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ORIGINAL REPORT



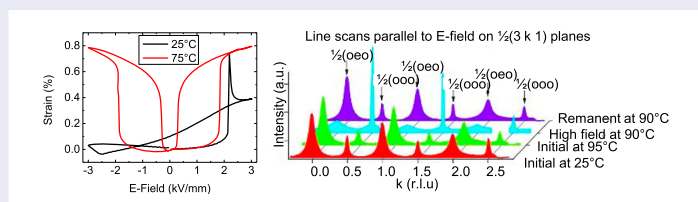
# Achieving large electric-field-induced strain in lead-free piezoelectrics

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## ABSTRACT

Lead-free piezoelectric single crystals of Fe-doped  $0.95(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}0.05\text{BaTiO}_3$  are shown to combine multiple mechanisms for high strain and an effective piezoelectric coefficient of up to 3260 pm/V. This is explained based on the analysis of superstructure reflections from diffuse synchrotron x-ray scattering. It depends on three factors: (1) the stabilization of a local tetragonal structure by  $(\text{Fe}'\text{-V}_{\text{O}}^{\bullet\bullet})^{\bullet}$  defect dipoles, (2) the reversible creation of a morphotropic phase boundary under field, and (3) the field-induced reversible transition between a short-range ordered relaxor and a long-range ordered ferroelectric state.



## IMPACT STATEMENT

The observation that a combination of three different physical mechanisms produces unprecedentedly high piezoelectric response in a lead-free piezoelectric presents a breakthrough in the fundamental understanding of optimizing piezoelectric properties.

## ARTICLE HISTORY

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## KEYWORDS

Piezoelectricity; relaxor ferroelectrics; field-induced phase transitions

## Introduction: mechanisms to achieve high piezoelectric strain

Piezoelectric materials couple electrical and mechanical energy and are widely employed for actuators, sensors or energy harvesters. For many applications, the strain  $S_{\text{max}}$  achieved at the electric field  $E_{\text{max}}$ , quantified by the effective piezoelectric coefficient  $d_{33}^* = S_{\text{max}}/E_{\text{max}}$ , is of particular importance. Values of  $d_{33}^* = 2500$  pm/V found in Pb-based single crystals [1] were explained with an electric-field-induced structure change [2]: starting from rhombohedral symmetry with a  $[111]_{(\text{pc})}$  polarization vector (where the subscript 'pc' denotes the parent pseudo-cubic perovskite unit cell), application of an electric field in the  $[001]_{(\text{pc})}$  direction rotates the polarization, resulting in a transition to tetragonal symmetry and a large strain along the field direction. Removing the field

returns the rhombohedral structure; thus, the strain is reversible.

Environmental concerns have created a need for lead-free piezoelectrics. Bi-based materials such as  $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$  (BNT-100xBT) are particularly promising [3,4]. They are relaxors over a wide compositional range; poling induces ferroelectric order [5,6]. A morphotropic phase boundary (MPB) exists for  $0.06 < x < 0.07$ , where the long-range structure is pseudo-cubic in the as-processed state, with lower symmetry existing at the local scale [7]. Upon poling, it transforms into a tetragonal/rhombohedral mixed phase [8,9], with strain values of up to  $S = 0.7\%$  in BNT-based ceramics [10,11]. Improved properties are expected from the single crystal analogues [12,13]. A non-reversible strain of  $S = 1.2\%$  was observed in BNT-6.5BT single

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crystals under a field in the  $[001]_{(pc)}$ -direction [14]. At elevated temperatures, BNT-6.3BT shows a reversible electric-field-induced rhombohedral-tetragonal transformation [15], leading to a strain of  $S = 0.6\%$  at  $E = 2.5$  kV/mm. Furthermore, in BNT-6BT modified with 2%  $K_{0.5}Na_{0.5}NbO_3$ , a strain  $S = 0.83\%$  was observed at  $E = 2.8$  kV/mm, equivalent to approximately  $d_{33}^* = 3000$  pm/V. Structural investigations showed a transition from a pseudo-cubic to a mixed tetragonal/pseudo-cubic phase [16].

