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Temperature-dependent volume fraction of polar nanoregions in lead-free $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ ceramics

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The formation and temperature evolution of polar nanoregions (PNRs) in relaxor ferroelectrics is an intriguing issue that is still under debate. Therefore, we present an approach to estimate the volume fraction of PNRs by the example of the relaxor ferroelectric, $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNT-xBT). A detailed analysis of the Young's modulus, which is highly sensitive to small structural distortions, at temperatures $25\,^\circ\mathrm{C} < T < 800\,^\circ\mathrm{C}$ for both poled and unpoled samples, is correlated to the temperature evolution of PNRs by utilizing a composite model. The extracted volume fraction of the PNRs and the increasing Young's modulus above the formerly suggested Burns temperature indicate that the formation of the PNRs does not occur at a defined temperature but rather in a broad temperature range starting around $\sim 720\,^\circ\mathrm{C}$.

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I. INTRODUCTION

Although relaxor ferroelectric (RFE) materials were discovered by Smolenskii and Agranovskaya [1] 60 years ago, their unique dielectric, electromechanical, and electro-optical properties as a result of site and charge disorder still attract considerable attention due to several unresolved questions. In particular, the understanding of the physical nature of the relaxor state is still scientifically intriguing and calls for further debate.

Within the years, different models [2–5] were proposed to describe the macroscopic features of relaxor systems. To date, the widely accepted picture of the relaxor state supported by several experimental studies [2,6–13] is related to the existence of dipolar entities described as polar nanoregions (PNRs) embedded in a nonpolar matrix. A deviation of the refraction index [14] and the dielectric susceptibility [15] from the standard displacive ferroelectric (FE) behavior was associated with the formation of PNRs at the so-called Burns temperature (T_B) during cooling. With decreasing temperature, the PNRs start to grow, resulting in different relaxation times and a frequency dispersion of the permittivity (ε). Dependent on the coupling between the PNRs and the surrounding matrix, the system can undergo a spontaneous phase transition from the RFE phase into a long-range FE phase with macroscopic domains during cooling [16,17]. In canonical relaxors such as that found at the morphotropic phase boundary in the $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNT-xBT) system [18,19], however, such a FE phase can be induced only by application of an electric field [2,7,20]. In comparison to the domain structure evolved from a spontaneous phase transition, the domains in a field-induced FE phase are aligned with the external field, i.e., the material is poled. However, the stability of the FE phase strongly depends on the temperature. Above the freezing temperature (T_f), the relaxor is in an ergodic state, and a field-induced domain structure would transform back to the initial relaxor state when the external field is removed. Below T_f, where the relaxor is in the nonergodic state, an induced FE phase remains stable, even after the removal of the external field. During heating from the FE phase, a phase transition into the relaxor phase at the RFE transition temperature (T_{F-R}) occurs.

Despite this commonly accepted picture, the mechanisms of the formation of PNRs and its temperature evolution remain unclear [13,21–23]. In the past, this question was approached by utilizing different experimental methods like neutron scattering [11,24], Brillouin spectroscopy [25–27], Raman analysis [13], and dielectric spectroscopy [22] performed on lead-based relaxor systems. These techniques are hampered by the small size of a few nanometers of the PNRs, which is smaller than the coherence length of the diffracting beam, and by multiple sources for dielectric signals such as ionic and interfacial polarization. However, the studies revealed an off-centering of the Pb ion and the concurrent presence of polarization, which persists well above T_B. Therefore, it was proposed that PNRs may already form at temperatures higher than T_B, and a model based on the fast and slow motion of off-centered Pb ions was considered [11,13,24]. The presence of local distortions in the high-temperature phase was also observed in BNT based systems via x-ray absorption fine structure (XAFS) spectroscopy [28] and transmission electron microscopy (TEM) studies [23]. In the case of BNT-xBT, a variety of reported Burns temperatures occurs, as well as its dependence on the BT content [23,29,30].

