Field-induced phase transition in $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ -based lead-free piezoelectric ceramicsManuel Hinterstein,^{a,b*} Michael Knapp,^c Markus Hölzel,^a Wook Jo,^a Antonio Cervellino,^d Helmut Ehrenberg^b and Hartmut Fuess^a^aInstitute for Materials Science, TU Darmstadt, Petersenstrasse 23, 64287 Darmstadt, Germany,^bInstitute for Materials Science, TU Dresden, Helmholtzstrasse 7, 01062 Dresden, Germany,^cCELLS, POB 68, 08193 Barcelona, Spain, and ^dSwiss Light Source, Paul Scherrer Institute, 5232

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The origin of the electric field-induced strain in the polycrystalline ceramic $0.92\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.02\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ was investigated using *in situ* high-resolution X-ray and neutron diffraction techniques. The initially existing tetragonal phase with pseudocubic lattice undergoes a reversible phase transition to a significantly distorted rhombohedral phase under electric field, accompanied by a change in the oxygen octahedral tilting from $a^0a^0c^+$ to $a^-a^-a^-$ and in the tilting angle. The polarization values for the tetragonal and rhombohedral phases were calculated based on the structural information from Rietveld refinements. The large recoverable electric field-induced strain is a consequence of a reversible electric field-induced phase transition from an almost nonpolar tetragonal phase to a ferroelectrically active rhombohedral phase.

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1. Introduction

Lead-containing materials, such as $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3$ and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3$ in either single-crystal or polycrystalline ceramic form, are currently applied in industry. However, the toxicity of lead oxide and its high vapour pressure during processing initiated a search for alternative lead-free environmentally friendly piezoelectric materials. Our investigation is based on two promising lead-free systems: $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$ (BNT–BT) (Takenaka *et al.*, 1991) and $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (KNN) (Cross, 1958). For reasons of convenience the system $(1-x-y)\text{BNT}\text{--}x\text{BT}\text{--}y\text{KNN}$ will in the following be denoted by $100(1-x-y)\text{--}100x\text{--}100y$. Previous work in our laboratory (Zhang *et al.*, 2007; Zhang, Kounga, Aulbach, Granzow *et al.*, 2008; Zhang, Kounga, Aulbach, Jo *et al.*, 2008) revealed that improved properties of the BNT–BT system could be achieved by adding several per cent of KNN. In particular, a large recoverable strain of up to 0.45% has been demonstrated under either unipolar or bipolar field-cycling conditions, higher than any obtained with prominent ferroelectric lead zirconate titanate (PZT) ceramics and comparable to strains obtained in Pb-based antiferroelectrics (Yu & Singh, 2003).

Extensive studies showed that morphotropic $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$ with an additional 1–3% of morphotropic $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ leads to the best piezoelectric response (Zhang *et al.*, 2007; Zhang, Kounga, Aulbach, Granzow *et al.*, 2008; Zhang, Kounga, Aulbach, Jo *et al.*, 2008). Dielectric studies revealed that $(1-x-y)\text{BNT}\text{--}x\text{BT}\text{--}y\text{KNN}$ ($0.05 \leq x \leq 0.07$, $0.01 \leq y \leq 0.03$) possesses a morphotropic phase

boundary separating a nonpolar from a ferroelectric phase (Zhang *et al.*, 2007). A combination of longitudinal and transverse strain measurements revealed a correlation between the large strain and an electric field-induced nonpolar-to-ferroelectric phase transition (Jo *et al.*, 2009). The compositions in the investigated range exhibit significantly different piezoelectric properties. The maximum strain (S_{max}) reaches up to 0.45%. $S_{\text{max}}/E_{\text{max}}$ (E_{max} is the field strength at S_{max}) reaches up to 560 pm V^{-1} , higher than values reported for other lead-free and untextured lead-containing polycrystalline ferroelectric ceramics (Saito *et al.*, 2004).