Another promising system is Fe-doped  $BaTiO_3$  [17]. Its high strain relies on the presence of local ‘symmetry conforming’  $(Fe'-V_O^{\bullet\bullet})^\bullet$  defect dipoles that clamp the ferroelectric domain structure [18]. A field perpendicular to the clamping direction causes reversible domain switching, resulting in a large strain of 0.75% at 200 V/mm.

Here, we show a strain of 0.8% reached at  $E = 3$  kV/mm in  $[001]$ -oriented Fe-doped BNT-5BT (BNT-5BT:Fe) single crystals over a broad temperature range. An effective piezoelectric coefficient  $d_{33}^* = 3260$  pm/V is obtained at  $E = 2.3$  kV/mm, exceeding that commonly observed in lead-based crystals. The analysis of superstructure reflections (SSR) in synchrotron x-ray diffraction (XRD) reveals a reversible transformation between tetragonal and rhombohedral phase contents. BNT-5BT:Fe combines three effects to generate high strain: (1) an electric-field-induced creation of an MPB state by a structural transformation, (2) a defect-induced stabilization of the tetragonal structure, and (3) a relaxor-to-ferroelectric transformation.

## Materials and methods

### Sample fabrication

Top-seeded solution crystal growth followed the procedure described in [19]: starting materials were powders of  $Bi_2O_3$ ,  $Na_2CO_3$ ,  $BaCO_3$ ,  $TiO_2$  and  $FeO$  with purity of 99.99%. As crystals are always Ba-deficient compared to the melt composition, powders were weighed and mixed according to the stoichiometry  $[(Bi_{1/2}Na_{1/2})_{0.9}Ba_{0.1}](Ti_{0.99}Fe_{0.01})O_{2.99}$ . The mixture was calcined in a platinum crucible in air at 1000°C for 10 h. 20 wt% of  $Bi_2O_3$  and  $Na_2CO_3$  were added as self-flux. Crystals were drawn from the melt using a  $\langle 100 \rangle_{(pc)}$ -oriented BNT-BT seed crystal. Analysis by inductively coupled plasma atomic emission spectroscopy revealed a composition of BNT-5BT with 1 mol% Fe. For electrical measurements, cuboid samples of  $2 \times 2 \times 0.8$  mm<sup>3</sup> oriented in the  $\langle 100 \rangle_{(pc)}$ -direction were prepared. Samples for structural investigations had dimensions of

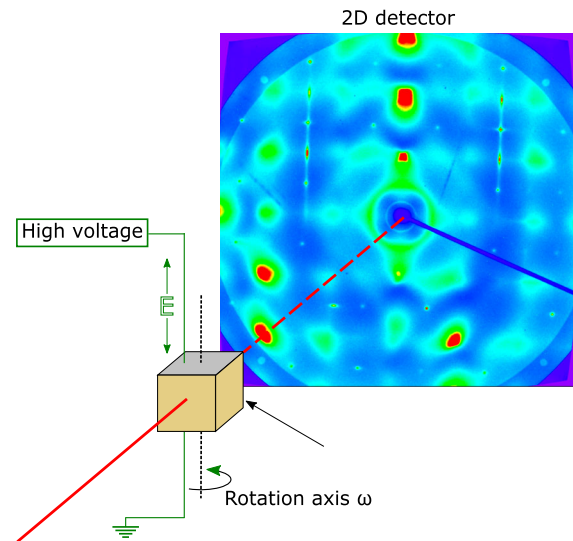


**Figure 1.** Experimental setup for synchrotron XRD with electric field applied *in-situ*.

$1 \times 1 \times 3$  mm<sup>3</sup>. All samples were electroded using silver paint fired at 400°C.

### Electrical and mechanical characterization

Temperature-dependent permittivity  $\varepsilon(T)$  was measured using an HP 4291 dielectric spectrometer (Hewlett Packard, USA) while heating in an LH30/12 box furnace (Nabertherm, Germany). For pyroelectric measurements, samples poled at room temperature at  $E = 5$  kV/mm were heated at 2 K/min while the depolarization current density  $j(T)$  was detected with a Keithley 6517B electrometer (Keithley, USA). The strain hysteresis  $S(E)$  was measured at different temperatures using an aixPES (aixACCT Systems, Germany). The  $E(t)$  signal was triangular with a frequency of 10 mHz and an amplitude of 3 kV/mm. Between measurements, the samples were depolarized at  $T = 150^\circ\text{C}$  for 20 min while short-circuited with aluminum foil.

