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Citation: Journal of Applied Physics 116, 104102 (2014); doi: 10.1063/1.4894630
View online: http://dx.doi.org/10.1063/1.4894630
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/116/10?ver=pdfcov
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Eva Sapper, Robert Dittmer, Dragan Damjanovic, Emre Erdem, David J. Keeble, Wook Jo, Torsten Granzow, and Jürgen Rödel

1Materials Science Department, Technische Universität Darmstadt, 64287 Darmstadt, Germany
2Ceramics Laboratory, École Polytechnique Fédérale de Lausanne, Lausanne 1015, Switzerland
3Institute of Physical Chemistry I, Universität Freiburg, 79104 Freiburg, Germany
4Division of Electronic Engineering and Physics, University of Dundee, Dundee DD1 4HN, United Kingdom
5School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan 687-798, South Korea
6Centre de Recherche Public—Gabriel Lippmann, L-4422 Belvaux, Luxembourg

(Received 7 May 2014; accepted 23 August 2014; published online 9 September 2014)

Aging of piezoelectric properties was investigated in lead-free (1 – x)(Bi_{1/2}Na_{1/2})TiO_3-xBaTiO_3 doped with 1at. % Fe. The relaxor character of the un-poled material prevents macroscopic aging effects, while in the field-induced ferroelectric phase aging phenomena are similar to those found in lead zirconate titanate or barium titanate. Most prominent aging effects are the development of an internal bias field and the decrease of switchable polarization. These effects are temperature activated, and can be explained in the framework of defect complex reorientation. This picture is further supported by electron paramagnetic resonance spectra indicating the existence of (Fe^{3+} – V_{O}) defect complexes in the Fe-doped material. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894630]

INTRODUCTION

Acceptor-doping of ferroelectrics is a key tool for tailoring piezoelectric properties since it lowers dielectric losses and increases the mechanical quality factor. Furthermore, it can modify the piezoelectric hysteresis such that the usable strain is increased when compared to un-doped materials. Aging is intrinsically connected to acceptor-doping, and is defined as the time-dependent change of piezoelectric properties. Thus, the application of acceptor-doped piezoelectrics calls for the quantification of aging effects as well as for a detailed understanding of the underlying mechanism. While aging is well-described in perovskite-structured materials with long-range-order, information on relaxors is scarce. In particular, effects in the field-induced ferroelectric state have not yet been investigated. Studies on aging in relaxors, so far, have been limited to the decrease of permittivity with aging time and the so-called memory-aging.

In conventional ferroelectrics such as BaTiO_3 (BT), PbTiO_3 (PT), and Pb(Zr_{x}Ti_{1-x})O_3 (PZT), two fundamental models have been developed to describe the aging mechanism. Both are based on the fact that acceptor-doping creates oxygen vacancies, which in the course of aging diffuse to lower energy lattice sites. The resulting electric field has a contribution from time-dependent clamping of the domain wall motion. Macroscopically, this leads to a decrease of the permittivity, an increased coercive field, or pinched polarization loops, and, in poled samples, to the development of an internal bias field $E_{bias}$. The “domain wall”- or “boundary”-model assumes the formation of space charges at domain walls, near grain boundaries or beneath electrodes. Charges move under the driving force of the depolarizing field, arising from the spontaneous polarization of domains. Subsequently, they pile up near initially uncompensated bound charges, e.g., at charged domain walls or grain boundaries in polycrystalline ceramics. The resulting asymmetric charge distribution then leads to the formation of an internal bias field. In contrast, the “defect dipole model” is based on the formation of defect dipoles within the unit cell, consisting of the acceptor ion and a bound oxygen vacancy. The defect dipole model was first described by Arlt and Neumann in BT, where Ti^{4+} on the B-site is replaced by Ni^{2+}. Together with an oxygen vacancy, created for charge compensation, Ni forms a defect dipole. This dipole can orient by vacancy diffusion within the oxygen octahedron. Calculations show that the lowest energy level in this system belongs to a defect dipole with its dipole moment $P_d$ in parallel to the spontaneous polarization of the cell $P_s$. This is the favored configuration also in PT doped with Fe or Cu. Acceptor dopants with an oxidation state different from 2+ (like, e.g., Fe^{3+}) can associate with oxygen vacancies as well. These aggregates, however, carry a net charge. Since dipoles are by definition neutral, charged defect combinations will be termed “defect complex” in the following. A microscopic explanation for aging in ferroelectrics and ferroelastics has been proposed by Ren and Otsuka. This model relates aging effects to symmetry-conforming short-range ordering of defects. Ferroelectric and ferroelastic states age due to atomic rearrangement in low-symmetry structures. Hence, so-called symmetry conforming defects are formed via short-range diffusion of atoms. These symmetry-conforming defects stabilize the structure and thus provide a restoring force when the material is subjected to electric field or mechanical deformation.

While the defect dipole (or defect complex) model can explain well the time and temperature dependence of aging,
its dependence on the doping level can only be modelled with the boundary model.\textsuperscript{12} Yet, single crystal experiments show the complete restoration of an aged domain pattern after a short excursion to the paraelectric state or after the application of a suitable electric field.\textsuperscript{19} These findings are only consistent with the defect complex model.\textsuperscript{20} Thus, it is complicated to assign aging effects to exclusively one model. Still, the diffusion-related character of aging, common to both models described above, is underlined by the fact that aging can be inhibited by fast cooling of the samples from the paraelectric state.\textsuperscript{21} Furthermore, repeated electrical cycling can introduce enough energy to randomize defects in the already aged state and reverse aging effects.\textsuperscript{3,21,22}

Versatile applications for hard-doped PZT motivated doping studies with acceptors also in (1−x)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$−xBaTiO$_3$ (BNT-100xBT) based materials,\textsuperscript{20,21} which are potential lead-free substitutes for PZT. In contrast to PZT or BT, however, the typical effects of acceptor-doping are less clear in BNT-based materials. This might be partially due to the fact that many of these compounds are relaxors with a polar structure different from that of ferroelectrics.\textsuperscript{23} Fe-doping in the base-compound BNT only leads to a slight increase of the coercive field, while pinching of the hysteresis was not observed in un-poled samples.\textsuperscript{24} Furthermore, the permittivity in Fe-doped samples ages more slowly than in un-doped BNT.\textsuperscript{25} This finding is contrary to the expectations and was explained with an increased relaxor character due to Fe-doping. Another indication of increasing relaxor character with acceptor-doping is the increased permittivity in Mn-doped BNT single crystals.\textsuperscript{26}