Detailed structural studies have been performed by Jones & Thomas (2002, 2000) for the system BNT. They found two temperature-dependent phase transitions: from the low-temperature ferroelectric phase *R3c* to the high-temperature phase *P4bm* in the range from 573 to 593 K, and the ferroelectric to paraelectric transition at 813 K. Both polar ferroelectric phases exhibit oxygen octahedral tilting, which can be described by the Glazer (1975) notation as $a^-a^-a^-$ for *R3c* and $a^0a^0c^+$ for *P4bm*. The octahedral tilting results in superstructure reflections (SR) of the type $1/2\{000\}$ for *R3c* and $1/2\{00e\}$ for *P4bm*, where ‘o’ represents odd and ‘e’ even Miller indices. Additionally *P4bm* possesses an unusual combination of antiparallel cation displacements along the polar *c* axis and in-phase oxygen octahedral tilts (Jones & Thomas, 2000). From dielectric measurements a rhombohedral–tetragonal morphotropic phase boundary was proposed for $(1-x)\text{BNT}\text{--}x\text{BT}$ at $x \simeq 0.06\text{--}0.07$ (Takenaka *et al.*, 1991). Ranjan & Dwiwedi (2005) confirmed a phase transition from rhombohedral to pseudocubic with increasing *x* by X-ray

diffraction. They found the structure to be pseudocubic for $x \geq 0.06$.

Since all structural studies yield only small distortions from cubic symmetry or even pseudocubic lattice parameters, the origin of the prominent piezoelectric properties is still unclear. Therefore characterizations under the influence of applied electric fields are mandatory. Such *in situ* studies have been performed with X-ray diffraction for capacitors (Menou, Muller, Baturin, Kuznetsov *et al.*, 2005; Menou, Muller, Baturin, Shur & Hodeau, 2005), single crystals (Hansen *et al.*, 2004), PZT-based thin films (Fong & Thompson, 2006) and bulk ceramics (Schoenau *et al.*, 2007; Hall *et al.*, 2004).

Recently a phase transition from rhombohedral to tetragonal symmetry in Mn-doped BNT–BT single crystals with an electric field applied along the $[001]_c$ direction has been reported (Ge *et al.*, 2009). The subscript 'c' denotes the pseudocubic perovskite unit cell. For relaxor ferroelectric systems such as $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$, Lebon *et al.* (2003) reported a similar behaviour. Starting from pseudocubic symmetry a ferroelectric tetragonal phase was induced by an external electric field applied along the $[001]_c$ direction. Moreover, a ferroelectric rhombohedral phase resulted by applying the electric field along $[111]_c$ to the same material. These phase transitions are connected to a change of disorder of the lead ions. High-energy X-ray diffuse scattering indicates a redistribution of the polar nanoregions (PNRs) during the field-induced rhombohedral phase transition (Xu *et al.*, 2006). These PNRs are considered to be precursors of the ferroelectric phase and are widely believed to be essential for relaxor properties (Cross, 1987).

For 93–07–00, a field-induced phase transition from pseudocubic to tetragonal was reported (Daniels *et al.*, 2009). From texture analysis using profile fitting the authors concluded a strong domain texture with the polarization of the induced phase aligning preferentially parallel to the electric field. Similar to this study most *in situ* neutron diffraction experi-

ments concentrate on the analysis of single reflections (Jones *et al.*, 2006; Daniels *et al.*, 2007).

In situ transmission electron microscopy (TEM) studies with applied electric field revealed for 91–06–03 a complete absence of any visible domain structures in the unpoled state (Kling *et al.*, 2010). Domains, however, appear with an applied electric field and disappear when the field is switched off. Recently we studied the composition 92–06–02 in comparison with 94–05–01 (Schmitt *et al.*, 2010). Similar to 91–06–03, no domain structures were visible in 92–06–02. The composition 94–05–01 clearly showed domain structures, and X-ray and neutron data exhibited a phase coexistence of $R3c$ and $P4bm$, while 92–06–02 was refined by a single-phase fit for $P4bm$. In 91–06–03, Schmitt & Kleebe (2010) observed the coexistence of $R3c$ and $P4bm$ within single grains. The composition 92–06–02 exhibits the highest strain under applied electric field in the investigated range. We therefore investigated this composition with high-resolution *in situ* synchrotron diffraction and *in situ* neutron powder diffraction under applied electric fields with specifically developed sample environments.

2. Experimental

Samples of the composition $0.92\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.02\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (92–06–02) were synthesized by conventional ceramic fabrication methods *via* calcination of Bi_2O_3 , Na_2CO_3 , K_2CO_3 , BaCO_3 , TiO_2 and Nb_2O_5 powders at 1173 K for 3 h and sintering at 1423 K for 3 h.