### Synchrotron x-ray diffraction

XRD experiments were undertaken at beamline ID15 of the European Synchrotron Radiation Facility (ESRF). A schematic of the geometry is shown in Figure 1 [20]. X-ray energy was 76.9 keV. Fields of 3 kV/mm were applied along the  $\langle 100 \rangle_{(pc)}$  direction. Data were collected using a Frelon charged-coupled device 2D detector coupled to an x-ray image intensifier. Images were taken as the sample was rotated around the  $\omega$ -axis, normal to the direction of the incident beam, through a total of 60° in steps of 0.2°.

## Experimental results

### Development of strain around the phase transition

Figure 2(a) displays the temperature dependence of permittivity  $\varepsilon$  and loss tangent  $\tan(\delta)$  measured upon heating at 1 kHz in poled  $\langle 100 \rangle_{\text{pc}}$ -oriented BNT-5BT:Fe, and the pyroelectric current density  $j(T)$ . A step-like anomaly in  $\varepsilon$  and maximum of  $\tan(\delta)$  at  $T_{F-R} = (93 \pm 2)^\circ\text{C}$  marks the transition from a ferroelectric to an ergodic relaxor state [14]. A maximum of  $j(T)$  indicates the depolarization temperature  $T_d = (94.3 \pm 1.3)^\circ\text{C}$ , where the macroscopic polarization vanishes. The results agree with the expectations for BNT-100xBT with predominantly rhombohedral symmetry close to the MPB [15].

Figure 2(b) presents the electric-field-induced strain  $S(E)$  measured at 25°C, 50°C, 75°C and 100°C. At 25°C and 50°C,  $S(E)$  is highly asymmetric. There are notable overshoots with the first increase of the field beyond  $E = 2.2$  and 1.9 kV/mm, respectively. The same behavior has been observed before in undoped BNT-6.5BT, i.e. in the MPB region, but not in the rhombohedral part of the phase diagram, and only if the field is applied

in  $\langle 001 \rangle$ -direction [14]. At 75°C, the overshoot has disappeared. The sample reaches  $S_{\text{max}} = 0.8\%$ , with no notable remanent strain. Positive and negative field loops are symmetric. The observation that the maximum strain remains nearly constant with temperature in the Fe-doped crystal is in contrast to undoped BNT-BT single crystals, which show a decrease in strain when  $T_d$  is approached [15]. Remarkably, with the low poling field of 1.8 kV/mm, the strain of 0.75% observed at 2.3 kV/mm translates to  $d_{33}^* = 3260$  pm/V. The behavior is similar at 100°C, though  $S_{\text{max}}$  is reduced slightly. Nevertheless,  $S = 0.76\%$  is reached at 3 kV/mm; at 2.3 kV/mm, it still reaches 0.69%, equivalent to  $d_{33}^* = 3000$  pm/V.

To elucidate the reason for the exceptionally high piezoelectric coefficient, the crystallographic structure was analyzed by synchrotron XRD. Figure 2(c) shows a polar plot of strain values measured at 90°C from Bragg reflections at 3 kV/mm, and with the field removed in the remanent state, as a function of scattering vector angle to the field. As expected, there is a significant lattice strain in poling direction under field. Removing the field reverts the structure back to the isotropic state without remanent strain. However, since the unpoled sample is a relaxor and

