obvious change of the grain size. The average grain sizes of the 0.6B\textsubscript{0.98MT-0.4PT, 0.6B\textsubscript{MT-0.4PT, 0.6B\textsubscript{1.02MT-0.4PT, and 0.6B\textsubscript{1.04MT-0.4PT are 0.89, 0.82, 0.91, and 0.83 $\mu$m, respectively. The grain size for all ceramics follows a Gaussian distribution. The appearance of liquid phase during sintering process could enhance the diffusion rate of ions across grain boundaries and/or weld the smaller grains.\textsuperscript{[16]} Several larger grains might be attributed to the liquid phase sintering mechanism.

Temperature dependence of the real part of permittivity ($\varepsilon$) and dielectric loss (tan $\delta$) for 0.6B\textsubscript{(1-x)MT-0.4PT ceramics measured from 1 kHz to 1 MHz is shown in Figure 3a–d, respectively. All compositions show the signatures of a ferroelectric transition that follows a relaxor transition upon cooling (similar phenomenon occurs on heating, which associates with the competition of different PNRs or core-shell structure or defect dipoles). The abnormal relaxor transition at the lower temperature $T_{\text{m}}$ is the so-called re-entrant relaxor transition. One important difference with the two dielectric anomalies is that the lower-in-temperature one around 680 K ($T_{\text{RR}}$) shows a strong frequency dispersion, while the higher-in-temperature one is a typical DPT. Here for 0.6Bi\textsubscript{(1-x)(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}-0.4PbTiO\textsubscript{3}, compared to a typical re-entrant relaxor transition, no broad permittivity plateau is found because the $T_m$ and $T_{\text{RR}}$ is very close. It suggests that the P4mm ferroelectric microdomains remains in the re-entrant relaxor and the frozen PNRs make a negative influence on the switching/growth of the microdomains. The higher-in-temperature DPT around 900 K is associated with the ferroelectric to paraelectric phase transition rather than the effect of space charges.\textsuperscript{[17]}

In order to gain further insights into the re-entrant relaxors, we employ the macroscopic and phenomenological approach\textsuperscript{[18,19]} to describe and fit the $\varepsilon'$ of 0.6Bi\textsubscript{(1-x)(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}-0.4PbTiO\textsubscript{3.} In this approach, the dielectric permittivity is proposed to following expressions\textsuperscript{[12,14]}

$$\varepsilon(T)_{\text{reentrance}} = \varepsilon_{11} + \varepsilon_{12} P_{11}(E_{\text{b1}}, T)$$

$$\varepsilon(T)_{\text{DPT}} = \varepsilon_{21} + \varepsilon_{22} P_{21}(E_{\text{b2}}, T)$$

$$\varepsilon(T) = \varepsilon(T)_{\text{reentrance}} + \varepsilon(T)_{\text{DPT}}$$

where $\varepsilon_{11}, \varepsilon_{12}, \varepsilon_{21}, \varepsilon_{22}, E_{\text{b1}}, E_{\text{b2}}, \theta_1$, and $\theta_2$ are constants at a given frequency. $E_{\text{b1}}$ and $E_{\text{b2}}$ are effective potentials of PNRs corresponding to re-entrant relaxor and DPT, which can be

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**Figure 2.** The surface SEM images of a) 0.6B\textsubscript{0.98MT-0.4PT, b) 0.6B\textsubscript{MT-0.4PT, c) 0.6B\textsubscript{1.02MT-0.4PT, and d) 0.6B\textsubscript{1.04MT-0.4PT ceramics. The statistic distributions of the gain size in ceramics using Gauss distribution.**
understood as activation energy to a certain extent. The insets of Figure 3 show that the fitting curves are in very good agreement with the experimental data, indicating that the model can accurately describe the re-entrant dipole glass-like behavior and the DPT behavior. The $E_{b1}$ of the re-entrant dipole glass-like behavior and frequency has an opposite trend, and the average value of $E_{b1}$ is in the range of 0.05(1)–0.07(5) eV, while the $E_{b2}$ of the DPT behavior is a constant value of 1.30(4)–1.31(3) eV (Table 2).