All high-resolution X-ray measurements were performed at the high-resolution powder diffraction station of the materials science (MS) beamline at the Swiss Light Source (SLS, Villigen, Switzerland) (Patterson *et al.*, 2005) at an incident wavelength of $\lambda = 0.4780 \text{ \AA}$ (26 keV) using the same geometry as previously reported for PZT (Schoenau *et al.*, 2007). This sample environment is set up in transmission geometry with the incoming X-ray beam parallel to the electric field. Data were recorded by a position-sensitive microstrip detector (Schmitt *et al.*, 2003; Bergamaschi *et al.*, 2010). The wavelength and the instrumental profile were determined with an LaB_6 standard (SRM NIST 660a). From polycrystalline sintered pellets with diameter 10 mm, discs were cut, thinned and polished to a thickness of 110 μm .

Neutron powder diffraction measurements were carried out on the SPODI powder diffractometer at the research reactor FRM II (Garching bei München, Germany) (Hoelzel *et al.*, 2007) at an incident wavelength of 1.548 $\text{\AA}$. Data were collected by a bank of 80 position-sensitive ^3He detectors covering a 160° scattering range. The wavelength and the instrumental profile were determined with a silicon (SRM NIST 640c) and a corundum standard, respectively. The polycrystalline sintered sample of cylindrical form had a height of 5.5 mm and a diameter of 10 mm.

For electric contacting, silver electrodes with a thickness of 15 nm for X-ray and 40 nm for neutron measurements were sputtered onto the samples from both sides using a mask of around 9 mm in diameter (Sputter Coater SCD 050, Balzers).

Figure 1

Schematic drawing of the high-voltage sample environment for neutron powder diffraction. The viewing direction is upstream of the primary beam. The diffraction plane is perpendicular to the drawn cross section.

The plasma current was 40 mA, operating under an Argon pressure below 5 Pa. The electrodes were fired at 623 K.

For *in situ* neutron measurements with electric field we developed a new sample environment (Fig. 1). A cylindrical aluminium container with a wall thickness of 2 mm, 120 mm height and a diameter of 120 mm constitutes the outer wall of the sample environment. All container walls as well as the aluminium contacts beyond the detection range of the detector are shielded with hexagonal boron nitride to avoid aluminium reflections and electrical short circuits. The sample is contacted from two opposite sides in the vertical direction with aluminium contacts. This way the electric field is perpendicular to the diffraction plane and the incident neutron beam. The sample environment is evacuated to around 100 Pa and then flooded with the electrically insulating gas SF₆ to a pressure of around 1.5×10^5 Pa to assure electric insulation and to avoid short circuits. The electric field is applied statically with a high-voltage power supply reaching a maximum voltage of 35 kV (FuG HCP 35–35000).

In contrast to all other existing *in situ* sample environments the electric field vector is perpendicular to the scattering plane in this case. This way the diffracting lattice planes for every reflection are parallel to the field vector, resulting in a constant observation angle with respect to the field for the whole diffractogram.

Full-profile Rietveld refinements were carried out using the software package *FullProf* (Roisnel & Rodriguez-Carvajal, 2001). To reduce the number of refined parameters an instrumental resolution file provided the instrumental contribution to the profile function. The peak profile shape was described by a Thompson–Cox–Hastings pseudo-Voigt function (Thompson *et al.*, 1987). The background of the diffraction pattern was fitted using a linear interpolation between selected data points in non-overlapping regions. The scale factor, lattice parameters, atomic parameters, zero angular shift, and microstructural and preferred orientation para-

eters were varied during the refinement. The lattice and atomic parameters were constrained for the combined refinement with X-ray and neutron data.

3. Results

3.1. Combined X-ray and neutron zero-field structure

We investigated the initial unpoled state of the sample with high-resolution X-ray and neutron diffraction. Fig. 2 shows the combined Rietveld refinement. Even with high-resolution X-ray diffraction almost no lattice distortion is visible (Fig. 2a). The main reflections do not show any splitting that could be interpreted as tetragonal or rhombohedral distortion. High-resolution neutron diffraction reveals strongly broadened SR of the type $1/2\{00\}$ (Fig. 2b), indicating the tetragonal phase *P4bm* with in-phase oxygen octahedral tilts along the *c* axis (Glazer notation $a^0a^0c^+$). A refinement with the centrosymmetric space group *P4/mbm* was not feasible. The results are in good agreement with a comparative study on the same composition using TEM and X-ray (XRD) and neutron diffraction (ND) (Schmitt *et al.*, 2010). This work gave evidence that the SR of this composition originate from octahedral tilting in a non-centrosymmetric phase. Additionally Schmitt & Kleebe (2010) discussed the origin of SR for 91–06–03 on the basis of electron diffraction.