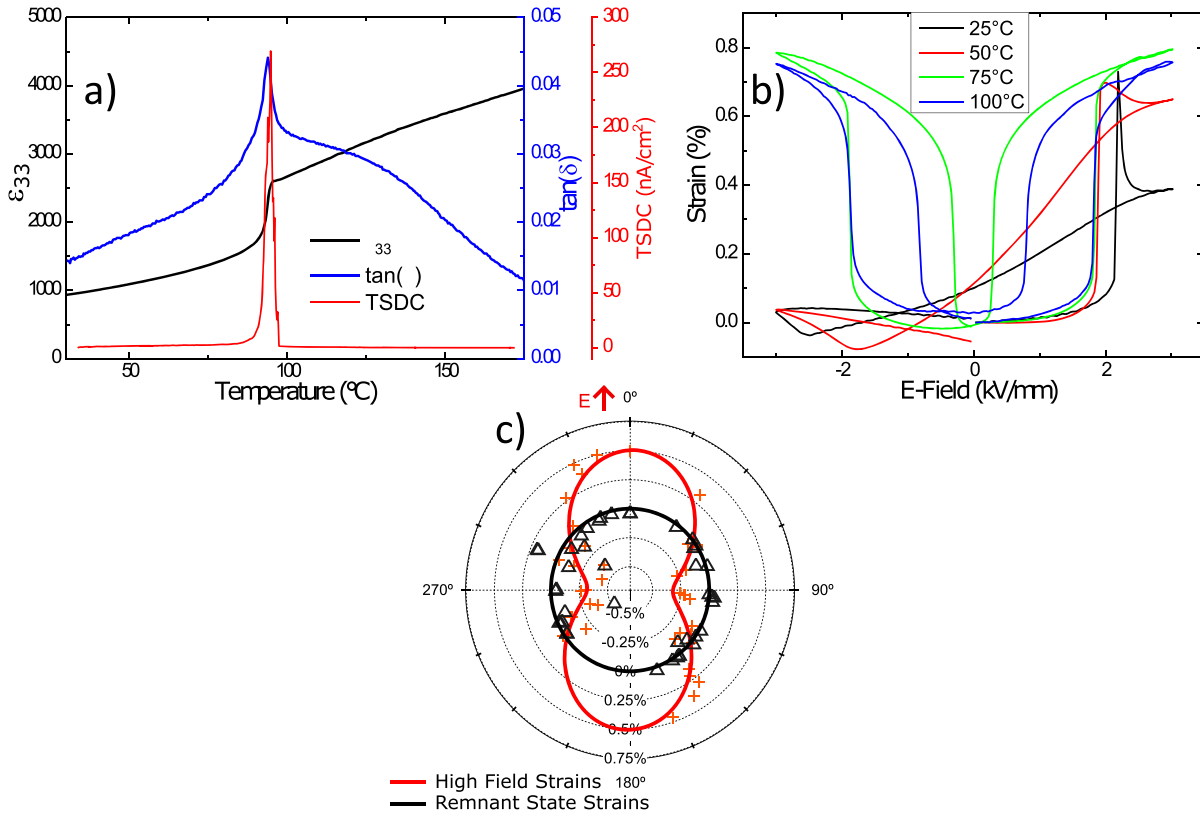


**Figure 2.** (a) Dielectric permittivity  $\varepsilon(T)$ , loss tangent  $\tan(\delta)(T)$  and thermally stimulated depolarization current density  $j(T)$  of BNT-5BT:Fe. (b) Strain hysteresis  $S(E)$  of BNT-5BT:Fe at various temperatures. (c) Polar graph of strain values from XRD measurements at 90°C, at 3 kV/mm and in the remanent state. Data points represent crystal reflections as function of azimuth angle. Solid lines are guides for the eye.

develops ferroelectric long-range order only upon poling, the information that can be gained from Bragg reflections is limited. Therefore, the focus is shifted to superstructure reflections (SSR) seen against the background of the diffuse x-ray scattering pattern.