A comparison of acceptor-doping with Fe$^{3+}$ and donor doping with Nb$^{5+}$ in 0.92(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$−0.06BaTiO$_3$−2(K$_{0.5}$Na$_{0.5}$)NbO$_3$ (BNT-6BT-2KNN) reveals that the ergodic relaxor character of the material partly conceals the effects of the dopants, since already the un-doped material displays a constricted $P(E)$ hysteresis. Therefore, hardening effects like pinching of the ferroelectric hysteresis curve, the increase of the coercive field, or the development of an internal bias in poled samples are hard to determine. In contrast to reports on Fe-doped BNT in Refs. 23 and 25, $P(E)$ and $S(E)$ loops in Fe-doped BNT-6BT-2KNN indicate that the ferroelectric order in BNT-6BT-2KNN is enhanced when compared to the un-doped or donor-doped material.\textsuperscript{27} Also in BNT-8BT modified with 0.3 wt. %, MnO hardening effects are observed in the form of an increased mechanical quality factor $Q_m$.\textsuperscript{28} Yet the results do not allow conclusions to be drawn if the increase in $Q_m$ is directly related to a microscopic hardening or simply due to a modified grain structure and improved poling behavior by Mn-addition. Acceptor-doping with Fe or Mn in 0.88[(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$]−0.08[(Bi$_{0.5}$K$_{0.5}$)TiO$_3$]−0.04[(Bi$_{0.3}$Li$_{0.5}$)TiO$_3$] leads to increased $Q_m$ as well.\textsuperscript{29} While some dopants improve the properties of BNT-100xBT, the effects of acceptor-doping in lead-free piezoelectric ceramics and their correlation to aging are not well-understood and systematic studies are missing. Therefore, it appears timely to evaluate the suitability of aging mechanisms known in PZT when applied to the lead-free system BNT-100xBT, and expand understanding on the possible role of the relaxor character of the material.

In this study, the time- and temperature-dependent changes in piezoelectric parameters are investigated in four different compositions of BNT-100xBT doped with 1 at. % Fe. The region of the morphotropic phase boundary (MPB) including rhombohedral and tetragonal symmetries was covered. Since crystal structure and domain structure change with the barium titanate content, the aging effects are expected to depend on the percentage of BaTiO$_3$. Piezoelectric properties after different aging treatments serve as a measure for the aging effects. In addition, electron paramagnetic resonance (EPR) provides insight into the microscopic mechanism of defect complex formation and the effect of electrical poling.

**EXPERIMENTAL**

Ceramic disc-shaped samples of BNT-100xBT:1Fe with $x=0.01, 0.04, 0.06,$ and 0.15 were prepared by the conventional solid state route described elsewhere.\textsuperscript{30} In all of the compositions 1 at. % of the Ti content was replaced by Fe. The ceramic powders were calcined at 700 °C and 900 °C for 2 h each and then pressed first uniaxially and then isostatically. The green bodies were then sintered at 1150 °C for 3 h. To prevent the loss of volatile species, the samples were embedded in powder of the original composition. The sintering conditions were kept constant in all compositions to avoid different defect concentrations due to different sintering protocols. After sintering, the sintered skin was removed by grinding and polishing the specimens to a final geometry of 7 mm in diameter and 500 μm in thickness. Samples for EPR measurements were further cut to 5 mm length and 1 mm width to reduce the microwave absorption of the samples. The density was determined on polished samples according to the Archimedes method and the microstructure of sintered samples was investigated by scanning electron microscopy (SEM). After polishing, the samples were annealed at 450 °C for 2 h to remove residual stress from the mechanical treatment. Annealing and aging temperature protocols were executed in a Nabatherm furnace. For the electrical characterization, silver electrodes were sputtered on and an additional layer of silver paste was applied and burnt in to ensure mechanical and thermal stability of the electrodes. In the case of quenched samples, air-dried silver paint was used as electrode to avoid the influence of the burn-in process on the thermal history of the sample. Comparative measurements proved that the coercive field and the remanent polarization were not influenced by the type of electrode.

The ferroelectric and piezoelectric characterizations were performed at around 22 °C with an aixPES piezoelectric evaluation system (aixACCT Systems, Aachen, Germany). To prevent electrical flashover, the samples were immersed in silicone oil during the measurement. All measurements were executed with a bipolar triangular signal starting in positive field direction at 100 mHz. For measurements of the field-dependent relative permittivity $\varepsilon_{33}(E)$, the piezoelectric coefficient $d_{33}(E)$, and the loss angle $\tan \delta(E)$, an additional sinusoidal wave with 1 kHz frequency and an amplitude of 20 V/mm modulated the base signal. The temperature-dependent relative permittivity was determined.
with an impedance analyzer (HP 4284A) connected to a Nabertherm furnace. The heating rate was 2 K/min. To induce aging, the samples were subjected to different temperature protocols in the un-poled state as well as in the poled state. In all cases, they were short-circuited with aluminum foil during the aging procedure.

Un-poled samples were characterized directly after annealing and furnace cooling with a maximum cooling rate of 2 K/min. In addition, the same characterization was performed on quenched samples. In this case, rapid cooling was accomplished by transferring the samples from 450°C into liquid nitrogen. Since poled samples were aged at elevated temperatures, as described later, un-poled samples were aged at the same temperature as reference. For these measurements, furnace cooled samples were heated to the aging temperature with 2 K/min, kept there for 10 h and then were furnace cooled back to room temperature.

In poled samples, aging was investigated at room temperature as well as at elevated temperatures (in the following termed as “high-temperature aging”). Before the poling procedure, the samples were annealed at 450°C and subsequently furnace cooled. Poling was performed with a single bipolar cycle at room temperature according to the measurement signal described above. In the case of BNT-15BT:1Fe, the high-temperature aging procedure was performed also on an electrically de-aged sample, since cycling leads to a larger degree of poling. Thus, larger aging effects were expected in a sample with a higher ratio of oriented domains. De-aging was accomplished with 10^5 bipolar electrical cycles at 10 Hz at the amplitude of 6 kV/mm. The use of a quenched sample for deaging was discarded, since high-temperature-stable electrodes could not be applied on quenched samples.