From the FWHM of the broadened SR we calculated a particle size of around 8 nm. The combined Rietveld refinement with neutron and X-ray data yields a weak tetragonal distortion of only 0.0258% and an octahedral tilting angle $\omega_1 = 2.25^\circ$. Tables 1–3 show a summary of refined and calculated parameters. The introduction of anisotropic displacement parameters (ADPs) for O atoms improved the fit. Therefore, ADPs were applied for all O atoms, while for the remaining atoms isotropic displacement parameters were used. The ADPs for O₁ show a pronounced flattening along the polar *c*

Figure 2

Combined Rietveld refinement with (a) X-ray diffraction and (b) neutron diffraction data. The insets show the (a) $\{110\}_c$ reflection and (b) broadened superstructure reflections.

Table 1

Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) of the refinements for the unpoled sample (0 kV mm^{-1}) and the sample with applied electric field (6 kV mm^{-1}).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
0 kV mm⁻¹, <i>P4bm</i>				
<i>A</i>	0.0	0.5	0.5293 (15)	0.0696 (5)
<i>B</i>	0.0	0.0	0.0	0.0170 (5)
<i>O</i> ₁	0.0	0.0	0.511 (5)	–
<i>O</i> _{2,3}	0.2598 (7)	0.2402 (7)	0.027 (5)	–
6 kV mm⁻¹, <i>P4bm</i>				
<i>A</i>	0.0	0.5	0.555 (5)	0.051 (3)
<i>B</i>	0.0	0.0	0.0	0.0047 (19)
<i>O</i> ₁	0.0	0.0	0.506 (7)	–
<i>O</i> _{2,3}	0.2604 (7)	0.2396 (7)	–0.001 (9)	–
6 kV mm⁻¹, <i>R3c</i>				
<i>A</i>	0.0	0.0	0.257 (2)	0.041 (4)
<i>B</i>	0.0	0.0	0.004 (3)	0.021 (3)
<i>O</i>	0.1341 (7)	0.3299 (18)	0.083	–

Table 2

Anisotropic displacement parameters ($\text{\AA}^2$) of the refinements for the unpoled sample (0 kV mm^{-1}) and the sample with applied electric field (6 kV mm^{-1}).

Atom	<i>U</i> ₁₁	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃
0 kV mm⁻¹, <i>P4bm</i>						
<i>O</i> ₁	0.029 (3)	0.0	0.0	0.029 (3)	0.012 (4)	0.0
<i>O</i> _{2,3}	0.0218 (18)	–0.0154 (20)	0.009 (5)	0.0218 (18)	0.081 (5)	–0.009 (5)
6 kV mm⁻¹, <i>P4bm</i>						
<i>O</i> ₁	0.040 (3)	0.0	0.0	0.040 (3)	0.058 (7)	0.0
<i>O</i> _{2,3}	0.0154 (20)	–0.014 (2)	–0.012 (6)	0.0154 (20)	0.141 (8)	0.012 (6)
6 kV mm⁻¹, <i>R3c</i>						
<i>O</i>	0.0113 (15)	–0.009 (3)	–0.015 (3)	0.029 (4)	0.023 (4)	–0.014 (4)

axis, while the ADPs for *O*_{2,3} are flattened along $\langle 110 \rangle$ with an elongation along the polar *c* axis (Table 2 and Fig. 3*a*). The atomic positions exhibited the same unusual antiparallel cation displacements as reported by Jones & Thomas (2000) (Table 1). The *A*-site cations are related to the most pronounced static atomic displacements ($0.114 \text{ \AA}$) together with large isotropic displacement parameters ($0.0696 \text{ \AA}^2$). This feature is frequently observed in lead-based relaxor ferroelectrics (Peng & Bursill, 1993; Zhou *et al.*, 2004; Maier *et al.*, 2010). Owing to the antiparallel static displacement, the resulting spontaneous polarization (*P*_s) is almost negligible. Therefore, this phase has to be considered as nonpolar (Jo *et al.*, 2009).