### Superstructure analysis by diffuse x-ray scattering

Superstructure reflections, which indicate oxygen octahedral tilt systems, are observed at  $\frac{1}{2}(hkl)_{(pc)}$  reciprocal space coordinates. Figure 3(a) shows the intensity distribution in the reciprocal  $(hk\frac{1}{2})_{(pc)}$ -plane in the initial state at room temperature. For the analysis, line scans at  $k = -1.5$  and  $h = 1.5$  (Figure 3(b,c), respectively) were taken as indicated by the dashed boxes in Figure 3(a). For the h-scans, the observed intensity is caused by structures on the  $(100)_{(pc)}$ -plane with a normal perpendicular to the direction of the applied field, whereas the normal of the features seen in the k-scan is oriented parallel to the field. Both h- and k-scans show clear SSR at all  $\frac{1}{2}(ooo)_{(pc)}$ -,  $\frac{1}{2}(eoo)_{(pc)}$ - and  $\frac{1}{2}(oeo)_{(pc)}$ -positions, where 'o' and 'e' denote odd and even Miller indices, respectively. In the initial state at 25°C, the intensity of the  $\frac{1}{2}(ooo)_{(pc)}$ -peaks is generally lower than that of the  $\frac{1}{2}(eoo)_{(pc)}$ - and  $\frac{1}{2}(oeo)_{(pc)}$ -peaks. The reflections do not change significantly upon heating to 95°C, i.e. above

the transition temperature  $T_{F-R}$  into the ergodic relaxor phase.

Under an electric field of 3 kV/mm in  $\langle 100 \rangle_{(pc)}$ -direction at 90°C, the intensity of the  $\frac{1}{2}(ooo)_{(pc)}$ -peaks increases and the full width at half maximum decreases both for the h-scan (Figure 3(b)) and the k-scan (Figure 3(c)). For peaks with one 'even' index, there is a difference between the two scanning directions: in the h-scan, the  $\frac{1}{2}(eoo)_{(pc)}$ -peaks, most notably the  $\frac{1}{2}(231)_{(pc)}$ -reflection, also increase, although not as much as the  $\frac{1}{2}(ooo)_{(pc)}$ -peaks. In contrast, the intensity of the  $\frac{1}{2}(oeo)_{(pc)}$ -peaks in the k-scan diminishes under the electric field.

When the field is removed, the pattern of the k-scan (Figure 3(c)) returns to the initial state, with little remanence. In the h-scan (Figure 3(b)), the intensity increase in the  $\frac{1}{2}(ooo)_{(pc)}$ -peaks is partially reversed, but a notable remanence exists, particularly for the  $\frac{1}{2}(131)_{(pc)}$ -reflection. In contrast, the  $\frac{1}{2}(eoo)_{(pc)}$ -peaks return close to the original intensities after field removal.

## Discussion

### Development of local structure

The SSR indicate local areas of oxygen octahedral rotation that distort the long-range cubic or pseudocubic