Details about the formation and temperature-dependent volume fraction of PNRs have remained elusive [11,31]. In this approach, we utilize the high sensitivity of the Young's modulus (Y) towards small structural changes as a signature for the interatomic forces, i.e., the lattice strain, described by the Lennard-Jones interatomic potential [32] to determine T_B and to give a quantified trend of the evolution of the PNRs.

The temperature dependent Young's modulus of a ceramic, in the absence of any structural changes, reveals an approximately linear decrease at elevated temperatures [33]. This behavior is based on the weakening of the atomic bonding due to the increase in the lattice constants with temperature also known as lattice anharmonicity. In the vicinity of a phase transition, e.g., at a FE to paraelectric transition, the Young's modulus presents a sharp decrease [34,35]. Studies of the temperature dependence of the elastic properties of several

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relaxor materials feature a broad asymmetrical minimum [36–38]. The deviation from the linear behavior during cooling was attributed to the formation of the PNRs below T_B [37,39].

Precursor softening in the paraelectric phase was found for several FEs; therefore, the well-established term can be found in the literature describing the observed softening in RFEs as well, beside the fact that the particularly large softening effect in such materials is driven by the coupling of the PNRs with the phonon interaction below T_B [25–27,40,41].

Salje *et al.* [40] referred the softening in the cubic phase in $BaTiO_3$ ceramics to the appearance of PNRs above the tetragonal-cubic phase transition temperature. Thereby, a temperature dependence in the form of Vogel-Fulcher dynamics was found and was correlated to the softer nature of the PNRs in comparison to the cubic matrix, while phonon soft mode interaction could be excluded due to the absence of a power law dependence.

In this paper, we would like to continue the idea of Salje *at al.* [40] and consider the difference in elastic modulus between the PNRs and the cubic matrix as the primary reason for the observed softening. Similar results were found in lead containing relaxors by measuring the acoustic wave velocity as well as Brillouin shift as function of temperature. Both can be related to the elastic properties and their anomalous behaviors during cooling are correlated with the onset of the formation of PNRs below T_B [42,43].

Although the temperature dependent elastic modulus has been determined for relaxors before, the data were not evaluated in order to provide physical insight into the evolution of the volume fractions of participating phases, such as PNRs, nor was the field-induced FE phase investigated due to the lack of measurements with poled samples.

II. EXPERIMENTAL DETAILS AND COMPOSITE MODEL

To study the temperature evolution of PNRs, the lead-free BNT-xBT ($x = 3,\ 6,\ 12$ mol%) relaxor system was investigated, utilizing resonance frequency damping analysis (RFDA) and dielectric spectroscopy. Thereby, measurements were expanded to electrically poled samples in order to give insight into the effect of field-induced FE phases on the elastic properties. The temperature evolution of PNRs could be determined by calculating the volume fraction of PNRs present in the relaxor phase.

To extract the volume fraction of the PNRs, the material is assumed as an isotropic composite, consisting of PNRs as spherical inclusions with a tetragonal ($P4bm$) structure, surrounded by a nonpolar cubic ($Pm\bar{3}m$) matrix. The Young's moduli of the two phases [cubic matrix: $Y_{\mathrm{cub}}(T)$, tetragonal PNRs: $Y_{\mathrm{tet}}(T)$] were assumed to be linear functions of temperature in the observed temperature regime from room temperature up to 800 °C. To obtain $Y_{\mathrm{cub}}(T)$, linear functions were fitted above the maximum in $Y(T)$ for each composition. At this temperature, only the cubic phase should be present, and additional measurements up to 900 °C (not shown here) confirmed the assumption that further heating results in an unchanged linear decrease of the Young's modulus. While the Young's modulus of the pure $P4bm$ structure could not been accessed directly, $Y_{\mathrm{tet}}(T)$ was determined from a linear fit between room temperature and 100 °C for BNT-12BT. Consistent across the different phase diagrams of BNT-xBT [23,44,45], BNT-12BT is observed to be in the FE tetragonal phase in this temperature range. Even though the tetragonal structure of BNT-12BT is $P4mm$ and therefore varies from the tetragonal $P4bm$ structure of the PNRs, no significant difference between the two Young's moduli is expected, especially with regard to $Y_{\mathrm{cub}}(T)$ and therefore are used interchangeably in the presented approach.

