Revealing the mechanism of electric-field-induced phase transition in antiferroelectric NaNbO_3 by *in situ* high-energy X-ray diffractionMao-Hua Zhang¹, Changhao Zhao^{1,*}, Lovro Fulanović¹, Jürgen Rödel¹, Nikola Novak², Alexander Schökel², Jurij Koruza^{1,*}¹Department of Materials and Earth Sciences, Nonmetallic Inorganic Materials, Technical University of Darmstadt, 64287 Darmstadt, Germany²Department of Condensed Matter Physics, Jozef Stefan Institute, 1000 Ljubljana, Slovenia³Deutsches Elektronen-Synchrotron (DESY), 22607 Hamburg, Germany**Abstract**

Antiferroelectric materials exhibit electric-field-induced phase transitions between antiferroelectric and ferroelectric states, which enable their use in energy storage and other applications. However, the mechanisms of these transitions are insufficiently understood. Here, we considered the electric-field-induced phase transition in the lead-free antiferroelectric NaNbO_3 . Macroscopic measurements of polarization and longitudinal, transverse and volumetric strain were complemented with simultaneous structural investigations using high-energy X-ray radiation yielding crystallographic strain and unit cell volume change. The field-induced behaviour can be divided into the structural antiferroelectric-ferroelectric phase transition at about 8 kV/mm and the clearly decoupled polarization switching process at about 12 kV/mm, which is associated with a large increase in polarization and strain. Decoupling of the field induced phase transition and polarization switching is related to the randomly-oriented grains and mechanical stress present at the phase boundary.

Antiferroelectric materials are characterized by a phase transition from an antiferroelectric (AFE) to a ferroelectric (FE) state induced by the application of an external electric field. This transition is often accompanied by the appearance of double polarization hysteresis loops, depending on whether the transition is reversible¹⁻⁴ or irreversible^{5,6}. Reversible AFE-FE transitions enable potential application of AFE materials in a wide range of devices, including high energy density capacitors⁷⁻¹⁰, non-volatile random access memory¹¹, and electrocaloric refrigerators^{12,13}.

Double polarization hysteresis loops were observed in PbZrO_3 -based^{1,14}, PbHfO_3 -based^{15,16}, and AgNbO_3 ^{17,18} AFE systems. However, in pure NaNbO_3 , one of the prototype lead-free AFE

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materials, double polarization loops were only verified in certain single crystals^{6,19}. Instead, the electric-field-induced phase transition was reported to be irreversible^{5,20}, resulting in characteristic FE polarization loops after the first electric field cycle. The nature of the irreversibility remains unclear, but may be related to the small energy difference between the AFE and FE phases (about 2 meV/f.u.)^{21,22}, which is much smaller than the 20 meV/f.u. difference reported for PbZrO₃²³. This irreversible transition was recently investigated *ex situ* by comparing the sample's states before and after the application of electric fields⁵. The field-induced transformation of the non-polar *P* phase (AFE, orthorhombic *Pbcm*)²⁴ into the polar *Q* phase (FE, orthorhombic *P2₁ma*)²⁵ is accompanied by a large longitudinal strain of 0.64 %, drop in the permittivity, disappearance of the translational AFE domain structure, and changes of the local Na environment⁵. The transition was previously suggested to be of the first order nature⁶.

However, the mechanism of AFE-FE transitions, which includes interactions between the structural transformations, induced lattice strain, and FE domain formation and reorientation, remains poorly understood. Park *et al.* reported that the tetragonal(AFE)-rhombohedral(FE) transition in polycrystalline Pb_{0.98}La_{0.02}(Zr_{0.66}Ti_{0.10}Sn_{0.24})_{0.995}O₃ occurs by orientation of the AFE phase, AFE-FE transition, and subsequent poling of the FE phase²⁶. This transition is also accompanied by an unusual auxetic behaviour²⁷. While macroscopic polarization and strain measurements can be used to detect the transition, they do not provide detailed insight into the underlying structural changes. This problem can be overcome by *in situ* X-ray diffraction (XRD), which has been utilized to study domain dynamics and lattice strain in ferroelectrics²⁸⁻³⁰. Recently, this approach has also been applied to study the electric-field-induced transitions in PbZrO₃-based AFEs³¹⁻³⁴. Ciuchi *et al.* reported that the transition in (Pb_{1-x}La_x)(Zr_{0.90}Ti_{0.10})_{1-x/4}O₃ includes an irreversible orientation of the domain structure and a reversible/irreversible change of the lattice, depending on the composition³¹. Indications for irreversible processes during AFE-FE transition were previously also reported by Lu *et al.*, investigating Pb_{0.97}La_{0.02}(Zr_{0.56}Sn_{0.33}Ti_{0.11})O₃ using *in situ* neutron diffraction³². Liu *et al.* found that the large strain during the reversible AFE-FE transition in Pb_{0.99}(Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.94}Ti_{0.06}]_{0.98})O₃ arises from the anisotropic lattice strain and preferential domain reorientation³³. A revised schematic of the AFE-FE transformation sequence was proposed³³. However, similar studies of the lead-free NaNbO₃-based compositions, exhibiting predominantly orthorhombic phases, are still missing.

