Cyclic electric field response of morphotropic Bi1/2Na1/2TiO3-BaTiO3 piezoceramics

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Cyclic electric field response of morphotropic Bi$_{1/2}$Na$_{1/2}$TiO$_3$-BaTiO$_3$ piezoceramics

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In this study, the evolution of field induced mechanisms in lead-free piezoelectric ceramics (1−x)Bi$_{1/2}$Na$_{1/2}$TiO$_3$−xBaTiO$_3$ with x = 0.06 and 0.07 was investigated by transmission electron microscopy, neutron, and X-ray diffraction. Preliminary investigations revealed a strong degradation of macroscopic electromechanical properties within the first 100 bipolar electric cycles. Therefore, this structural investigation focuses on a comparative diffraction study of freshly prepared, poled, and fatigued specimens. Transmission electron microscopy and neutron diffraction of the initial specimens reveal the coexistence of a rhombohedral and a tetragonal phase with space group R3c and $P4_{2}bm$, respectively. In situ electric field X-ray diffraction reveals a pronounced field induced phase transition from a pseudocubic state to a phase composition of significantly distorted phases upon poling with an external electric field of 4 kV/mm. Although the structures of the two compositions are pseudocubic and almost indistinguishable in the unpoled virgin state, the electric field response shows significant differences depending on composition. For both compositions, the application of an electric field results in a field induced phase transition in the direction of the minority phase. Electric cycling has an opposite effect on the phase composition and results in a decreased phase fraction of the minority phase in the fatigued remanent state at 0 kV/mm. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922145]

More than sixty years after the discovery of strong and stable piezoelectric effects in lead zirconate titanate (PZT),$^1$ PZT is still the dominant ceramic for piezoelectric applications. However, a revised ecological awareness all over the world has driven legislation against the continuous use of toxic lead-containing compounds and in favor of lead free materials, which do not raise the same concerns, particularly in regards to potentially toxic by-products during manufacture and disposal. Recently, the European Union revised the two main pieces of legislation addressing these issues: The Directive on waste electrical and electronic equipment (WEEE Directive)$^2$ and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive).$^3$ These measures sparked the world has driven legislation against the continuous use of toxic lead-containing compounds and in favor of lead free materials, which do not raise the same concerns, particularly in regards to potentially toxic by-products during manufacture and disposal. Recently, the European Union revised the two main pieces of legislation addressing these issues: The Directive on waste electrical and electronic equipment (WEEE Directive)$^2$ and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive).$^3$ These measures sparked the

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et al.\textsuperscript{14} They demonstrated that the initial system, which can be regarded as a pseudocubic phase with slight tetragonal and rhombohedral lattice distortions, irreversibly transformed to a predominantly rhombohedral modification. The poled sample featured the presence of distorted tetragonal and rhombohedral phases. In addition, Hinterstein et al. reported that the giant recoverable strain in (K\textsubscript{0.5}Na\textsubscript{0.5})\textsubscript{0.7}Bi\textsubscript{0.3}TiO\textsubscript{3}-modified BNT-xBT arises from a reversible field induced phase transition between the initial pseudocubic structure and the distorted field induced phases.\textsuperscript{15}

With high-energy X-ray diffraction, the irreversible electric field induced phase transition in BNT-7BT from initial pseudocubic to tetragonal phase was investigated.\textsuperscript{16} Due to a variation in intensity ratio of the 002/200 reflections as a function of the angle between scattering vector and applied electric field, the authors concluded the presence of a remarkable domain texture within the tetragonal phase. Bipolar\textsuperscript{17,18} and unipolar\textsuperscript{18} fatigue behavior of BNT-6BT were examined with neutron\textsuperscript{17} and X-ray\textsuperscript{18} diffraction and revealed a continuous decrease in properties, such as polarization, strain as well as $\varepsilon_{33}$ and $d_{33}$, as a function of cycle number.