After poling, samples were kept at the aging temperature and characterized after defined aging times. Aging at elevated temperatures was performed slightly below the transition temperature from the induced-ferroelectric to the relaxor state, \( T_{\text{F-R}} \) (Table I) to accelerate the aging process, while the sample was still in the ferroelectric state. \( T_{\text{F-R}} \) was determined from \( \varepsilon'(T) \) measurements of poled samples (not shown here) as described before for different sample compositions.\(^{31}\) The aging process consisted of heating with a constant rate of 2 K/min to the aging temperature, aging at constant temperature and furnace cooling back to room temperature. The aging temperatures were 150°C for BNT-1BT:1Fe, 120°C for BNT-4BT:1Fe, 60°C for BNT-6BT:1Fe, and 180°C for BNT-15BT:1Fe.

X-Band (9.86 GHz) EPR spectra were collected at 22°C using a Bruker EMX Spectrometer on both poled and un-poled ceramic samples. The poling procedure was the same as that used for the electrical measurement samples. The silver paint electrodes were removed with acetone prior to measurements. The differences in permittivity between un-poled and poled samples resulted in changes in resonator Q-factor. Therefore, spectra were compared by normalizing to the maximum intensity, assuming the Fe\(^{3+} \) concentration is not altered by the poling procedure. Spectra were simulated using the MATLAB toolbox EasySpin.\(^{32}\)

**RESULTS**

This section is divided into two parts. The first part covers aging phenomena in the un-poled state of BNT-100xBT:1Fe and the effect of the poling procedure. In the second part, the formation of the internal bias field and the decrease of switchable polarization \( 2P_e \) are quantified for compositions with \( x = 0.01, 0.04, 0.06, \) and 0.15.

**Basic properties of un-aged materials and EPR results**

The general characteristics of as-sintered samples are summarized in Table I. Scanning electron microscopy (SEM) investigations of the microstructure revealed that the grain size of the doped material varies with the BT-content. It is also larger than in un-doped material sintered under the same conditions, where the grain size is usually below 2 \( \mu m.\)\(^{33}\) The trend in \( T_{\text{F-R}} \) with BT content and room temperature permittivity at 1 kHz is comparable to that in un-doped BNT-100xBT.\(^{34}\) To quantify the relaxor character of the material, the frequency dispersion of un-poled samples was determined at 35°C according to Eq. (1)

\[
\Delta f = \frac{\varepsilon'(1\text{MHz}) - \varepsilon'(100\text{Hz})}{\varepsilon'(100\text{Hz})}.
\]

\( \Delta f \) is lowest in BNT-15BT:1Fe. This is consistent with the finding of a spontaneous relaxor-to-ferroelectric transition upon cooling reported for the un-doped material of comparably high BT content.\(^{35,36}\)

To investigate the oxidation state and the site of incorporation of the dopant, EPR was performed. EPR is an effective tool for probing ions with unpaired electrons such as Fe\(^{3+} \) (\( S = \frac{5}{2} \)).\(^{37}\) The spectra of BNT-1BT:Fe and BNT-15BT:Fe ceramic samples in the un-poled and the poled state shown in Figure 1 (black: poled, grey: un-poled). In literature, so far, only spectra of powder samples have been presented for this material. Thus, the influence of electrical poling has not been reported yet. Samples with \( x = 0.04 \) and \( x = 0.06 \) deliver spectra similar to BNT-1BT:1Fe.

Furthermore, simulated spectra of defect complexes formed by Fe\(^{3+} \) and oxygen vacancies are shown for comparison. Such complexes have been detected in other ferroelectric perovskites previously.\(^{6,38-40}\) The defect complex spectra were simulated with zero-field splitting parameters of \( |B_{2}^{2}| = 12 \text{ GHz} \) for a tetragonal center (i) and \( |B_{2}^{2}| = 6 \text{ GHz} \) and \( |B_{2}^{2}| = 2 \text{ GHz} \) for a rhombic center (ii). In both cases, the line width was 30 mT. The simulated spectra represent different relative orientations of a defect complex with respect to the spontaneous polarization of the unit cell (Figures 1(i)

**TABLE I.** General characteristics of bulk ceramic samples.

<table>
<thead>
<tr>
<th>( x )</th>
<th>Grain size (( \mu m ))</th>
<th>( T_{\text{F-R}} ) (°C)</th>
<th>( \varepsilon' ) 1 kHz un-poled</th>
<th>( \Delta f ) un-poled</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>19.5</td>
<td>185</td>
<td>650</td>
<td>0.22</td>
<td>94</td>
</tr>
<tr>
<td>0.04</td>
<td>7.0</td>
<td>155</td>
<td>830</td>
<td>0.21</td>
<td>96</td>
</tr>
<tr>
<td>0.06</td>
<td>2.5</td>
<td>90</td>
<td>1500</td>
<td>0.24</td>
<td>95</td>
</tr>
<tr>
<td>0.15</td>
<td>7.6</td>
<td>215</td>
<td>570</td>
<td>0.14</td>
<td>95</td>
</tr>
</tbody>
</table>
and (ii)) as well as “free iron,” which is not associated with an oxygen vacancy (Figure 1(iii)).

The most prominent resonance in experimental spectra of both compositions appears at 170 mT with a shoulder at approximately 100 mT. A third resonance occurs at higher fields around 300 mT in un-polled and around 350 mT in poled samples. Due to relatively broad lines, the position of the shoulder at 100 mT is not well resolved. Its relative intensity with respect to the 170 mT resonance, however, is obviously higher in BNT-15BT:1Fe than in BNT-1BT:1Fe. The position of the low-field resonances at 100 mT and 170 mT matches the simulation for defect complexes in both compositions, while the high-field resonance fits the simulation only in the case of poled samples. In un-polled BNT-100xBT the signal at 300 mT can be modelled in a cubic structure, only if an unrealistically high effective g-factor of 2.2 is assumed. For an ideally cubic structure, an effective g-factor of 2.0 is expected. In contrast to the situation in un-polled samples, the resonance at 350 mT in poled samples corresponds well with a g-factor of 2.0. Experimental spectra of poled and un-polled samples differ in signal intensity as well as in line width. Since EPR spectra are conventionally displayed as derivative of the absorption, the intensity of a signal is accessed by integration. In poled samples, the intensity of the signals assigned to defect complexes is increased with respect to the un-polled state. The resonance of free iron on the other hand is broadened, shifted to 350 mT and has a lower intensity than in the un-polled state.