The overall bulk modulus (κ) of an isotropic composite with spherical inclusions can be derived with the model from Weng [46]:

$$\kappa = \kappa_M + \frac{\kappa_M c_I}{\frac{3c_M\kappa_M}{3\kappa_M+4\mu_M} + \frac{\kappa_M}{\kappa_I-\kappa_M}}, \tag{1}$$

where c_i is the volume fraction and μ_i is the shear modulus of the corresponding phase, indexed with the indices M and I for the matrix and inclusion, respectively. With the coupling between κ, μ, Y and the Poisson's ratio (ν),

$$\kappa = \frac{Y}{3(1-2\nu)}, \tag{2}$$

$$\mu = \frac{Y}{2(1+\nu)}, \tag{3}$$

and the condition that the volume fraction of the phases in fractional units must sum to unity ($c_M + c_I = 1$), it is possible to solve Eq. (1) for c_I. Therefore, it is possible to determine c_I as function of temperature by taking $Y_{\mathrm{cub}}(T)$, $Y_{\mathrm{tet}}(T)$, and the measured Young's modulus $Y(T)$ into account.

The BNT-xBT samples were synthesized using the conventional solid-state oxide route described elsewhere [47]. Two sample geometries were prepared: (i) cylindrical pellets for the dielectric measurements, with a thickness of 0.7 mm and diameter of 7 mm, and (ii) rectangular bars for the RFDA of $4 \times 26 \times 3\ \mathrm{mm}^3$. Internal stresses induced by the processing steps were relieved by annealing at 400 °C. Electrical contact for the poling process was provided through sputtered silver electrodes. Poling was carried out at 150 °C with a field of 2 kV/mm for 5 minutes followed by field-cooling to room temperature. The temperature-dependent permittivity of the pellets was measured in a box furnace (LE4/11/R6, Nabertherm GmbH, Lilienthal, Germany) with an impedance analyzer (HP-4192A, Hewlett-Packard Co., Palo Alto, CA, USA) at a heating rate of 2 °C/ min between room temperature and 500 °C. The measurement frequencies were 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

The Young's modulus was measured using a resonance frequency and damping analyzer (RFDA-HT1750, IMCE, Genk, Belgium). In this nondestructive method, the poled bars were mechanically excited by a light impulse of an electromagnetic cylinder, hitting the sample in the face center, parallel to the poling direction. The sample was held by two wires at the nodes of the standing resonance wave. Therefore, it could oscillate freely, and the time-dependent acoustic signal was recorded with a microphone. The calculation of the frequency spectrum was performed by processing the signal via fast Fourier transformation. With the obtained resonance frequency (between 15 kHz and 18.5 kHz), the sample geometry, mass, and Poisson's ratio ($\nu = 0.27$ [48]), the Young's modulus was calculated according to ASTM E