3.2. Time-resolved *in situ* X-ray diffraction

A time-resolved X-ray measurement with a frame rate of 0.5 Hz during a constant increase of the electric field of around $0.0088 \text{ kV mm}^{-1} \text{ s}^{-1}$ and a switch-off after reaching 4.6 kV mm^{-1} displays the reversible character of the poling with electric fields (Fig. 4). The depolarization occurs immediately, which is in good agreement with the polarization [*P*(*E*)] and strain [*S*(*E*)] hysteresis loops of 91–06–03, where a

Table 3

Structural parameters.

0 kV mm⁻¹, <i>P4bm</i>	
<i>a</i> ($\text{\AA}$)	5.52166 (3)
<i>c</i> ($\text{\AA}$)	3.90541 (4)
<i>V</i> ($\text{\AA}^3$)	119.0712 (16)
<i>V</i> _c ($\text{\AA}^3$)	59.54
Tetragonal distortion (%)	0.0258 (16)
ω_t (°)	2.25 (11)
<i>P</i> _s ($\mu\text{C cm}^{-2}$)	4 (2)
<i>R</i> _B (ND/XRD)	7.92/7.48
χ^2 (ND/XRD)	3.51/1.14
6 kV mm⁻¹, <i>P4bm</i>	
<i>a</i> ($\text{\AA}$)	5.51020 (10)
<i>c</i> ($\text{\AA}$)	3.9186 (4)
<i>V</i> ($\text{\AA}^3$)	118.977 (12)
<i>V</i> _c ($\text{\AA}^3$)	59.49
Tetragonal distortion (%)	0.572 (12)
<i>P</i> ($\mu\text{C cm}^{-2}$)	5 (4)
Phase fraction (%)	29.13 (16)
ω_t (°)	2.39 (12)
<i>R</i> _B (ND)	7.58
χ^2 (ND)	2.58
6 kV mm⁻¹, <i>R3c</i>	
<i>a</i> ($\text{\AA}$)	5.50818 (9)
<i>c</i> ($\text{\AA}$)	13.5286 (10)
<i>V</i> ($\text{\AA}^3$)	355.47 (3)
<i>V</i> _c ($\text{\AA}^3$)	59.24
α_r (°)	89.90
Rhombohedral distortion (%)	0.269 (9)
<i>P</i> ($\mu\text{C cm}^{-2}$)	11 (6)
Phase fraction (%)	70.87 (16)
<i>s</i>	0.007 (2)
<i>t</i>	0.004 (3)
<i>d</i>	0.0009 (5)
<i>e</i>	0.0154 (8)
ω_r (°)	6.106 (6)
$\zeta \times 10^2$	–0.75 (7)
<i>R</i> _B (ND)	5.53
χ^2 (ND)	2.58

Figure 3

Illustration of the unit cell with ADPs for the O atoms of (a) *P4bm* in the unpoled state and (b) *P4bm* and *R3c* at 6 kV mm^{-1} .

Table 4
Structural descriptions given in the space groups *R3c* and *P4bm* (Megaw & Darlington, 1975).

Space group	Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>
<i>P4bm</i>	<i>A</i>	2(<i>b</i>)	0	1/2	1/2 + $\delta_{z,A}$
	<i>B</i>	2(<i>a</i>)	0	0	0
	<i>O</i> ₁	2(<i>a</i>)	0	0	1/2 + $\delta_{z,O1}$
	<i>O</i> _{2,3}	4(<i>c</i>)	1/4 - $\delta_{x,O23}$	1/4 + $\delta_{x,O23}$	0 + $\delta_{z,O23}$
<i>R3c</i>	<i>A</i>	6(<i>a</i>)	0	0	1/4 + <i>s</i>
	<i>B</i>	6(<i>a</i>)	0	0	<i>t</i>
	<i>O</i> ₁	18(<i>b</i>)	1/6 - 2(<i>e</i> - <i>d</i>)	1/3 - 4 <i>d</i>	1/12

very low remanent polarization for samples poled up to about 5.0 kV mm⁻¹ was found (Kling *et al.*, 2010). Fig. 4 shows that the first clearly visible reactions to the applied field occur at around 250 s, representing a field strength of around 2.2 kV mm⁻¹, which is also in good agreement with the published *S(E)* data (Zhang, Kounga Aulbach, Granzow *et al.*, 2008; Jo *et al.*, 2009; Kling *et al.*, 2010).