Here, we utilize *in situ* high-energy diffraction measurements to simultaneously study the macroscopic changes in polarization/strain and the structural/microstructural evolution during the AFE-FE transition in the lead-free prototype antiferroelectric NaNbO_3 . Three stages were observed with the sequence: AFE (*P* phase) $\rightarrow$ FE (*Q* phase) without macroscopic polarization and strain $\rightarrow$ FE (*Q* phase) with macroscopic polarization and strain, whereby the phase transition was found to be clearly decoupled from the polarization switching process.

Polycrystalline NaNbO_3 was prepared by the solid-state reaction⁵. *In situ* XRD measurements were carried out on bars ($0.5 \times 1 \times 5 \text{ mm}^3$), sputter-coated with platinum ($1 \times 5 \text{ mm}^2$ surfaces). All samples were annealed at 600°C for 2 h prior to the measurement. The diffraction patterns were collected at the DESY PETRA III P02.1 beamline in transmission geometry using a Pilatus CdTe 2M area detector (Dectris Ltd., Switzerland). The beam energy and spot size were 60 keV ($\lambda=0.20673 \text{ \AA}$) and $0.3 \times 0.3 \text{ mm}^2$, respectively. During the measurement, the samples were loaded with an unipolar electric field with a frequency of 0.05 Hz, while the frame exposure time was 415 ms. The two-dimensional XRD patterns were converted into one-dimensional patterns by integrating the intensity in different azimuthal ranges using Fit2D³⁵, while LeBail fitting was conducted with the GSAS program³⁶. The polarization and strain were simultaneously measured using a modified Sawyer-Tower circuit and an optical displacement sensor, respectively. The sample exhibited a piezoelectric coefficient $d_{33}=40 \text{ pC/N}$ after the measurement, confirming the irreversible inducement of the FE phase. Electric-field-induced longitudinal and transverse strains were additionally obtained using linear variable differential transformers³⁷.

Both, *P* and *Q* phase, exhibit orthorhombic symmetry with rhombic primitive cells ($a \neq b \neq c$, $\gamma \neq 90^\circ$; **Figure 1**). However, they differ in the arrangement of successive layers along the $[001]_{\text{PC}}$ axis. In the *Q* phase, a repeating unit is constituted by two successive primitive cells along $[001]_{\text{PC}}$ axis, as indicated by the green dashed squares in **Figure 1b**. Within the repeating unit, all the atoms are mirrored across the (002) plane. The Nb displacements (yellow arrows) are the same and close to $[110]_{\text{PC}}$ direction, as indicated by blue arrows. The Na(1) displacement is also close to $[110]_{\text{PC}}$, but larger than that of Nb. The tilt system in the *Q* phase is $a^-a^-b^+$ (**Figure 1f**). In the *P* phase, the repeating unit of the *Q* phase is operated by a screw diad along $[001]_{\text{PC}}$ direction, constituting a new repeating unit with antiparallel arrays of Nb and Na(1) displacements, as indicated by Nb/Nb' and Na(1)/Na(1)', respectively (**Figure 1a**). The tilt system is different in successive octahedra layers, *i.e.*, $a^-a^-b^+$ for layers 1&2 and layers 3&4, and $a^-a^-b^-$ for layers 2&3 (**Figure 1c-e**). The primitive cell in the *Q* and *P* phases is multiplied

by 2 and 4 in the $[001]_{\text{PC}}$ direction, respectively. Therefore, their superlattice reflections are characterized by half-integer indices and quarter-integer indices, respectively³⁸. In the following all lattice parameters will be presented based on one primitive cell with a pseudocubic configuration.