For actuator fabrication, the understanding of fatigue plays a crucial role in improving materials performance. Several mechanisms,\textsuperscript{9,20} like microcracking\textsuperscript{21,22}, drift of charge carriers,\textsuperscript{23,24} and structural changes,\textsuperscript{25} have been reported to contribute to fatigue. This investigation is focused on structural changes caused by electric cycling, which leads to material degradation and thus fatigue. Therefore, in this study structure evolution of the two MPB compositions BNT-xBT with $x = 0.06$ and 0.07 was investigated by diffraction studies in the initial versus poled and fatigued state.

In the present study, two piezoceramics of the binary system $(1-x)$Bi\textsubscript{12/3}Na\textsubscript{12/3}TiO\textsubscript{3}·xBaTiO\textsubscript{3} with $x = 0.06$ and 0.07 were investigated using X-ray, neutron, and electron diffraction. A detailed description of the sample synthesis is given elsewhere.\textsuperscript{26} Neutron diffraction experiments were carried out at the high-resolution powder diffractometer SPODI at research reactor FRM-II (Garching, Germany)\textsuperscript{27} with an incident wavelength of $\lambda = 1.5484$ Å. High resolution X-ray diffraction measurements were performed at the high resolution powder diffraction beamline B2 at HASYLAB (DESY, Hamburg, Germany) with a scintillation counter with an analyzer crystal at an incident wavelength of $\lambda = 0.538$ Å using transmission geometry. For X-ray diffraction, sintered pellets were polished to a thickness of 100 μm. After measuring the initial state, silver electrodes were sputtered on the top and bottom faces of the sample. During in situ X-ray diffraction, a maximum voltage of 400 V was applied to the samples, which corresponds to an electric field of 4 kV/mm. Two samples of each composition were fatigue ex situ under a bipolar triangular load at the frequency of 50 mHz and a maximum electric field of 6 kV/mm. In order to reach a fatigued state, the samples were exposed to 100 bipolar cycles.

Data analysis was performed by Rietveld refinement with the program packages Fullprof\textsuperscript{28} and MAUD.\textsuperscript{29} The structure models consisted of a rhombohedral R3c phase and a tetragonal $P4bm$ phase. For the textured, poled samples an exponential harmonics model accounted for the preferred orientation during the refinement.\textsuperscript{30} TEM sample preparation of initial and ex situ fatigued specimen included polishing, ultrasonic disc cutting, dimpling, and ion-thinning. TEM experiments were performed on an FEI CM20 (FEI, Eindhoven, The Netherlands) operated at 200 kV.

The results of the TEM investigations of both compositions are depicted in Fig. 1. Bright field micrographs of the initial, unpoled state along the [130]$_C$ zone axis for BNT-6BT (Fig. 1(a)) and BNT-7BT (Fig. 1(b)) show an almost homogeneous contrast. For BNT-6BT several grains featured a core-shell structured contrast, comparable to K\textsubscript{0.3}Na\textsubscript{0.7}Bi\textsubscript{0.3}TiO\textsubscript{3} doped BNT-6BT.\textsuperscript{31} In BNT-7BT, some grains exhibited domains, as recently reported.\textsuperscript{11} The corresponding selected area electron diffraction (SAED) pattern are depicted in the inset of Figs. 1(a) and 1(b). In the following, the subscript C denotes the pseudocubic perovskite unit cell, whereas $R$ denotes rhombohedral and $T$ tetragonal indexing. Both types of superlattice reflections (SR) $\frac{1}{2}$ 000 and $\frac{1}{2}$ 0 0 0, where $a$ and $c$ denote odd and even Miller indices,\textsuperscript{32,33} are present, even though with different intensities and widths.

The Rietveld refinements with neutron diffraction data of the initial, unpoled structures of compositions BNT-6BT and BNT-7BT are presented in Figs. 2(a) and 2(b), respectively. With the neutron diffraction data, the SR arising from the octahedral tilting become visible. The insets depict the positions of the $\frac{1}{2}$310$_C$ and $\frac{1}{2}$311$_C$ SR. Although a very weak intensity of the $\frac{1}{2}$311$_C$ reflection is observable for both compositions, the structures could only be refined with a single phase $P4bm$ model. Due to the weak intensity of the SR and the weak lattice distortion, a phase coexistence with $R3c$ could not be established within the refinements.