3.3. *In situ* neutron diffraction

Since the structure of BNT–BT–KNN is dominated by oxygen octahedral tilting and the X-ray geometry is not sufficiently sensitive to this investigated system, we studied the sample using the *in situ* sample environment for the high-resolution neutron powder diffractometer SPODI at FRM II. In the neutron diffraction experiment the direction of the applied electric field is perpendicular to the scattering plane, allowing a full-pattern Rietveld refinement. For the same composition we could reach an even higher field of 6.0 kV mm⁻¹ without short circuits. Fig. 5 shows the two-phase refinement of the poled sample at 6.0 kV mm⁻¹ with space groups *P4bm* and *R3c*. The two insets on the left show the most intense rhombohedral superstructure reflections arising

with applied electric field and the inset on the right shows the split {331}_c reflection. The superstructure reflections of the new phase are of the type 1/2{000} and indicate a phase transition to rhombohedral symmetry with an *a*⁻*a*⁻*a*⁻ tilt system.

The *R3c* phase can be described as a rhombohedrally centred hexagonal lattice projected down the threefold axis. The rhombohedral structure is referred to on hexagonal axes, whose lattice parameters *a*_h and *c*_h are specified in relation to the double pseudocubic cell (2*a*_c × 2*b*_c × 2*c*_c) by the matrix

$$\begin{pmatrix} 0.5 & 0 & -0.5 \\ -0.5 & 0.5 & 0 \\ 1 & 1 & 1 \end{pmatrix}.$$

This setting allows the definition of only four structural parameters, *e*, *d*, *s* and *t*, and leads to the set of atomic fractional coordinates given in Table 4 (Megaw & Darlington, 1975). The parameter *e* is related to the tilt angle ω , which indicates the rotation of the oxygen octahedra around the triad axis:

$$\tan \omega = 4e3^{1/2}. \quad (1)$$

The distortion of the oxygen octahedra, keeping the triad axis symmetry and influencing the relation between the upper and the lower faces, is described by the parameter *d*. Finally, the shifts of the *A* and *B* cations along the ferroelectric axis are derived from the parameters *s* and *t*, respectively. They determine the strength of the polarization.

The tilt angle and the hexagonal cell parameters are coupled through an additional parameter called the octahedral strain:

$$\zeta = \cos \omega \left(\frac{c_h}{6^{1/2}a_h} \right) - 1. \quad (2)$$

Figure 4
Time-dependent X-ray diffraction measurement with frame rate 0.5 Hz and poling velocity 0.0088 kV mm⁻¹ s⁻¹. The intensity along the vertical line at 2θ = 9.845° is shown on the right. The intensity plot along the horizontal line at time = 520 s (*E* = 4.5 kV mm⁻¹) is shown at the top.

Figure 5
Rietveld refinement of 92-06-02 at 6 kV mm⁻¹. The insets show the superstructure reflections (SR) of both phases and the rhombohedral split {331}_c reflection.

The octahedra are elongated along c_h if $\zeta > 0$ and compressed for $\zeta < 0$, while $\zeta = 0$ results in no strain (Megaw & Darlington, 1975).

The two-phase Rietveld refinement with space groups $R3c$ and $P4bm$ yields a rhombohedral distortion angle $\alpha_r = 89.90^\circ$ and an octahedral tilting angle $\omega_r = 6.106^\circ$ with an octahedral strain $10^2\zeta = -0.75$. The rhombohedral phase fraction of around 71% indicates a pronounced phase transition to $R3c$. The ADPs of the rhombohedral O atom are elongated along the polar $\langle 111 \rangle_c$ and flattened along all other $\langle 111 \rangle_c$ directions (Fig. 3*b*). The tetragonal phase exhibits a tetragonal distortion of 0.572%. The atomic positions at 6.0 kV mm^{-1} reveal the same unusual polar displacement along the c_t axis as in the unpoled state. With $\omega_t = 2.39^\circ$ no significant change was observed for the octahedral tilting angle. For the tetragonal phase the ADPs of O_1 show an elongation along $\langle 001 \rangle_t$. The ADPs of $O_{2,3}$ are significantly reduced along $\langle 110 \rangle_t$ compared with the unpoled state, still exhibiting an elongation along $\langle 001 \rangle_t$ (Fig. 3*b*).