Remarkably, we are able to estimate the size of dipole clusters (or PNRs) in the relaxor and DPT regions using $E_{b1}$ and $E_{b2}$. The size of the PNRs is such that the direction of polarization is reoriented by thermal fluctuations of the lattice. This is consistent with the concept of a ferroelectric order crystal which includes features, such as lattice distortion, ionic disorder, and charge mismatch, which limit the coherence of the spontaneous polarization. The density of the features determines the size of PNRs (coherently polarizing volume), $\lambda$. In the simplest case, each initially isotropic region is subject to distortion, on cooling through Burns temperature $T_B$, to a ferroelectric order characterized by a local, temperature-dependent polarization, $P_s$. The reorientation of the polarization vector of a single PNR, between the variants allowed by the crystal symmetry, is considered to be a thermally activated process with an activation energy $E_{b1}$. In terms of an energy density, $\Delta G$, the activation energy is dependent on the PNRs size ($E_{b1} = \Delta G \lambda^3$).[20] Therefore, $E_{b1}$ or $E_{b2}$ can be expressed as $\Delta G^*V$, where $V$ is the volume of a single PNR. The Landau–Devonshire formalism of free energy[1,12] shows the typical values of $\Delta G$ is in the range of $10^5$–$10^7$ J m$^{-3}$. The volume of a PNR of re-entrant relaxor and PNR of DPT is calculated to be in the range of $(0.16–1.20) \times 10^{-27}$ m$^3$ and $(20.86–21.00) \times 10^{-27}$ m$^3$, respectively, corresponding to a lateral size in the range of 0.93–1.06 nm and 2.75–2.76 nm, respectively. The size of PNRs of re-entrant relaxor and DPT depends on the stoichiometry of bismuth due to the off-center displacement of Bi$^{3+}$ ion with lone pair of electrons creating local polarization.[21] Compared to Bi-deficient sample, the PNRs in both the relaxor and DPT regions are larger for the Bi-excess samples, suggesting that the size of PNRs can be modified by the concentration of bismuth.

The function $\omega_1(T)$ describes the ability of dipoles to overcome the potential wells at different temperatures, as shown in Figure 4a, which is similar to the Fermi–Dirac function. It is close to 1 at low temperature, while it is close to 0 at high temperature.[8] The function $\omega_1(T)$ shows frequency dispersion,
suggesting multiple relaxation time of dipoles in the system. Different from the function $\omega_1(T)$, the function $\omega_2(T)$ associated with DPT behavior shows a rapid decrease without frequency dispersion near the Curie temperature as shown in Figure 4b. It suggests that the appearance/disappearance of ferroelectric domain is very different from that of polar clusters. The phase transition of the pseudo-cubic and the tetragonal symmetry to the cubic symmetry undergo a thermal evolution giving rise to a sharp dielectric maximum.

The empirical Vogel–Fulcher law can be employed to relate the probing frequency $f_0$ and the temperature corresponding to the maximum of the $\varepsilon''(T_{\text{m}})$ for the re-entrant dipole glass-like behavior and as shown in Figure 5a–d.[22] The equation is given by

$$f = f_0 \exp\left(\frac{-E_a}{k_B(T_f - T_{\text{m}})}\right)$$  \hspace{1cm} (4)

where $E_a$ is the activation energy, $f_0$ represents the inverse attempt frequency, $k_B$ is the Boltzmann constant ($8.617 \times 10^{-5}$ eV K$^{-1}$), and $T_f$ is the freezing temperature of dipoles or PNRs. The fitting parameters of $E_a$, $T_f$, and $f_0$ are cataloged in Table 3. The $f_0$ for all samples are on the order of $10^{12}$ Hz, which is close to the typical lattice frequencies (near THz).[23] The $E_a$ is from 0.03 to 0.08 eV depending on the Bi stoichiometry, which falls in the activation energy values of re-entrant relaxors (0.2–0.3 eV) and the canonical ferroelectric relaxors (0.01–0.05 eV), suggesting a strong interaction between PNRs that give rise to the similarity to canonical ferroelectric relaxors. The increase of Bi concentration of 0.6B$_{1-x}$MT-
0.4PT results in a decrease of $T_f$ and an increase of $E_a$, which is closely related to the fact that dipoles (and therefore polarization) arise due to the Bi off-center displacements. The more the Bi makes the creation of local polarization or PNRs easier, the higher the $E_a$ reveals a weaker interaction between PNRs in comparison to the increased interaction inside a PNR.