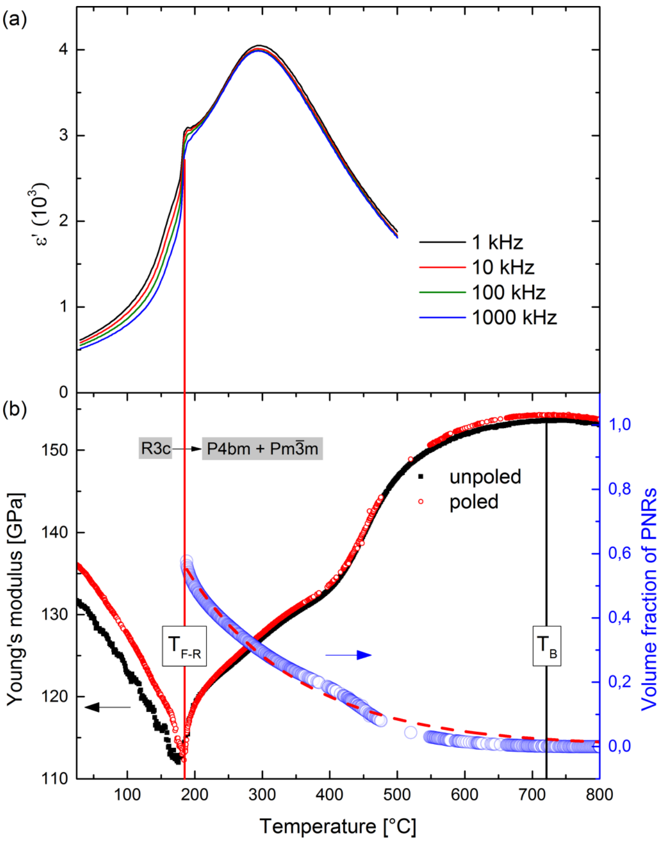

FIG. 1. Frequency-dependent permittivity of poled (a) and Young's modulus for poled and unpoled (b) BNT-3BT during heating. Evolution of the volume fraction of the PNRs (b) is calculated between T_{F-R} and 800 °C and fitted by an exponential decay function (dashed line).

1876–99 [49]. Temperature dependent measurements were performed in a furnace with a heating rate of 2 °C/min between room temperature and 800 °C.

III. RESULTS AND DISCUSSIONS

The temperature dependent real part of the permittivity (ε') for poled BNT-3BT is provided in Fig. 1(a). The BNT-3BT features FE behavior at room temperature with a rhombohedral structure ($R3c$) [23,50]. Upon heating, BNT-3BT undergoes a phase transition from FE $R3c$ to relaxor phase at $T_{F-R} = 180°\mathrm{C}$. The FE-RFE transition is accompanied by a steep increase of the permittivity. Previous x-ray diffraction (XRD) analysis suggested a structural phase transition from rhombohedral to the higher symmetry cubic phase at T_{F-R} for compositions 3 mol% $\leqslant x \leqslant$ 5 mol%. However, neutron powder diffraction studies revealed also a structural phase transition at which rhombohedral distortion vanishes, and tetragonal ($P4bm$) distortion appears [50]. Hence, the structural studies suggest that the high-temperature relaxor phase in BNT-3BT consists of PNRs with tetragonal structure. In addition to permittivity measurements, the temperature evolution of Y for BNT-3BT is depicted in Fig. 1(b). The room temperature value of the unpoled sample is in agreement with the results of Ogawa ($Y = 130$ GPa) [51]. With increasing temperature, a sharp minimum at 175 °C signifies the transition from FE to relaxor phase. The poled sample features an enhancement in Y from room temperature to T_{F-R}, in compliance with the results for classical FE, which is referred to lattice and domain wall contribution due to the reorientation of domains with different Y along the axes of the unit cells [52]. For the poled sample, a shift of T_{F-R} of $\sim$10 °C to higher temperatures is observed, consistent with permittivity measurements (not shown for the unpoled sample). The alignment of the domains with the poling field increases the internal electrical fields and therefore increases the energy barrier, which needs to be overcome to transit from the FE to the relaxor phase. Above T_{F-R}, the unpoled and poled sample feature the same temperature dependence, indicating no structural differences between them. The Young's modulus increases monotonically with a change in slope at about 410 °C. The physical reason behind the occurrence of the slope change is still under discussion: Cordero *et al.* [30] related a tetragonal to cubic phase transition. This anomaly fades away for compositions $x > 5$ mol%, suggesting that the correlation length of the tetragonal distortions must be very small [30]. Carpenter *et al.* [53] observed the change in slope in $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ as well and related it to the condensation of quasistatic PNRs during cooling.