From the atomic positions, the octahedral tilting angle could be calculated to $\omega_T = 2.49(12)^\circ$ for BNT-6BT and $\omega_T = 2.25(11)^\circ$ for BNT-7BT. With 0.009(3)% for BNT-6BT and 0.008(3)% for BNT-7BT the lattice distortions of the unpoled material are small enough to be almost within the error range.

A direct comparison of the two neutron diffraction patterns is depicted in Fig. 3(a). The SR of both compositions is almost exactly the same as already indicated by the tilt angles from the refinements. Close inspection with high resolution X-ray diffraction also reveals only minor differences (Figs. 3(b) and 3(c)). The 111$_C$ reflection of BNT-6BT features a small shoulder which indicates a small fraction of a rhombohedral distorted phase (Fig. 3(b)). However, the intensity is too low to quantify the amount with a refinement.
The 200C reflection of the same composition exhibits a small broadening indicating a higher tetragonal lattice distortion (Fig. 3(c)), but with a full width at half maximum (FWHM) of 0.019°/C14, the reflection is still very sharp. The high resolution X-ray diffraction patterns of BNT-6BT and BNT-7BT revealed the presence of a pseudocubic structure in the unpoled state. The in situ measurements were performed in transmission geometry with the electric field parallel to the incident beam (ψ = 0°) (Fig. 4). With the application of an electric field of 4 kV/mm, a field induced phase transition takes place. For both compositions, the pronounced lattice distortion can be observed at the 110C reflection. In addition to the lattice distortion, a texturing can be observed (see arrows in Fig. 4). In the remanent state (poled, 0 kV/mm), the texturing is reduced while the lattice distortion is maintained.

Apart from the pronounced splitting of the 110C reflection, BNT-6BT is characterized by a pronounced splitting of the 111C reflection and a splitting of the 200C reflection. Due to a strong texturing, the 111R reflection almost vanishes (arrow, Fig. 4(a)). The lattice distortions can be calculated as $\eta_T = \frac{c_T}{a_T} - 1$ and $\eta_R = \frac{\sqrt{2}c_T}{2\sqrt{3}a_T} - 1$. A refinement of the lattice parameters reveals a lattice distortion of $\eta_T = 0.244\%$ and $\eta_R = 0.8567\%$ with 16.5% tetragonal and 83.5% rhombohedral phase in the remanent state after poling (0 kV/mm). With applied electric field (poled, 4 kV/mm), a phase transition to 33.8% tetragonal and 64.9% rhombohedral takes place. While the tetragonal lattice distortion changes to $\eta_T = 0.432\%$, the rhombohedral lattice distortion shows no significant change ($\eta_R = 0.8626\%$).

BNT-7BT reveals an opposite behavior. Here, the 200C reflection provides a significant splitting and strong texturing with an almost vanishing 002T reflection (arrow, Fig. 4(b)). The 111C also shows splitting comparable to the 200C reflection of BNT-6BT. The refinement reveals a lattice distortion of $\eta_T = 1.2656\%$ and $\eta_R = 0.314\%$ with 66.6% tetragonal and 36.4% rhombohedral phase in the remanent state (poled, 0 kV/mm, Table I). Under the influence of an applied field (poled, 4 kV/mm), BNT-7BT shows a phase transition in the direction of rhombohedral symmetry (54.4% tetragonal and 45.6% rhombohedral phase). The lattice distortion of the

![FIG. 2. Rietveld refinement of neutron diffraction data showing the initial structure of (a) BNT-6BT and (b) BNT-7BT. The insets show the 1/2{310}C and 1/2{311}C superlattice reflections.](image)

![FIG. 3. Comparison of (a) the neutron diffraction pattern and (b) and (c) X-ray diffraction pattern of BNT-6BT and BNT-7BT.](image)

![FIG. 4. High resolution X-ray diffraction pattern at $\psi = 0°$ of the remanent state at 0 kV/mm and the applied field state at 4 kV/mm in comparison to the unpoled state of (a) BNT-6BT and (b) BNT-7BT.](image)
rhombohedral phase increases to $\eta_{R} = 0.363\%$ and to $\eta_{T} = 1.277\%$ for the tetragonal phase.