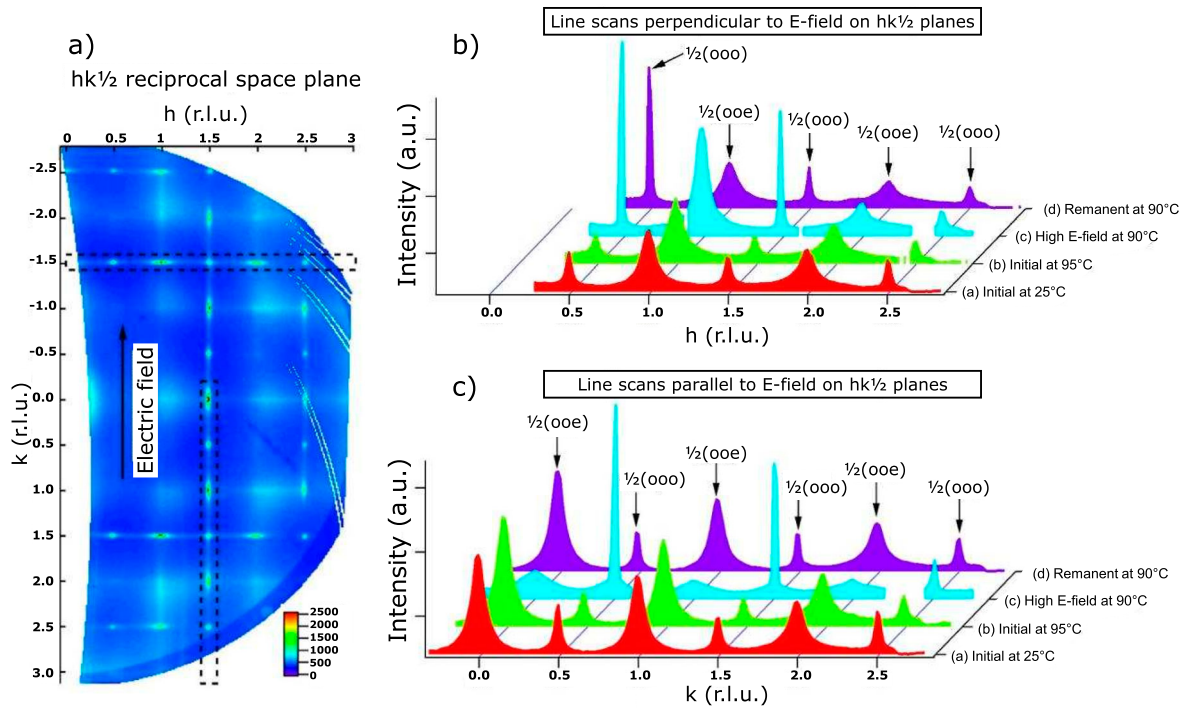


**Figure 3.** (a) Section of the  $(hk\frac{1}{2})_{(pc)}$  reciprocal space plane showing superstructure intensities. (b) Line scans along the h-axis at  $(h\frac{3}{2}\frac{1}{2})_{(pc)}$  for the sample unpoled at 25°C, field-free at 95°C, under  $E = 3$  kV/mm at 90°C and the remanent state at 90°C after field removal. (c) Line scans along the k-axis at  $(\frac{3}{2}k\frac{1}{2})_{(pc)}$  under the same conditions.

symmetry [6].  $\frac{1}{2}(\text{ooo})_{(\text{pc})}$ -peaks are associated in polycrystalline BNT-6BT with an out-of-phase  $a^-a^-a^-$  tilt system (Glazer notation [21,22]), corresponding to a rhombohedral distortion with space group  $R3c$ . SSR with one even index (e.g.  $\frac{1}{2}(\text{eoo})_{(\text{pc})}$ - and  $\frac{1}{2}(\text{oeo})_{(\text{pc})}$ -peaks) are linked to the in-phase  $a^0a^0c^+$  tilt system, associated with the polar tetragonal space group  $P4bm$  [9, 23]. The former have also been observed in the synchrotron diffraction pattern of undoped polycrystalline BNT-5BT, but the latter are absent in the undoped system [8]. The existence of both types of SSR implies that both rhombohedral regions of out-of-phase tilting and in-phase tilted tetragonal regions are present. The notable presence of tetragonal nanoregions seems to contradict the expectation that the rhombohedral structure is dominant in BNT-5BT [8,9]. An explanation can be found in the Fe-doping, which creates  $(\text{Fe}'\text{V}_\text{O})^\bullet$  defect dipoles of intrinsically tetragonal symmetry. They stabilize tetragonal nanoregions in the sample. A similar stabilization of the tetragonal phase by acceptor doping has been reported before for ferroelectrics and relaxors [24–26]. In the present case, the acceptor doping does not induce a spontaneous long-range-ordered ferroelectric phase. That only develops after poling, as can clearly be seen by the sharp, non-frequency dependent anomaly in  $\varepsilon(T)$  and  $\tan(\delta)(T)$  in Figure 2(a).

The increase in intensity of the  $\frac{1}{2}(\text{ooo})_{(\text{pc})}$ -peaks under an electric field at 90°C indicates both a growth of the size of individual rhombohedral regions and an increase of the volume fraction of these regions, in agreement with the assumption that the local order of the relaxor is replaced by a long-range ferroelectric order during electric field application. Tetragonal regions oriented perpendicular to the poling direction also grow, but surprisingly, the volume fraction of tetragonal regions parallel to this direction appears to decrease, as indicated by the diminished intensity of the  $\frac{1}{2}(\text{oeo})_{(\text{pc})}$ -peaks in the k-scan.