It should be emphasized that the increase in Y is driven by structural changes, namely the evolution of PNRs with temperature. The Burns temperature for BNT-3BT is reported to be at $T_B \sim 421$ °C [29]. It is expected that Y reflects a linear decrease at temperatures above T_B due to the temperature-dependent softening of a stable cubic phase [53]. However, an increase in Y is still observed above T_B, indicating that the material did not transform completely into a pure cubic phase. An onset of the expected linear decrease was finally observed at 723 °C. The increase of Y above T_B can be interpreted as a consequence of the local distortion present in the cubic structure. This implies that PNRs are not formed at particular temperature but rather in a broad temperature range. This suggestion is supported by the neutron diffraction studies on lead-based relaxors done by Egami *et al.* [21], who observed distortions in the structure up to temperatures several hundreds of degrees above T_B. Furthermore, TEM studies on BNT-xBT ceramics also revealed the presence of a cubic structure with local distortion in the high temperature region [23]. Therefore, we define T_B in consistence with Carpenter *et al.* [53] at the maximum of Y. This approach is additionally supported by Tsukada and Kojima [42] and Smirnova *et al.* [43], who correlated the onset temperature of the deviation of the observed linear behavior during cooling in the Brillouin shift and wave velocity as T_B in lead-containing RFE.

To reflect the evolution of PNRs as a function of temperature, the volume fraction of PNRs was calculated using the model of spherical inclusions in an isotropic matrix. The determined volume fraction of PNRs decreases with increasing temperature [Fig. 2(b)]. In a first approximation, the temperature profile of the volume fraction of PNRs can be fitted by the simple exponential decay ansatz,

$$c_I(T) = c_0 e^{-(T-T_0)/\lambda}, \tag{4}$$

where $c_0 = 0.55$ is the initial volume fraction of the PNRs at $T_0 = T_{F-R}$ and $\lambda = 167$ °C is the exponential decay constant.

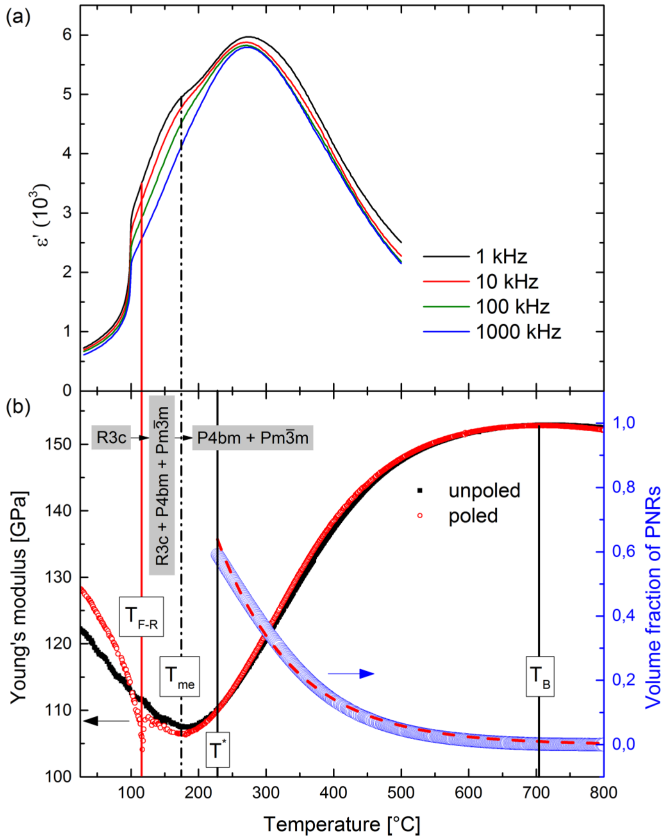

FIG. 2. Frequency-dependent permittivity of poled (a) and Young's modulus for poled and unpoled (b) BNT-6BT during heating. Evolution of the volume fraction of the PNRs is calculated between T^* and 800 °C and fitted by an exponential decay function (dashed line).

When approaching T_B, the volume fraction of the PNRs becomes almost zero, as expected from theory. The change in slope of the Young's modulus is also reflected in the extracted volume fraction.