**Aging in un-polled samples**

The ferroelectric hysteresis in Figure 2 display the influence of different temperature protocols on un-polled samples with \( x = 0.01 \) (Figure 2(a)) and \( x = 0.15 \) (Figure 2(b)). Each graph provides \( P(E) \) curves measured directly after the virgin cycle. Pinching of the loop at zero-field, as it appears in Fe-doped PZT, is not observed after any of the treatments. The intermediate compositions BNT-4BT:1Fe and BNT-6BT:1Fe are not shown here do not display signs of hysteresis pinching after furnace cooling, either.

After annealing and furnace cooling BNT-1BT:1Fe (Figure 2(a), black solid line) exhibits a rectangular hysteresis. The switchable polarization \( 2P_r = |P_c| + |P_c| \) is 66 \( \mu \)C/cm\(^2\) and the coercive field \( E_c \) is 5.2 kV/mm. In BNT-15BT-1Fe (Figure 2(b), black solid line), the same temperature protocol results in a narrow and slanted loop with a switchable polarization \( 2P_r \) of only 20 \( \mu \)C/cm\(^2\) and a coercive field of 2.2 kV/mm.

**FIG. 1.** EPR spectra of BNT-1BT:1Fe (a) and BNT-15BT:1Fe (b) un-polled after furnace-cooling (grey) and poled after furnace-cooling (black). (i) Simulated spectrum of a defect complex with tetragonal symmetry, (ii) simulated spectrum of a defect complex with rhombic symmetry, and (iii) simulated spectrum of free iron with two different g-values. All spectra were recorded at 22°C.

**FIG. 2.** \( P(E) \) after different cooling procedures in BNT-1BT:1Fe (a) and BNT-15BT:1Fe (b).
Fast cooling from 450 °C does not induce changes in the hysteresis of BNT-1BT:1Fe (Figure 2(a), red dashed line). Likewise, in compositions with $x = 0.04$ and $x = 0.06$, no prominent effects are observed in quenched samples. The remanent polarization after quenching is comparable to the values after furnace cooling. In BNT-15BT:1Fe, on the other hand, quenching from 450°C significantly increases the loop area (Figure 2(b), red dashed line). $2P_r$ increases to 50 μC/cm$^2$ and the coercive field is 3.4 kV/mm. Furthermore, the slope of the hysteresis curve is considerably steeper than after furnace cooling.

After 10 h of aging at 150°C or 180°C, respectively, no changes are observed in BNT-1BT:1Fe. In BNT-15BT:1Fe, however, $2P_r$ is lowered to 18 μC/cm$^2$ (Figure 2(b), green dotted line), while $E_C$ does not change with respect to the furnace-cooled sample.

### Aging in poled samples

Aging in the poled state leads to shifted and deformed hysteresis curves in all compositions. Exemplarily, BNT-1BT:1Fe (Figure 3) and BNT-15BT:1Fe (Figure 4) are considered in the following. Changes in the hystereses due to high-temperature aging in the poled state of BNT-4BT:1Fe and BNT-6BT:1Fe are qualitatively similar to the effects in BNT-1BT:1Fe and therefore not displayed here. The observed changes of $2P_r$ and the internal bias field $E_{bias}$ are reversed by annealing the samples at 450°C for 2 h.

High-temperature aging phenomena in furnace-cooled and subsequently poled BNT-1BT:1Fe samples are presented in Figure 3. $2P_r$ and the maximum strain $S_{max}$ decrease with increasing aging time at 150°C (Figures 3(a) and 3(b)). The decrease in polarization occurs mostly in the positive poling direction, while the negative value stays constant. At the same time, the $P(E)$ hysteresis shifts along the field-axis towards the positive direction. The shift is defined as internal bias field $E_{bias}$ according to Eq. (2):

$$E_{bias} = -\frac{E^+_C + E^-_C}{2}. \quad (2)$$

Thus, a shift in positive field direction corresponds to a negative bias field. Together with the shift, a contraction of the loop along the x-axis occurs. This is reflected in decreasing $2E_C$ values, where $2E_C = |E_C| + |E_C|$. Due to the combination of both effects, the shift of $|E_C|$ is higher in negative field direction than in positive field direction. In addition, the hysteresis slants gradually and the slope near $E_C$ is reduced.

The strain curve in the u-aged state is symmetric with respect to the y-axis and displays a butterfly shape typical for ferroelectrics (Figure 3(b)). Upon aging, the maximum strain diminishes in both field regimes. Furthermore, the strain curve distorts, since in the positive field regime, the strain $\Delta S^+$ decreases faster than the strain in the negative field regime $\Delta S^-$. The field dependent permittivity displays an overall reduction with aging time (Figure 3(c)). The strongest decrease is observed around $-E_C$, while at positive maximum field, it stays nearly constant. Like the polarization, the piezoelectric coefficient $d_{33}$ in the positive remanent state is reduced more strongly than in the negative state (Figure 3(d)). The shift of the $d_{33}(E)$ loops along the x-axis mirrors the trend observed in the $P(E)$ curves. Near $E_C$, $d_{33}(E)$ displays local maxima, which become less distinct during aging.