Compared to the unpoled state the reduced cell volume – as this geometry is not sensitive to the presumably dominant elongation parallel to the field vector – showed an apparent decrease of around 0.08% for the tetragonal phase and around 0.51% for the rhombohedral phase. From the atomic positions and the lattice parameters the polarization P is calculated (Table 3). The estimation of P is based on the dipole moment equation $P \simeq (1/V) \sum_i q_i r_i$, where the summation is over all point charges q_i at positions r_i in a primitive cell volume V (Frantti *et al.*, 2002). The calculation of P results in very low values for $P4bm$ in the unpoled state as well as in the poled state. For $R3c$ P is slightly higher but still significantly lower than for common ferroelectrics ($\sim 40 \text{ } \mu\text{C cm}^{-2}$; Frantti *et al.*, 2002; Muller *et al.*, 2000).

A refinement of preferred orientation with the March–Dollase model (Dollase, 1986) did not improve the fit considerably. For the tetragonal phase the introduction of this additional degree of freedom resulted either in a negative tetragonal distortion or a preferred orientation perpendicular to the applied electric field due to the low phase fraction of $P4bm$. For $R3c$ no significant change could be observed by applying a preferred orientation.

4. Discussion

The structural results of the sample in the unpoled state are unexpected for a material with ferroelectric properties. With almost no ferroelectric distortion and weak evidence of a superstructure, the sharp reflections especially from X-ray diffraction indicate a long-range-ordered pseudocubic lattice (Fig. 2). The antiparallel cation displacement together with a tetragonal distortion of only 0.26% result in almost no spontaneous polarization. The combination of static displacements and large isotropic displacement parameters for the A-site cations indicates a broad deviation of local displacements as found for relaxor ferroelectrics (Peng & Bursill, 1993; Zhou *et al.*, 2004; Maier *et al.*, 2010). Since the mean displacement, calculated from the isotropic displacement parameters

(0.264 Å), is twice as high as the static polar displacement (0.114 Å), the average structure has a nonpolar character. This is endorsed by the absence of anisotropic displacements.

The profile analysis of the SR from neutron diffraction shows that the oxygen octahedral tilting is a short-range-ordered variation of the average pseudocubic structure. This is underlined by the ADPs of the O atoms (Fig. 3*a*). The strong flattening along $\langle 110 \rangle_t$ for the O atoms responsible for the octahedral tilting ($O_{2,3}$) indicates a broad variation of tilting angles, also reflected by the relatively large error of 5% (Table 3).

With the application of an electric field the structure changes considerably. A strong reversible splitting of reflections is visible with X-ray diffraction (Fig. 4). As a result of strong texturing, a Rietveld refinement of the structure model based on these patterns was not feasible, but since the pseudocubic $\{hh0\}_c$ and $\{hhh\}_c$ reflections are split with an applied field while the $\{h00\}_c$ reflections are only shifted, we assume a phase transition to rhombohedral symmetry. The threshold field strength for the first response to the applied electric field is in good agreement with the strain measurements in the literature (Zhang, Kouna, Aulbach, Granzow *et al.*, 2008; Jo *et al.*, 2009; Kling *et al.*, 2010). The direct correlation of macroscopic strain and structural changes is thus confirmed. Since the change of lattice constants is due to a field-induced phase transition from tetragonal to rhombohedral, the large macroscopic strain is directly linked to this phase transition.

Kling *et al.* (2010) showed that the application of an electric field to a domain-free material (91–06–03) results in the formation of domain structures. Since 91–06–03 and 92–06–02 show very similar dielectric and electromechanical behaviour, the X-ray observations indicate a correlation between the field-induced phase transition with accompanying rhombohedral distortion and domain formation. Additionally, both compositions show a very low remanent strain and polarization for poling with fields up to 4.5 kV mm^{-1} . The results from X-ray diffraction agree with this observation, because after switching off the electric field, the structure returns to the initial state. Accordingly, the TEM study reports the disappearance of the domain structures by removing the electric field (Kling *et al.*, 2010).

With the data from the *in situ* neutron diffraction sample environment a further analysis was possible. The refinement with the data from the poled sample yields an intense phase transition from 100% tetragonal to 29% tetragonal and 71% rhombohedral for 6.0 kV mm^{-1} . This field-induced phase transition results in the formation of rhombohedral SR. Compared to the octahedral tilting angle of the initial state ($\omega_t = 2.25^\circ$), the rhombohedral tilting is stronger ($\omega_r = 6.106^\circ$).