Although the two compositions show an almost indistinguishable structure in the unpoled state, BNT-6BT transforms to a predominantly rhombohedral modification under the influence of an electric field, while BNT-7BT transforms to a predominantly tetragonal modification. This is in agreement with the phase diagram, where BNT-6BT is more on the rhombohedral side and BNT-7BT more on the tetragonal side of the MPB. With electric field both compositions reveal a phase transition in the direction of the minority phase. In the process the lattice distortion of the minority phase increases significantly compared to that of the majority phase. This behavior is similar to the field induced behavior of actuator materials based on lead zirconate titanate.

When we consider the unpoled sample as a polycrystalline material with pseudocubic structure, all grains have random orientation. The electric field induces either a rhombohedral or a tetragonal phase. While the tetragonal phase offers 8 polarization directions along 111, dependent on grain orientation, one of the phases is favorable concerning the orientation of the polarization vector with respect to the electric field vector. If no other factors would influence the field induced structure, the applied field state should show $\frac{\eta_{R}}{\eta_{T}} = 57.1\%$ rhombohedral and $\frac{\eta_{R}}{\eta_{T}} = 42.9\%$ tetragonal phase. Our results unambiguously demonstrate that both compositions provide a trend towards this phase composition under the influence of an electric field.

After electric cycling, the samples ex situ by 100 bipolar cycles, the remanent polarization $P_r$ decreased to 57% and 66% relative to its initial values for BNT-6BT and BNT-7BT, respectively. Fig. 5 displays BF and SAED of specimens (a) BNT-6BT and (b) BNT-7BT in the fatigued remanent state at 0 kV/mm. The presence of domains is visible in both compositions. A recently performed in situ electric-field TEM investigation on lanthanum doped BNT-5BT supported the idea of evolving domain configurations as salient features in the fatigue processes. In BNT-6BT, a high amount of grains feature a core-shell structure. Presence of some several nanometer sized pores near to the core region is frequently observed. These pores could act as seeds for the phase transformation, due to a higher local electric field. In BNT-7BT, a homogenous distribution of domains within the grains was observed. The corresponding [130]C diffraction patterns reveal the presence of both types of SR.

![FIG. 5. BF image of (a) BNT-6BT and (b) BNT-7BT after ex situ fatiguing. Corresponding electron diffraction pattern along [130]C is shown in the inset.](image)

![FIG. 5. BF image of (a) BNT-6BT and (b) BNT-7BT after ex situ fatiguing. Corresponding electron diffraction pattern along [130]C is shown in the inset.](image)
lattice distortions during poling. The initial pseudocubic structure transforms to a phase coexistence of distorted rhombohedral and tetragonal phases with preferred orientation. While BNT-6BT provides a strong rhombohedral and a weak tetragonal lattice distortion, BNT-7BT is characterized by a strong tetragonal and a weak rhombohedral lattice distortion. Similar to commercial lead containing piezoceramics, the phase coexistence is the key for the enhanced piezoelectric properties. Additionally, BNT-xBT reveals similar to the lead phase coexistence is the key for the enhanced piezoelectric properties. Additionally, BNT-xBT reveals similar to the lead containing material that cycling has the opposite effect on the phase composition compared to applying a single electric field. Therefore, this study indicates that the phase composition is not only dependent on the chemical composition but also on the state and nature of the applied field state.

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8C. Ma and X. Tan, Solid State Commun. 150, 1497 (2010).