High-temperature aging effects in BNT-15BT:1Fe are displayed in Figure 4. After furnace-cooling and poling, the $P(E)$ loop (Figure 4(a)) is slanted and has a comparably low $2P_r$ of 20 μC/cm$^2$. Aging of the poled sample at 180°C has effects different from those observed in BNT-1BT:1Fe. $P(E)$ curves in the aged state are less slanted than the initial ones. Furthermore, $2P_r$ increases slightly. The curves, nevertheless, display the development of an internal bias field with aging. Also the strain curve in the annealed and furnace-cooled state of BNT-15BT:1Fe (Figure 4(b)) differs in shape from the corresponding loop in BNT-1BT:1Fe. The negative strain, which is defined as the difference between the

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** Piezoelectric characterization of annealed and furnace-cooled BNT-1BT:1Fe after different times of aging in the poled state at 150°C. (a) Ferroelectric polarization, (b) piezoelectric strain, (c) field-dependent permittivity, and (d) field-dependent piezoelectric coefficient.
minimum of the strain curve and the remanent strain, is
clearly lower in BNT-15BT:1Fe. It accounts for only a quar-
ter of the total strain in this composition, while in un-aged
BNT-1BT:Fe, the negative strain delivers 50% of the total
strain. With aging, the strain curve of BNT-15BT:1Fe tilts
and after 5 h and 100 h, $\Delta S^-$ is slightly higher than in the ini-
tial state. Aging also distorts the field dependent permittivity
curve displayed in Figure 4(c). While the values drop in the
negative field regime, the permittivity stays constant at maxi-
mum positive field and even increases around $+E_C$ with
respect to the initial state. At the same time, the $d_{33}(E)$ curve
(Figure 4(d)) is shifted towards negative remanent values.

Since the low remanent polarization in BNT-15BT:1Fe
indicates that aging already takes place during furnace-
cooling even in the un-poled state, high-temperature aging
was performed also with an electrically de-aged sample, as
displayed in Figure 5. After cycling, $E_C$ has increased from
2.2 kV/mm in the furnace-cooled state to 2.7 kV/mm (Figure
5(a)). At the same time, $2P_r$ has changed from 20 $\mu$C/cm$^2$ to
38 $\mu$C/cm$^2$. Furthermore, the slope of $P(E)$ near $E_C$ is steeper
in the cycled state as compared to the furnace-cooled state
and the negative strain takes up a larger part of the total
strain (Figure 5(b)) than in the furnace-cooled condition
(Figure 4(b)). Starting from the de-aged state, the effects of
high-temperature aging are similar to those in BNT-
1BT:1Fe. The $P(E)$ curve (Figure 5(a)) shifts towards the
positive field direction and the strain loop (Figure 5(b)) tilts.
In contrast to BNT-1BT:1Fe, however, the $P(E)$ loop does

![Figure 4. Piezoelectric characterization of annealed and furnace-cooled BNT-15BT:1Fe after different times of aging in the poled state at 180 °C. (a) Ferroelectric polarization, (b) piezoelectric strain, (c) field-dependent permittivity, and (d) field-dependent piezoelectric coefficient.](image1)

![Figure 5. Piezoelectric characterization of BNT-15BT:1Fe after different times of aging in the electrically de-aged and poled state at 180 °C. (a) Ferroelectric polarization, (b) piezoelectric strain, (c) field-dependent permittivity, and (d) field-dependent piezoelectric coefficient.](image2)
not constrict along the x-axis during aging. Like in BNT-1BT:1Fe, $e_{33}(E)$ decreases to the largest extent around the negative coercive field (Figure 5(c)) and $d_{33}$ decreases mostly in the positive direction (Figure 5(d)).

The most prominent parameter of aging, $E_{bias}$, is summarized in Figure 6 for room temperature aging of furnace-cooled and poled samples (Figure 6(a)) as well as for high-temperature aging at individually set aging temperatures (Figure 6(b)). For the sake of clarity, only electrically de-aged BNT-15BT:1Fe is included in Figure 6(b) and in the following graphs. In all compositions, the bias field develops more quickly during aging at elevated temperatures. The largest effects are observed in rhombohedral BNT-1BT:1Fe and tetragonal BNT-15BT:1Fe, while the intermediate mixed phase compositions BNT-4BT:1Fe and BNT-6BT:1Fe show smaller effects.

Figure 7 demonstrates correlation of $2P_r$ (Figure 7(a)) and $2E_C$ (Figure 7(b)) with aging time in high-temperature aged samples. Both parameters are normalized with respect to the starting value. With increasing aging time, $2P_r$ decreases in all compositions. In the compositions with $x = 0.01$, 0.06, and 0.15, the loss of switchable polarization is comparable: $2P_r$ after 100 h of aging is reduced by about 25% of the initial value. The effect is lower in BNT-4BT:1Fe, where after 100 h $2P_r$ is still at 83% of the initial value. Interestingly, $2E_C$ displays a different trend. BNT-15BT:1Fe scatters around the initial value, while it has decreased by about 10% in the other compositions after the final aging step.

**DISCUSSION**

The first part of the discussion concentrates on the validity of the defect complex model for BNT-100xBT:1Fe ceramics. Furthermore, the impact of relaxor properties on aging is discussed in comparison with conventional ferroelectrics like PZT. In the second part, the effects of aging in the induced ferroelectric state are addressed.

**EPR spectra of un-poled and poled samples**

The EPR resonances of BNT-100xBT:1Fe depicted in Figure 1 prove the presence of Fe$^{3+}$ in all samples, since Fe$^{3+}$ resonances do not appear in X-band spectra. The ionic radius of Fe$^{3+}$ (65 pm) is similar to that of Ti$^{4+}$ (61 pm), but is markedly smaller than the Ba$^{2+}$ radius (143 pm). Thus, Fe$^{3+}$ is incorporated at the B-site of the perovskite structure (FeTi$^{0}$ in Kröger-Vink notation) and is negatively charged with respect to the lattice. To maintain charge balance, oxygen vacancies are created. For lead titanate and PZT, it has been demonstrated that oxygen vacancies can form (FeTi$^{0}$/Vo$^{••}$) defect complexes with the dopant. Since EPR spectra are highly sensitive to distortions in the local environment of the probed ion, they enable the differentiation between charged (FeTi$^{0}$/Vo$^{••}$) complexes (Figures 1(i) and 1(ii)) and isolated FeTi$^{0}$ defects within a complete oxygen octahedron (Figure 1(iii)). Furthermore, the position of EPR resonances contains information about the relative orientation of defect complexes within the host unit cell. In so-called axial or tetragonal defect complexes (Figure 1(i)), the spontaneous polarization is oriented in parallel or antiparallel with the polarization of the unit cell in which it is embedded, i.e., along the crystallographic ⟨001⟩ direction. Defect complexes in so-called rhombic symmetry either originate from defects in unit cells with rhombohedral crystal symmetry or from defect complexes in tetragonal unit cells, where the polarization of the complex
is oriented perpendicular with respect to the polarization of the unit cell (Figure 1(ii)).