The temperature dependence of the $P-E$ loop can directly show the relaxors behavior in ferroelectric materials. Polarization–electric field ($E$) and polarization current density ($J$) of the 0.6B(1–x)MT-0.4PT measured at the temperature below $T_f$ are shown in Figure 6. Similar to the canonical relaxor ferroelectrics, all $P-E$ loops exhibit a profile between the relaxor ferroelectric (thin $P-E$ loop) and the normal ferroelectric (square $P-E$) independent of temperature. It suggests that $P_{4mm}$ ferroelectric microdomains are retained in the re-entrant relaxor and the frozen PNRs make a pinning effect on $P_{4mm}$ ferroelectric microdomains. However, the temperature evolution of $P_{\text{max}}$ increases linearly with the increasing temperature. The increase of $P_{\text{max}}$ is attributed to the thermal activated PNRs as the $P_{\text{r}}$ is independent of temperature.$^{[24,25]}$ It suggests that the configuration of tetragonal ferroelectric microdomains remains unchanged in this temperature region (below $T_f$), since the frozen PNRs prevent the switching of tetragonal domains under electric field.$^{[24]}$ It is interesting that both Bi-deficient and Bi-excess sample show higher $P_{\text{max}}$, and the former could be associated with bismuth vacancies and oxygen vacancies, which make the PNRs susceptible to reorientation under electric filed, while the lattice is attributed to low fraction of tetragonal phase (the PNR contributes to the $P_{\text{max}}$ as discussed earlier).$^{[26]}$

To clearly describe the re-entrant relaxor behavior, impedance spectroscopy with a broader and more continuous frequency spectrum was employed for the electric response of 0.6B(1–x)MT-0.4PT ceramics. The temperature evolution of the imaginary part of the electrical modulus ($M''$) is calculated for the 60B(1–x)MT-40PT ceramics and is depicted in Figure 7a–d. With increasing temperature, all $M''$ peaks rapidly shift to higher frequencies, which exhibit a thermally activated behavior. The electric modulus physically corresponds to the relaxation of the electric field in the materials, while the electric displacement remains constant so that the electric modulus represents the real dielectric relaxation process.$^{[27]}$ To understand such electric modulus via relaxation mechanism, the Fourier transform of a relaxation function ($\phi(t)$) was employed to describe.$^{[28,29]}$

### Table 3. Fitting parameters for different compositions of 0.6B$_{(1-x)}$MT-0.4PT ceramics obtained using the Vogel–Fulcher.

| Composition       | $T_f$ [K] | $f_0$ [Hz] | $E_a$ [eV] | Ref.      |
|-------------------|-----------|------------|------------|-----------|
| 0.6B$_{0.98}$MT-0.4PT | 691.48    | 2.58 × 10$^{12}$ | 0.03       | This work |
| 0.6BMT-0.4PT       | 665.67    | 2.65 × 10$^{12}$ | 0.04       |           |
| 0.6B$_{1.04}$MT-0.4PT | 655.30    | 2.98 × 10$^{12}$ | 0.05       |           |
| 0.6B$_{1.08}$MT-0.4PT | 645.14    | 4.39 × 10$^{12}$ | 0.08       |           |
| 95BT-5BS           | 222.21    | 2.31 × 10$^7$  | 0.02       | [5]       |
| 50KNN-50BNT        | 214.63    | 5.41 × 10$^{13}$ | 0.20       | [13]      |
| 35 SBS-20PT-0.025PCN | 630.25    | 1.79 × 10$^{13}$ | 0.05       | [24]      |
| PMN-10PT           | 296.13    | 2.4 × 10$^{12}$ | 0.04       | [8,18]    |