Since the electric field vector in the neutron diffraction setup is perpendicular to the scattering plane, all diffracting lattice planes originate from unit cells with different orientations with respect to the electric field. In particular, unit cells oriented with the polarization direction along the applied electric field give no contribution to the diffraction of the lattice planes perpendicular to the polar axis. Thus a signifi-

cant amount of information is not accessible. Therefore, a decrease in unit-cell volume and almost no increase of the polarization can be observed in the poled state.

In this case of unidirectional loading the gathered information originates from observations perpendicular to the field vector. This is the reason for the contradictory results from the refinement. With an applied field the volume decreases and the oxygen octahedra are compressed along the polar axis ($\zeta < 0$) together with weak displacements of the *A* and *B* cations. Since the volume of the material is almost constant during the expansion along the electric field direction (Jo *et al.*, 2009), unit cells with the polar axis perpendicular to the electric field will be compressed.

The volume change of the rhombohedral phase is significantly higher than for the tetragonal one. With -0.08% the tetragonal volume change is in the range of 6.0 kV mm^{-1} (Jo *et al.*, 2009). For *R3c* the volume change is larger because only the compressed unit cells contribute to the diffraction pattern, whereas the stretched unit cells aligned along the electric field do not fulfil the diffraction condition and thus do not contribute.

This indicates that only *R3c* responds to the electric field. The tetragonal distortion of the remaining phase fraction of *P4bm* is the result of the compression perpendicular to the field direction, while the rhombohedral distortion is an active reaction to the applied electric field. The passive character of the tetragonal phase is confirmed by the constant values of polarization and ω_i . During unidirectional poling a preferred orientation is induced, resulting in a systematic increase or decrease of specific reflections, and hence in an error in the Rietveld refinement, as the integrated intensities cannot be modelled correctly. The refinement of ADPs can compensate for these effects. Since all ADPs show reasonable values and χ^2 as well as R_B are not worse for *in situ* data than for untextured zero-field data, preferred orientation effects are small and the ADPs are still significant. However, the shape of the ADPs is an artefact of the texturing, and the elongation along the polar axes indicates a broad deviation of polarizations of the contributing domains. Thus a complete structure analysis is only possible with the measurement of a sufficient number of different sample orientations with respect to the electric field vector.

The phase transition from pseudocubic to rhombohedral is the reason for the high macroscopic strain of BNT–BT–KNN. The tetragonal phase in the unpoled state is close to cubic, so every $\langle 111 \rangle_c$ direction can be converted to a rhombohedral polar axis with equal probability during the field-induced phase transition. Thereby, the generated lattice strain is compensated by tilting of the oxygen octahedra and the formation of domain walls.

During the poling process the tetragonal phase is not involved. The tetragonal distortion of the *P4bm* phase highlights the fact that, owing to macroscopic deformation induced by the phase transition to a rhombohedrally distorted phase, the tetragonal phase is forced to a deformation. It, therefore, acts as a kind of buffer between the polar rhombohedral domains. Regarding the initial structure of the sample, the nonpolar tetragonal phase can be considered as a locally

ordered precursor for the ferroelectrically active rhombohedral phase. The reversibility of this phase transition is the reason for the large recoverable strain of BNT–BT–KNN.

These results indicate a strong analogy to the polar nano-regions in relaxor ferroelectrics. The initial structure exhibits pseudocubic structure with short-range ordering of the octahedral tilting and *A*-site cation displacements. Additionally, the nonpolar tetragonal phase with pseudocubic lattice represents the precursor for the ferroelectrically active rhombohedral phase. Therefore, the pinched shape in the *P(E)* curves with traces of remanent polarization during bipolar cycling reported by Jo *et al.* are very likely to originate from this relaxor-like behaviour.

5. Conclusions

The development of a new type of *in situ* sample environment for neutron powder diffraction enabled a detailed analysis of lead-free 0.92BNT–0.06BT–0.02KNN. The large macroscopic strain and domain formations with applied electric field could be correlated with a field-induced phase transition from *P4bm* to *R3c*. This phase transition is accompanied by a change of the oxygen octahedral tilt system from $a^0a^0c^+$ to $a^-a^-a^-$. Together with *in situ* X-ray diffraction a detailed analysis correlates macroscopic properties and the microstructure with structural changes.

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