In PZT, the resonance around 100 mT has been assigned to a tetragonal defect complex, while that at 170 mT is attributed to a rhombic complex. Interestingly, a signal for a tetragonal configuration is found in BNT-1BT:1Fe, which appears rhombohedral in XRD measurements. In contrast to tetragonal symmetries, where both tetragonal and rhombic defect complex orientations are possible, in the rhombohedral structure, only rhombic orientations should occur.

Due to relatively broad lines, a conclusive assignment of the shoulder signal at 100 mT is not possible with the present measurements. Either the shoulder stems from a second rhombic defect complex within a cell with different zero-field splitting or on a very local scale tetragonal symmetry is also present in BNT-1BT:1Fe but not resolved by x-ray diffraction (XRD). The presence of platelets with tetragonal symmetry with a thickness of only a few unit cells has, for example, been reported in transmission electron microscopy studies on BNT.

In BNT-15BT:1Fe, the intensity ratio of the resonances assigned to tetragonal and rhombic complexes is clearly higher than in BNT-1BT:1Fe. This is consistent with the tetragonal diffraction pattern found in XRD measurements of BNT-15BT:1Fe.

The signal at 350 mT was rationalized before with the existence of Fe₂O₃ second phase at grain boundaries in BNT due to limited solubility. Another interpretation for the relaxor Pb(Mg₁/₃Nb₂/₃)O₃ doped with Fe, however, postulates an isolated Fe₂O₃ (also termed “free” iron) within a complete oxygen octahedron of the hosting perovskite as origin of this signal. The strong reaction to poling, which entails a field-induced distortion of the unit cell, favors the latter interpretation. The question of why the position of the signal assigned to free iron changes during poling cannot be answered conclusively with the present measurements. However, the changing intensity ratio of the high-field (free iron) and low-field (complexed iron) resonances due to poling indicates that poling increases the number of defect complexes at the expense of free iron. Thus, we propose the following picture for the defect complex situation in Fe-doped BNT-100xBT: Un-poled samples consist of a non-polar matrix with embedded polar nanoregions (PNR), according to the random-bond random-field model for relaxors.

The dopant ions Fe⁺⁺⁺ are assumed to be distributed evenly in the sample. In the non-polar fraction of the specimen, the free iron configuration is preferred, similar to the situation in the non-polar perovskite SrTiO₃. At the same time, some defect complexes (Fe⁺⁺⁺–O⁻⁻⁻⁻⁰) exist in the locally distorted structure of PNR, giving rise to the defect complex EPR resonances in un-poled samples. Electrical poling induces non-cubic distortion of the whole material and a domain structure throughout the sample, including the originally non-polar fractions. The induced distortion of the cell provides a driving force for the association of defect complexes due to the formation of local energy minima. Free iron from the initially non-polar phase forms defect complexes with oxygen vacancies, which have not been bound to Fe⁺⁺⁺ in the non-polar phase. The complexation proceeds via oxygen vacancy hopping from unit cells containing Ti on the B-site to unit cells containing Fe on the B-site. The assumption of high VO⁻⁻⁻⁻⁰ mobility, which is necessary for this mechanism, is supported by conductivity studies in BNT, showing that the material is an excellent VO⁻⁻⁻⁻⁰ conductor.

Thus, poling increases the concentration of defect complexes, while the concentration of acceptor dopant and oxygen vacancies remains constant. This process is represented by the shift of resonance intensity from the free iron signal to the defect complex resonances after electrical poling. The persistence of the free iron resonance even in poled samples is rationalized with the mechanism of charge compensation in BNT-100xBT:Fe. Fe⁺⁺⁺ on a Ti⁺⁺⁺ site is singly charged with respect to the host lattice, while an oxygen vacancy can be singly or doubly charged. Assuming only the formation of doubly charged oxygen vacancies VO⁻⁻⁻⁻⁰, the concentration of oxygen vacancies VO⁻⁻⁻⁻⁰ formed for charge compensation is half of the concentration of FeTi⁺⁺⁺. Consequently, some FeTi⁺⁺⁺ ions remain free after all available oxygen vacancies have been bound in complexes.

Since the low field resonances of experimental spectra (Figure 1) match the simulated spectra for defect complexes, we conclude that defect complexes are present in BNT-100xBT:1Fe and base the following discussion primarily on the defect complex model. Nevertheless, it is possible that space charges contribute to aging as well, since the experimental differentiation between those two mechanisms is complicated.

Aging of un-poled samples

The effect of acceptor-doping in un-poled BNT-100xBT samples after furnace cooling is clearly different from that in conventional ferroelectrics like PZT. The pinching of the polarization hysteresis, which commonly occurs in PZT:Fe at a doping level of 1% even without special aging treatment, is not observed here, independent of the thermal history (Figure 2). To explain this finding, we recapitulate that pinching in conventional ferroelectrics such as PZT or BT is rationalized with the gradual stabilization of a domain structure with randomly oriented Pᵥ vectors. During aging, defect complexes reorient in parallel with the spontaneous polarization of their hosting domain. The stabilized domain structure switches at higher fields than an un-stabilized structure. At common measurement frequencies, the defect complexes themselves largely retain their original alignment even under high field, since the diffusion of vacancies that is required for defect complex reorientation is slow. When the field is removed, they restore the initial domain pattern and inhibit the formation of remanent polarization. In contrast to ferroelectric PZT, un-poled BNT-1BT:1Fe at room temperature is in a non-ergodic relaxor state characterized by Pᵥ embedding in a non-polar matrix without a long-range domain structure. This situation is schematically depicted in Figure 8(a), while Figure 8(b) represents the ferroelectric state achieved after poling. Due to the absence of long-range order in the relaxor state, a given concentration of defect complexes stabilizes a smaller volume fraction of material (hatched regions in Figure 8) in the relaxor state than in the ferroelectric state. Furthermore, the EPR spectra indicate...
that the relative amount of free iron is larger in the relaxor state than in the ferroelectric state. Even at the same concentration of acceptor ions, the concentration of stabilizing defect complexes is therefore lower in the relaxor state when compared to the ferroelectric state. Hence, only the ferroelectric state develops a considerable restoring force recovering the original domain pattern after a field excursion. In contrast, the majority of PNR in the relaxor state remains un-stabilized. The PNR can be oriented in an external field without hindrance and transform to a ferroelectric long range order. Thus, little defect complex induced depolarization occurs in the relaxor upon field removal, and pinching of the \( P(E) \) curves is absent or small. A similar correlation between the existence of a PNR state and the degree of dielectric aging has been proposed for the relaxor system \((1-x)\)PMN-xPT with \( x < 0.3 \).  