Figure 6. Polarization–electric filed ($P-E$) at different temperatures. Inset: $P_r$ and $P_{\text{max}}$ versus temperature of a) 0.6B$_{0.98}$MT-0.4PT, b) 0.6BMT-0.4PT, c) 0.6B$_{1.04}$MT-0.4PT, and d) 0.6B$_{1.08}$MT-0.4PT ceramics.
The function \( \varphi(t) \) is modified by the function of Kohlrausch–Williams–Watts (KWW), and the imaginary part of the electric modulus can be described

\[
M'' = M''_{\text{max}} \left\{ (1 - \beta) + \frac{\beta}{1 + \beta} \left[ (\omega_{\text{max}}/\omega) + (\omega/\omega_{\text{max}})^{\beta} \right] \right\}
\]

where \( M''_{\text{max}} \) is the peak value of \( M'' \) and \( \omega_{\text{max}} \) is the corresponding frequency of \( M''_{\text{max}} \). The index \( \beta \) (0.1) indicates a deviation of dielectric relaxation from ideal Debye relaxation. Increasing the value of \( \beta \), the relaxations approach the ideal Debye relaxation. In an ideal Debye medium, molecules are independent, and there are no interactions among them, and the dipole moment of the molecules is constant. The molecules will only freeze at 0 K.\(^{[12]}\)

The material under investigation here is certainly not an ideal Debye medium, and the deviation can be deduced from the value of \( \beta \). The temperature dependence of \( \beta \) in 0.6B\(_{0.98}\)MT-0.4PT ceramics is shown in Figure 8a–d. The high-temperature minimal value corresponds to \( T_B \) while the low-temperature one is \( T_F \), as listed in (Table 4), which are lose to the results of \( V-F \) fitting and Curie-Weiss law. Furthermore, the temperature dependence of relaxation frequency \( \omega \) also follows \( V-F \) law as shown in inset of Figure 8. The change of \( \beta \) can be understood with the following discussion.

The sketch of the dynamics of two kinds of PNRs of a re-entrant relaxor is shown in Figure 9. From a very high temperature, when the temperature decreases the lattice is slightly distorted and ions displaced, and as the interaction between dipoles are enhanced, PNRs appear at \( T_B1 \). The dynamic of PNRs and phase transition can be determined according to the value of \( \beta \). Initially, PNRs with \( P4mm \) symmetry emerge at high temperature (\( T_B1 \)), and the interaction between them increases with decreasing temperature. The DPT behavior of 0.6B\(_{1-x}\)MT-0.4PT appears at near 900 K (\( T_m \)) when the \( P4mm \) PNRs collaborate and become \( P4mm \) microdomains. Further decreasing the temperature, the freezing of PNRs and the growth of microdomains weaken the interaction between them; therefore, \( \beta \) increases. However, what makes re-entrant relaxors so special is that, at about 800 K, a new type of PNRs (rhombohedral

\[
M'' = M''_{\infty} \left[ 1 - \int_{0}^{\infty} \exp(-\omega t)(-\frac{\omega \varphi}{\omega})dt \right]
\]

![Figure 7. Frequency dependence of the imaginary part of the electric modulus for 60BMT-40BCT measured at various temperature of a) 0.6B\(_{0.98}\)MT-0.4PT, b) 0.6BMT-0.4PT, c) 0.6B\(_{1.02}\)MT-0.4PT, and d) 0.6B\(_{1.04}\)MT-0.4PT ceramics.](image)

**Table 4.** The freezing temperature of dipoles (\( T_F \)), and the temperature of diffuse phase transition (\( T_B \)) of the 0.6B\(_{1-x}\)MT-0.4PT ceramics obtained using the deviation of dielectric relaxation from ideal Debye relaxation.