One would expect that an electric field in the  $\langle 100 \rangle_{(\text{pc})}$ -direction favors tetragonal over rhombohedral symmetry, analogous to the behavior of Pb-based crystals [2]. A possible explanation lies in the fundamental symmetry of BNT-5BT. As noted, this composition should strongly favor the rhombohedral symmetry; only the presence of defect dipoles stabilizes local tetragonal regions. Application of an electric field creates a long-range order. As the influence of the defect dipoles is limited to their immediate vicinity, the long-range order parallel to the poling field is dominated by regions without defect dipoles: rhombohedral regions grow, and tetragonal regions in the poling direction shrink, independent

of the orientation of the field with respect to the pseudo-cubic axes.

Once the field is removed, most of the original structure of the ergodic relaxor reasserts itself; only some of the rhombohedral regions remain stable in the direction perpendicular to the poling direction.

### Origin of high strain

Three aspects have to be taken into account to explain the high field induced strain around the depolarization temperature:

- (1) The reversible field-induced transformation from a macroscopically cubic ergodic relaxor to ferroelectric long-range order. This mechanism and the negligible remanent strain have been identified before as the main reason for the high strain in BNT-100xBT polycrystalline ceramics [5,27].
- (2) This relaxor-to-ferroelectric transition couples with a reversible polarization rotation from tetragonal to rhombohedral symmetry, creating an MPB through electrical poling, comparable to the behavior of undoped polycrystalline BNT-6BT reported in [9]. At 25°C and 50°C, increasing the field further leads to ‘overpoling’, pushing the sample towards a stable rhombohedral structure with lower piezoelectric strain [9] and causing the appearance of the overshoot in the strain hysteresis. As the transformation is not reversible at low temperatures, the high strain values are not observed in the following cycles and thus do not result in a high effective piezoelectric coefficient. At elevated temperatures, however, there is no stable long-range structure without field, ‘overpoling’ does not occur, comparable to the case of undoped polycrystalline BNT-7BT in [9], the sample remains in the MPB, and the high strain is maintained at high field. The transformation is reversible and contributes to a high  $d_{33}^*$ . In undoped BNT-BT, the field stabilizes the tetragonal phase against the rhombohedral. In the present case, the defect-induced tetragonal structure drives toward rhombohedral symmetry, seen in the intensity increase of the  $\frac{1}{2}(\text{ooo})_{(\text{pc})}$ -reflections and the reduction of the  $\frac{1}{2}(\text{oeo})_{(\text{pc})}$ -reflections in the k-scan.
- (3) The influence of the acceptor dopant. Without it, BNT-5BT in the vicinity of  $T_{F-R}$  would be a macroscopically cubic relaxor with short-range ordered polar nanoregions (PNRs) of predominantly rhombohedral symmetry, with only few tetragonal PNRs. To account for the dominance of tetragonal PNRs in

the Fe-doped system apparent in the diffraction pattern, it is suggested that defect dipoles introduced by Fe-doping stabilize tetragonal PNRs, driving the structure towards the MPB. This interplay between defect symmetry and crystal structure is comparable to the effect that is responsible for the high strain in Fe-doped BaTiO<sub>3</sub> [17,18], but has not yet been seen in BNT-based systems [28]. In analogy to this concept of ‘symmetry conforming defects’, where the average symmetry of the defect dipoles adapts to that of the surrounding matrix in a long-range ordered ferroelectric [17,29], this could be referred to as a ‘defect-conforming symmetry’, since in the present case it is the defect that imprints its symmetry locally on the surrounding matrix.

## Conclusion

While the dielectric data and depolarization behavior of BNT-5BT:Fe do not set the system apart from other BNT-BT-based ceramics and single crystals described in literature, the SSR seen in the x-ray scattering pattern reveal the remarkable peculiarity of the system: the presence of tetragonal nanoregions stabilized by defect dipoles. The high strain in BNT-5BT:Fe is based on a combination of the three mechanisms: (1) a relaxor-to-ferroelectric transformation, (2) the interplay between symmetry and defect dipoles, and (3) a symmetry change under electric field, creating a field-induced MPB in the system. This combination has the potential to provide the groundwork for the next generation of high-performance lead-free piezoelectrics that will further enhance the capabilities of current actuators.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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