The fact that high-temperature aging in the un-poled state does not affect BNT-1BT:1Fe (Figure 2(a)) but decreases \( 2P_r \) in BNT-15BT:1Fe (Figure 2(b), green dotted line) indicates that clamping effects are present in the un-poled BNT-15BT:1Fe. The slanted curves can be modelled with a series circuit of a ferroelectric and a non-ferroelectric layer. Low \( 2P_r \) and \( E_C \) values indicate that in BNT-15BT:1Fe, a fraction of the sample is completely clamped after furnace-cooling. This result implies that at least some parts of the sample are not in a non-ergodic relaxor state, but have spontaneously developed a ferroelectric long-range order during furnace cooling. This picture is further supported by the small frequency dispersion of permittivity in the un-poled state does not affect BNT-1BT:1Fe (Figure 2(a)) but strengthens this hypothesis that not only the long-range order remains un-stabilized in the un-poled state.  

FIG. 8. Stabilizing effect of acceptor doping in un-poled samples with PNR structure (a) and ferroelectric long range order (b). Stabilized volume is indicated by hatched regions. At the same concentration of acceptor ions, the fraction of stabilized volume is larger in the ferroelectric state due to the existence of long range order and due to the larger amount of defect complexes aligned with polarization compared to the relaxor state.

The simultaneous increase of \( E_C \) and polarization \( P \) in BNT-15BT:1Fe with the coexistence of fully clamped and un-clamped domains in furnace-cooled BNT-15BT:1Fe. \( E_C \) is higher in quenched samples because domains, which were immobile in the furnace-cooled state, now dominate the switching process. Their coercive field is lowered by quenching; therefore, it is accessible to the experiment. It is, however, still higher than \( E_C \) of the portion, which still switches after furnace-cooling. This picture is further supported by the different slopes of \( P(E) \) curves near \( E_C \) in furnace cooled and quenched samples. The effect of quenching in BNT-1BT:1Fe on the other hand is small, since there is no driving force for the orientation of defects.

Even though defect complexes have been detected by EPR in the un-poled state of BNT-100xBT:1Fe for all investigated BT contents, they stabilize \( P_r \) only in BNT-15BT:1Fe due to the predominant ferroelectric order, while the relaxor compositions with \( x = 0.01; 0.04; \) and 0.06 are not affected in the un-poled state. However, the EPR spectra also indicate that electrical poling increases the number of defect complexes, therefore, increasing their overall clamping effect.

**Aging in poled samples**

The results on poled samples clearly reveal that the field-induced phase transition in BNT-100xBT ceramics plays a key role in the aging behavior of Fe-doped samples. After poling, aging similar to that in conventional acceptor-doped ceramics is observed in BNT-1BT:1Fe (Figure 3), which did not display aging in the un-poled state. Consistently, the signal ratio of the “defect complex resonances” with the respect to the “free iron” resonance in the EPR spectra increases, indicating an increase in defect complex concentration due to poling. Since samples were aged in the negatively poled state, this poling direction is stabilized (Figure 3(a)). This effect occurs in a similar manner in acceptor-doped PZT. Accordingly, the decreasing remanent polarization in positive field direction \(+P_r\) as well as the developing asymmetry of the \( S(E) \) curve (Figure 3(b)) indicate the time-dependent development of a negative internal bias field. The immobilization of non-180° domain walls furthermore leads to an overall decrease of the field-induced strain (Figure 3(b)).

The assumption that aging hampers domain wall motion is at first glance inconsistent with the decrease of \( 2E_C \) during the aging process. An effective stabilization should harden the material and therefore increase \( 2E_C \). The simultaneous reduction of \( 2P_r \), however, indicates that a portion of the sample is completely clamped during the aging process and does not contribute to switching anymore. Thus, by clamping domains with high \( E_C \), the macroscopic \( E_C \) is decreased. The small signal parameters \( e_{33}(E) \) and \( d_{33}(E) \) depicted in Figures 3(c) and 3(d) indicate that not only the long-range mobility of domain walls is reduced during aging but also short-range vibrations due to small fields are affected. In accordance with the negative \( E_{bias} \) observed in \( P(E) \) curves, the
stabilization effect on \( \varepsilon_{33}(E) \) is strongest in the negative field regime. The asymmetric decrease of \( \varepsilon_{33}(E) \) near the negative coercive field \( -E_C \) and the positive coercive field \( +E_C \) points towards different domain wall density or domain wall mobility in both field regimes.

As discussed before, in un-poled BNT-15BT:1Fe, the slanted \( P(E) \) curve indicates that the sample has experienced aging during furnace-cooling, and a randomly oriented domain structure is stabilized. Poling of this sample will orient only the fraction of domains, which still react to the external field. Under subsequent high-temperature aging, the formation of an internal bias field similar to that in BNT-1BT:1Fe shifts the \( P(E) \) curve towards the positive field direction (Figure 4(a)). The increase of \( 2P_r \) during aging can be rationalized with the reorientation of domains at elevated temperature. During poling at room temperature, only a part of the domains is oriented according to the external field. Randomly clamped portions are thus embedded in domains oriented with the external poling field. High temperatures mobilize the clamping defects and allow the oriented domains to grow at the expense of originally clamped parts. Therefore, \( |-P_t| \) increases as well as the remnant piezoelectric coefficient in negative field direction \( -d_{33} \).