The evolution of the main and the superlattice reflections upon application of an electric field to a virgin NaNbO_3 sample is displayed in **Figure 2a,b** (full-range diffractograms are provided in Supplementary Figure S1), while the simultaneous changes of polarization and strain are given in **Figure 2c**. The $\frac{1}{4}\{843\}_{\text{PC}}$ peak is a characteristic reflection of the AFE P phase, which is the only phase present in virgin NaNbO_3 ⁵. The integrated area of this peak was thus used to quantify the P phase fraction (**Figure 2c**). Single-phase models with the $Pbcm$ or $P2_1ma$ space groups were adopted. The structure of the sample during the application of field does not meet the isotropic average assumption, which prevents quantification by Rietveld refinement. Therefore, LeBail fitting³⁹ was performed to track the changes of the lattice parameters, as shown in **Figure 3**. The evolution of the d -spacings during individual stages, extracted from the diffraction data, is presented in **Figure 4**.

The results presented in **Figures 2-4** reveal that the behavior is divided into three main stages. During stage I, between 0 and 8 kV/mm, the sample consists of the AFE P phase, as evident by the quarter-indices superlattice reflections (**Figure 2b**). No structural changes can be observed and the macroscopic strain is absent. The minor polarization increase could be related to the dielectric displacement and a minor leakage current contribution. The strain increase has a linear correlation with the square of polarization, indicating purely electrostrictive contribution with an electrostrictive coefficient of $0.012 \text{ m}^4/\text{C}^2$. Interestingly, towards the end of this stage (at $\sim 6 \text{ kV/mm}$) the P phase fraction starts to decrease and the cell parameter c_{PC} slightly increases, which is reflected in a small increase in the cell volume.

This increase indicates the initiation of stage II (8–12 kV/mm). At 8 kV/mm, significant changes in main reflections are observed, e.g., $\{100\}_{\text{PC}}$ and $\{200\}_{\text{PC}}$ shift to lower 2θ values and exhibit strong increase in intensities, while $\{110\}_{\text{PC}}$ shifts to lower 2θ values and reduces in intensity. Moreover, the $\frac{1}{4}\{843\}_{\text{PC}}$ superlattice reflection disappears, $\frac{1}{2}\{312\}_{\text{PC}}$ appears, and the superlattice peaks $\frac{1}{2}\{310\}_{\text{PC}}$ and $\frac{1}{2}\{311\}_{\text{PC}}$ show changes in their intensities and positions. The parameters a_{PC} , b_{PC} , and γ_{PC} increase, while c_{PC} slightly decreases (**Figure 3a**). These changes clearly indicate the disappearance of the AFE P phase and the appearance of the FE Q phase at 8 kV/mm (**Figure 2c**), which is accompanied by a large increase in the cell volume

(Figure 3b). The d -spacings of 220, 200/020, and 002 reflections parallel to the electric field increase, while the d -spacings of 220 and 002 reflections perpendicular to the electric field decrease (Figure 4). Interestingly, although the strain curve exhibits a minor continuous non-linear increase, no other changes are observed in the macroscopic behavior at 8 kV/mm (Figure 2c).

The sample enters into stage III at about 12 kV/mm. Reflections $\{100\}_{\text{PC}}$ and $\{200\}_{\text{PC}}$ shift slightly to higher 2θ values and their intensities decrease. The changes in superlattice reflections are negligible, which indicates that the phase composition remains almost unchanged and the behavior in stages II and III is mostly related to microstructural changes. A slight decrease in a_{PC} , b_{PC} and γ_{PC} , as well as a slight increase in c_{PC} are observed near 12 kV/mm. Note that the values of γ_{PC} , a_{PC} and b_{PC} in stage III are still larger than in stage I. These structural changes correspond to the onset of the macroscopic polarization and strain increase, which reach the inflection point at 13.3 kV/mm. The small delay of the macroscopic response can be partially ascribed to the limited time resolution of the measurement (patterns were collected over a time of 415 ms, during which the field increased by 0.67 kV/mm). The critical electric fields for the transitions between individual stages are also expected to be frequency⁵ and grain size⁴⁰ dependent. Structural and microstructural changes during the stages will be discussed in more detail below.

To gain further insight into the transition mechanism, we simultaneously recorded the electric-field-induced longitudinal (S_{33}), transverse (S_{11}), and volumetric (S_V) strains (Figure 3c). For reference, the same measurement was conducted on a lead-based AFE with an irreversible phase transition $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.75}\text{Sn}_{0.13}\text{Ti}_{0.12})\text{O}_3$ (PLZST) and on a classical ferroelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), as displayed in Supplementary Figure S2. The large increase of S_{33} in NaNbO_3 at about 13 kV/mm is accompanied by a small decrease of S_{11} . Note that the strain ratio $-S_{11}/S_{33}$ remains positive throughout the process (inset in Figure 3c). This reveals that NaNbO_3 does not exhibit the same auxetic behaviour as PLZST, *i.e.*, simultaneous expansion in longitudinal and transverse directions (Figure S2a and Refs.^{27,41}). The corresponding macroscopic volume strain (S_V) in NaNbO_3 reaches a value of 0.26% at 16 kV/mm (Figure 3c), which is comparable to the volume change obtained by diffraction (0.29%; Figure 3b). No changes in S_{11} and S_V could be detected below 12 kV/mm (stages I and II), confirming the macroscopic measurement in Figure 2c. However, the large change in S_V at about 13.3 kV/mm is accompanied by a pulse-like behaviour (small decrease and increase just before and after the