|                | 0.6B\(_{0.98}\)MT-0.4PT [K] | 0.6BMT-0.4PT [K] | 0.6B\(_{1.02}\)MT-0.4PT [K] | 0.6B\(_{1.04}\)MT-0.4PT [K] |
|----------------|-----------------------------|------------------|-----------------------------|-----------------------------|
| \( T_F (V-F) \)| 691.48                      | 665.67           | 655.30                      | 645.14                      |
| \( T_B (M''_1) \)| 689.67                      | 664.15           | 653.59                      | 643.55                      |
| \( T_B (M''_2) \)| 910.37                      | 904.50           | 895.18                      | 890.25                      |
| \( T_B (M''_4) \)| 904.29                      | 900.52           | 890.36                      | 888.85                      |
symmetry) appears in the tetragonal (or the residual cubic) matrix at $T_{B2}$, which leads to some new dynamics and a new frequency dispersion for the temperature-dependent dielectric permittivity, resulting in the re-entrant relaxor behavior. The dielectric anomaly near 680 K ($T_{RR}$) shows a strong frequency dispersion, suggesting the formation of re-entrant relaxor. The new PNRs grow up with the decrease in temperature, and its size reaches maximum at $T_c$ when the interaction between PNRs is the strongest and $\beta$ has the smallest. Finally, the new PNRs are frozen below $T_c$. Below $T_c$, the temperature dependence of $P_c$ is attributed to the $P4mm$ ferroelectric microdomains and frozen PNRs. Meanwhile, $P_c$ slightly increases with temperature because of the re-orientation of the thermally activated PNRs.

**3. Conclusions**

The complex perovskite oxide $0.6B_{1-x}MT-0.4PT$ near the morphotropic phase boundary (MPB) between the tetragonal and the pseudo-cubic phase was prepared. Re-entrant dipole glass behavior of $0.6B_{1-x}MT-0.4PT$ ceramics was characterized by the Vogel–Fulcher law and the phenomenological statistical model. As the key feature of relaxors, the size of PNRs in paraelectric and ferroelectric states is found to be in the range of 0.93–1.06 nm and 2.75–2.76 nm, forming the re-entrant relaxor transition and the DPT, respectively. Furthermore, it is found that three critical temperatures can be seen both in $\beta$ and in relaxation time, associated with the freezing and formation of PNRs, which is affected by the stoichiometry of bismuth. This investigation
makes the dynamic behavior of PNRs clear and provides insights as modifying the re-entrant relaxor behaviors.

4. Experimental Section

The ceramics 0.66Bi(1−x)(Mg1/2Ti1/2)O3-0.4PbTiO3 with x = −0.02, 0.00, 0.02, 0.04 (06Bi1−xMT-0.4PT), which have a perovskite structure, were prepared with high purity raw materials and sintered at 1050–1100 °C for 3 h in air by a two-step procedure.[24]

Room temperature crystal symmetry of the ceramics was analyzed by a PANalytical X-Pert-PRO powder X-ray diffractometer with CuKα radiation (λ = 1.54059 Å). Full-profile Rietveld refinements were performed using the software package FULLPROF. The peak profile shape was described by a pseudo-Voigt function. For each composition, thermal etching was performed at 1000 °C for 30 min. The surface microstructure of the ceramics was examined using a field emission scanning electron microscope (FE-SEM, Model S4800, Hitachi, Japan). The samples were polished and coated with silver paste on both sides for electric measurements. The dielectric properties of the ceramics were measured using an impedance analyzer (Agilent 4294A, America) connected to a tube furnace. The probing frequency ranges from 100 Hz to 1 MHz, and the temperature ranges from 300 to 960 K. The ferroelectric hysteresis loop P(E) and the leakage current were measured using a ferroelectric test system (TF 2000 aixACCT Systems GmbH, Germany) with triangular voltage waveform at 1 Hz in the temperature range from 293 to 453 K. Impedance spectroscopy was collected using an impedance analyzer (Agilent 4294A, America) from 520 to 960 K.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
dielectric relaxation, ferroelectrics, polar nanoregions, re-entrant dipole relaxor

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