High-temperature aging of the electrically de-aged BNT-15BT:1Fe on the other hand displays the same trends in \( 2P_r \) and \( E_{bias} \) as BNT-1BT:1Fe (Figure 5(a)). Also the asymmetry in \( S(E) \), \( \varepsilon_{33}(E) \), and \( d_{33}(E) \) (Figures 5(b)–5(d)) is similar to the effects in BNT-1BT:1Fe hysteresis loops. Electrical cycling, therefore, randomizes the orientation of defect complexes and lowers the stabilizing effect. Hence, a larger portion of the sample can be poled as compared to the furnace-cooled state and the stabilization effect on the poling direction is larger as well.

The comparison of internal bias fields obtained at room temperature (Figure 6(a)) shows that the internal bias is composition-dependent and is highest in the tetragonal composition. Within the defect complex model, this effect can be explained with the relative alignment of polarization vectors in the unit cell, since the driving force for the reorientation of defect complexes is coupled to the spontaneous polarization of the unit cell. The higher distortion in the tetragonal cell entails a higher dipole moment as compared to the rhombohedral cell. The correlation between \( E_{bias} \) and the composition, i.e., the crystal structure, is consistent with results in PZT doped with 1.5 mol. % Fe. There, \( E_{bias} \) is highest in tetragonal compositions, has a minimum around the MPB and rises again in rhombohedral compositions. Furthermore, the difference between internal bias fields obtained during room-temperature aging (Figure 6(a)) and high-temperature aging (Figure 6(b)) emphasizes that the development of \( E_{bias} \) is thermally activated. Therefore, it fits well into the picture of defect-mediated clamping of domain walls. The trend of increasing bias field with increasing aging temperature has been found in Fe-doped PZT as well. The log-linear behavior found in PZT is not reproduced in BNT-100xBT:1Fe, though. After long aging times, the effect saturates in BNT-15BT:1Fe, indicating that all available defects are oriented. The absolute values of \( E_{bias} \) obtained during room temperature aging in BNT-100xBT:Fe (0.3 kV/mm after 2 \( \times \) 10^5 s aging time) are lower than those observed in PZT:Fe at comparable doping level and aging conditions (1.7 kV/mm after 2 \( \times \) 10^5 s aging time). On the basis of calculations for the defect dipole model, this finding can be tentatively related to different spontaneous polarizations and different permittivities in PZT:Fe and BNT-100xBT:Fe. A detailed discussion, however, will also have to include conductivity measurements and domain size investigations, which we plan to do in the future.

The effect of domain clamping during aging is reflected in the temperature dependence of \( 2P_r \) (Figure 7(a)) and \( 2E_C \) (Figure 7(b)) normalized to the starting values. The general decrease of \( 2P_r \) in all compositions is consistent with the development of an internal bias field. Interestingly, it is not correlated directly with the strength of the internal bias field after a specific aging time, since in BNT-4BT:1Fe, the effect is lower than in all the other compositions. The clamping effect indicated by the change in \( 2E_C \), on the other hand, is similar in compositions with \( x = 0.01 \), \( x = 0.04 \), and \( x = 0.06 \). The missing decrease of \( 2E_C \) in BNT-15BT:1Fe as compared to the other compositions can be rationalized in this case with the de-aging treatment. During electrical cycling, polarization directions along the field directions become already clamped and do not contribute to the subsequent aging process anymore.

To quantify the aging effect on small signal characteristics, the loss tangent before and after aging was investigated as shown in Figure 9. The difference between the curves of fresh and aged samples \( \Delta \tan(\delta) = \tan(\delta)_{aged} - \tan(\delta)_{fresh} \) reveals in which field regions the loss (produced by small-scale domain wall movement) changes due to aging. Regions of high loss indicate a flattening of the energy barrier for domain wall movement. Peaks in the grey-shaded, negative area indicate that \( \tan(\delta) \) is higher after aging, while peaks in the positive regime mark regions, where \( \tan(\delta) \) is higher before aging. In general, the area under the peaks for positive \( \Delta \tan(\delta) \) is larger than that for negative \( \Delta \tan(\delta) \), indicating that the losses decrease during aging, irrespective of the composition. Still, the comparison of un-aged and aged samples reveals composition-dependent differences. In BNT-1BT:1Fe (Figure 9(a)), aging shifts the maximum in the negative field regime towards the positive field direction, which is also evident in the \( P(E) \) hysteresis (Figure 3). Interestingly, the shift is not apparent in the positive increasing field branch. The increased \( \tan(\delta) \) on the decreasing field branch, however, indicates enhanced back-switching after aging. This finding is consistent with the stabilizing effect of defect complexes postulated earlier. The shift of lossy processes in the negative field regime is also observed in BNT-4BT:1Fe and BNT-6BT:1Fe (Figures 9(b) and 9(c)). The back-switching feature is missing in these compositions, though. Again, the shift of the \( P(E) \) hysteresis is reflected only in the negative field direction. BNT-15BT:1Fe on the other hand simply mirrors the shift of the hysteresis curve in both field regimes (Figure 9(d)). This is evident in both aging of the furnace-cooled sample (red curve) as well as aging of the electrically deaged sample (black curve). Lossy processes are shifted towards lower
absolute fields in the negative field branch and retarded in positive field direction. Pronounced effects on the decreasing field branch are present only in the furnace-cooled and aged sample. Figure 9 demonstrates clearly that a true shift of the hysteresis along the field axis only occurs in BNT-15BT:1Fe. The other compositions, while featuring stabilization along the poling direction during aging as well, rather indicate the reduction of lossy processes in the positive field regime, which is consistent with the reduction of $2E_C$ in these samples.

**SUMMARY AND OUTLOOK**

Noticeable aging effects are present in the polied state of BNT-100xBT:1Fe, but are low or absent in the relaxor state. The combination of EPR studies and electrical measurements indicates that the observed aging effects can be attributed to the orientation of defect complexes with respect to the spontaneous polarization of the unit cell and are accelerated with increasing temperature. Pronounced aging effects in the poled state, particularly in the tetragonal phase, underline that hard-doping is possible in BNT-100xBT and thus opens the field of sensor applications for this material.

**ACKNOWLEDGMENTS**

Helpful discussions with Professor Yuri Genenko (Technische Universität Darmstadt) and the support of EPR measurements by Professor Stefan Weber (Universität Freiburg) were gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft under SFB 595, Project D1. The work of Dragan Damjanovic was supported by the Fonds National Suisse under PNR62 Project 406240-126091.

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