large change, respectively; see **Figure 3c**). Such behaviour has not been observed in PLZST, despite the larger S_V ; however, similar features can be seen in the vicinity of the coercive field in PZT (Supplementary Figure S2b), which supports our conclusion that the polarization and strain increase at 13.3 kV/mm (stage II→III) are related to polarization reorientation, rather than a phase transition.

Based on the results of combined structural analysis and macroscopic measurements, we propose a three-stage phase transition mechanism. The virgin sample (AFE P phase) exhibits Na(1) displacements in a direction close to $\langle 110 \rangle_{PC}$, whereby the sequence of these displacements is antiparallel in consecutive cells along the $[001]_{PC}$ axis⁴² (**Figure 1**). The domain structure consists of orientational domains with antipolarization^{43,44}. During stage I, the E -field is not strong enough to induce the AFE-FE phase transition and electrostatically neutral domains are not affected. No change in the diffraction patterns were observed at this stage, which is consistent with an *in situ* neutron diffraction study by Lu *et al.*³². These results are different from the model of Park *et al.*, which observed the formation of preferred orientation within the AFE state as soon as the E -field was applied.

The transition from the P phase to the Q phase occurs when the critical electric field of about 8 kV/mm is reached, which marks the beginning of stage II (onset at ~6 kV/mm; **Figure 2**). This induces the displacement of Na(1)' in the same direction as Na(1) (**Figure 1**) and the disappearance of the quarter-index superlattice reflections. The transition to stage II is accompanied by a significant increase in the d -spacings of 220, 200/020, and 002 reflections parallel to the electric field, and a simultaneous decrease in the d -spacings of 220 and 002 reflections perpendicular to the electric field (**Figure 4**). The primitive cells oriented in the $\langle 110 \rangle$ direction exhibit a tensile stress in the direction parallel to the field and a compressive stress in the direction perpendicular to the field. The presence and the previously-predicted first order nature of the transition⁶ were additionally confirmed by detecting slight cooling of the sample between 6 and 8 kV/mm, indicative of the absorbed latent heat (Figure S3). Due to the first order nature of this transition, both phases coexist over a certain period (certain E -field range). In addition, a distribution of critical fields is expected due to polycrystallinity^{45,46}. These two phenomena induce mechanical stress at the phase boundary, related to the crystal lattice adaptation in the phase boundary vicinity^{47,48}. This stress influences the phase transition and the orientation of the phase boundary. Note that a unit cell expansion was observed during the phase transition (**Figure 3b**). In addition, a reorientation of the primitive cells occurs. The cells with

their $[110]_{PC}$ axes (long face diagonal of the (110) plane) are parallel to the field. Hence, texturing is induced, as evident from the azimuthal dependence of the $\{220\}_{PC}$ and $\{200\}_{PC}$ reflections in XRD patterns (Figure S4). The primitive cell expansion observed at 8 kV/mm (Figure 3) and texturing are expected to induce straining of the grains (Figure 3c); however, the absence of the macroscopic strain suggests that this effect is compensated by the randomly-oriented grains. This includes compensation by grain boundaries and pores, twinning, and intragranular stress buildup. Although polarization variants with the direction closer to the applied electric field are energetically favored, their reorientation in stage II is prevented by the mechanical stress and thus the macroscopic polarization does not exhibit a sudden change.

At about 13 kV/mm (stage II $\rightarrow$ III), the electric field is strong enough to counteract the internal mechanical stresses and polarization switching takes place, accompanied by the significant increase in macroscopic polarization and strain. The Na(1) are displaced along the $[110]_{PC}$ direction, while the primitive cells are elongated in the $[110]_{PC}$ direction and contracted in $[1\bar{1}0]_{PC}$ direction. The mechanical energy accumulated in stage II gets released and a significant change in d -spacings is observed (Figure 4). The cells with the orientation of 220, 200/020 and 002 exhibited tensile stress in the direction parallel to the electric field in stage II and thus the corresponding d -spacings of 220, 200/020, and 002 reflections parallel to the electric field decreased at the stress release from stage II to stage III. On the other hand, the cells with the orientation of 220 were compressed in the direction that is perpendicular to the electric field in stage II and correspondingly their d -spacings increase. Polarization switching also results in a 0.24% volumetric dilatation, which does not relate to the very small decrease of the unit cell volume observed at this field. This additional volume is suggested to be due to microcracking stemming from large intragranular strain incompatibility. Evidence for microcracks has been found in the polished microstructures (see Figure S5). The microcrack volume can be estimated by⁴⁹.