Unlike the BNT-3BT, which undergoes a spontaneous phase transition from relaxor to FE phase, BNT-6BT remains in a relaxor phase with pseudocubic structure if cooled in the absence of external electric field [54]. Upon poling, BNT-6BT undergoes a field induced phase transition, developing a FE $R3c$ domain structure [19,31,54,55]. Therefore, the permittivity curves for poled BNT-6BT exhibit a steep increase in the permittivity depicted in Fig. 2(a) during heating, corresponding to the FE-RFE transition [54,55]. The macroscopic domains are stable until $T_{F-R} = 100-110\,^\circ$C, where the domains dissolve into an ergodic RFE state, composed of rhombohedral $R3c$ and tetragonal $P4bm$ PNRs surrounded by a cubic $Pm\bar{3}m$ matrix [19,31,55,56]. Beyond this transition, strong frequency dispersion was observed, which vanishes several degrees below $T_m = 272\,^\circ$C; this feature is typical for the BNT-6BT composition [54,56]. Jo *et al.* [55] rationalized its origin by the coexistence of $P4bm$ and $R3c$ PNRs at temperatures below the shoulder. Above the shoulder, only $P4bm$ PNRs and the cubic $Pm\bar{3}m$ matrix exist. Both features can be found in the evolution of Y as well [Fig. 2(b)]. The T_{F-R} manifests itself as a very sharp minimum at 117 °C, which is absent for measurements on the unpoled sample. This comparison proves how sensitive the elastic properties are in respect to structural changes and that the observation of Y as function of temperature can be exploited to determine T_{F-R}. At temperatures close to the shoulder of the permittivity, a broad minimum is found in Y ($T_{\text{me}} = 175\,^\circ$C), correlating well with the results reported in the literature [30,57]. Yao *et al.* [57] interpreted the broad minimum as a strain glass transition. However, we consider the minimum to belong to the diffuse transition of the PNRs from $R3c$ to $P4bm$ [55]. Comparison between the poled and unpoled sample below T_{F-R} reveals an increase in Y attributed to similar effects discussed already for BNT-3BT. In contrast to BNT-3BT, the poled and unpoled Young's modulus differ above T_{F-R} and only coincide about 100 °C above it, denoted here as T^*. The deviation between the unpoled and poled Y for $T_{F-R} < T < T^*$ indicates that there are still structural differences in both samples due to the poling procedure. This could be explained due to remaining FE domains as well as remaining rhombohedral PNRs in the previously poled sample up to T^*. This is consistent with the persistence of a piezoelectric coefficient [58,59] and a depolarization current [60] in BNT-6BT even above T_{F-R}. Therefore, the calculations of the volume fraction, based on a two-phase-composite model, can be applied only at temperature above T^*, where it is assumed that only $P4bm$ PNRs exists. The exponential decay with $T_0 = T^*$ describes the evolution with an initial volume fraction of $c_0 = 0.64$ and $\lambda = 114\,^\circ$C. In contrast to BNT-3BT and in agreement with Cordero *et al.* [30], no change in slope is observed in BNT-6BT. With increasing temperature, the volume fraction of PNRs decreases and finally disappears at the maximum of Y around $T_B \sim 704\,^\circ$C, which is about 100 °C higher in comparison to literature [23,30].

The unpoled BNT-12BT exhibits a spontaneous phase transition into a FE phase upon cooling similar as BNT-3BT. In contrast to the $R3c$ structure of the domains in BNT-3BT, the structure is observed to be $P4mm$ [23,61]. Upon heating, the FE-RFE phase transition is reflected in a steep increase in the permittivity and a minimum in the Young's modulus, depicted in Fig. 3. With poling, T_{F-R} is shifted from 140 to 175 °C, and the minimum is more pronounced. Similar to BNT-6BT, the overlapping of Y between the unpoled and the poled state does not occur immediately above T_{F-R} but at a higher temperature, $T^* = T_0 = 274\,^\circ$C. A fitting of the calculated temperature-dependent volume fraction of the PNRs with Eq. (4) revealed an initial volume fraction of $c_0 = 0.62$ and $\lambda = 116\,^\circ$C. The Burns temperature of $T_B \sim 715\,^\circ$C was determined considering the maximum in Young's modulus.