$$V = \frac{16(1-\nu^2)}{3E} \sigma a^3, \quad (1)$$

where ν is the Poisson ratio, E the Young's modulus and a the size of the microcrack. Taking crack tip toughness of related (K,Na)NbO₃⁵⁰ and penny-shaped microcracks of diameter a equal to half of the average grain size, yields a microcrack volume of 0.27% of the grain volume. This is in agreement with the measured volumetric strain (Figure 3c) and would also rationalize the tendency of NaNbO₃-based compositions to exhibit slanted polarization hysteresis curves (related to the field-drop across the microcracks and broader distribution of switching fields) and dielectric break-down after electric field cycling. As a result, the primitive cell volume

decreases in stage III (**Figure 3b**) and reaches the value of $59.59 \text{ \AA}^3$, which closely matches previous reports for the Q phase⁵¹.

In summary, we investigated the electric-field-induced phase transition in the prototype lead-free AFE material NaNbO_3 . Three stages were observed, whereby the structural AFE-FE transition takes place much before macroscopic changes in polarization and strain are observed, the latter being related to polarization reorientation in the FE phase. These results show that the AFE-FE phase transition sequence in NaNbO_3 is distinctively different from PZ-based AFEs. Moreover, insight into the mechanism of this irreversible transition may facilitate further design of AFE materials with reversible transitions, which are desired for applications.

Supplementary Material

See Supplementary Material for details on the collected XRD patterns (Figure S1), unipolar strain and polarization hysteresis loops of the reference materials PLZST and PZT (Figure S2), temperature change of the sample during E-field loading (Figure S3), texturing indications following $\{220\}_{\text{PC}}$ and $\{200\}_{\text{PC}}$ reflections in the directions with 0° , 45° , and 90° to the electric field (Figure S4), and micrographs of polished samples before and after E-field loading (Figure S5).

Data availability statement: The data that support the findings of this study are available from the corresponding authors upon request.

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Figure captions

Figure 1. Crystallographic structures of P (AFE) and Q (FE) phases of NaNbO_3 . (a,b) View along the $[1\bar{1}0]_{\text{PC}}$ direction, where the Na(1) and Nb displacements are indicated by the orange and blue arrows, respectively. The Na(1) ion is located at a screw diad axis for P phase. Please note that the Na(2) atoms were taken as the reference frame. (c-f) Representation of the oxygen octahedra tilting, as viewed along the $[001]_{\text{PC}}$ direction.

Figure 2. (a) Evolution of the XRD reflections with increasing electric field; (b) superlattice reflections $\frac{1}{2}\{312\}_{\text{PC}}$ and $\frac{1}{4}\{843\}_{\text{PC}}$, which are characteristic for Q and P phases, respectively. The patterns from the bottom to the top were recorded every ~ 0.6 kV/mm upon linearly increasing the electric field up to 16 kV/mm. (c) P phase fraction determined from the integrated area of the $\frac{1}{4}\{843\}_{\text{PC}}$ reflections and the *in situ* macroscopic polarization (Pol) and longitudinal strain (S_{33}).

Figure 3. (a) Pseudocubic lattice parameters and (b) primitive cell volume as a function of electric field amplitude, obtained from LeBail fitting using single-phase models. (c) Simultaneously recorded longitudinal (S_{33}) and transverse (S_{11}) strains, used to calculate the volume strain (S_V). The instantaneous strain ratio $-S_{11}/S_{33}$ is shown in the inset.

Figure 4. Evolution of the d -spacings of the (a) $\{220\}_{\text{PC}}$ and (b) $\{200\}_{\text{PC}}$ reflections in directions parallel and perpendicular to the electric field. Note that the $2\bar{2}0$ and 202 reflections are too close to be resolved in the diffraction pattern and thus the associated d -spacings are assumed to be the same. The possible orientations in $\langle 220 \rangle_{\text{PC}}$ -oriented and $\langle 200 \rangle_{\text{PC}}$ -oriented cells are depicted at the right. The red thin arrows on the surfaces of the cells indicate the polar directions. The bold arrows represent the internal stress of differently oriented cells at stage II (8–12 kV/mm).

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