The initial volume fractions of PNRs were evaluated to lie between 0.55 and 0.64 for the three compositions. There is very limited literature available, which attempted quantification of this key parameter. Groszewicz *et al.* [31] utilized nuclear magnetic resonance and determined a volume fraction of the noncubic phase of 0.75 for BNT-6BT, albeit at room temperature, which appears consistent to our result. Jeong *et al.* [11], using neutron pair distribution function, found a maximum volume fraction of 0.30 of PNRs with a broad decay of ~500 °C until the volume fraction reaches zero, but in $Pb(Mg_{1/3}Nb_{2/3})O_3$. These data again appear consistent, but more so demonstrate the utility of our approach, utilizing Y to extract temperature-dependent volume fractions.

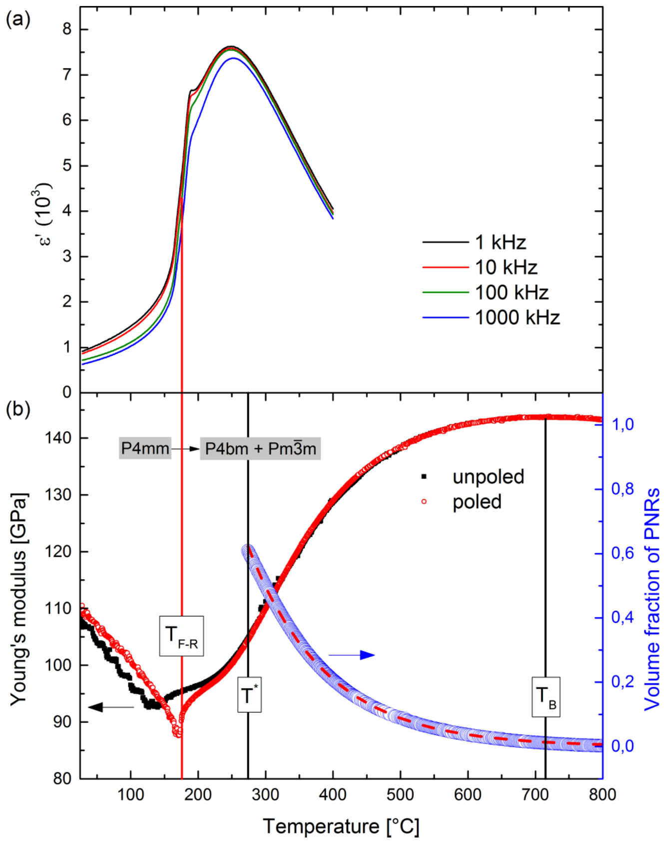

FIG. 3. Frequency-dependent permittivity of poled (a) and Young's modulus for poled and unpoled (b) BNT-12BT during heating. Evolution of the volume fraction of the PNRs is calculated between T^* and 800 °C and fitted by an exponential decay function (dashed line).

IV. CONCLUSIONS

In summary, both the dielectric response and the evolution of the Young's modulus with temperature of the BNT-xBT ceramic have been investigated by impedance analysis and RFDA. In all three compositions, the FE to relaxor transition temperature could be observed by explicit features in the measurements. The results of BNT-6BT are remarkable, in which the FE phase was induced by poling. In comparison to the unpoled sample, a sharp minimum was observed at T_{F-R}. This underpins the utility of elastic studies as a tool to determine the mentioned transition temperatures in relaxor materials as an alternative to dielectric measurements. Even more, the absence of the linear decrease in Young's modulus expected above the reported Burns temperature suggests the existence and the formation of the PNRs at much higher temperatures. Therefore, an approach to determining the volume fraction of the PNRs, utilizing a two-phase-composite model, was presented. The temperature evolution of the PNRs was described with an exponential decay function, which revealed an initial volume fraction of 0.55 to 0.64 for BNT-xBT. In addition, the volume fraction of the BNT-3BT features a small anomaly, which may suggest two competing decay mechanisms of PNRs or an additional phase transition present in the relaxor phase.

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