Multi-step stochastic mechanism of polarization reversal in rhombohedral ferroelectrics

Y. A. Genenko1*, R. Khachaturyan2, I. S. Vorotiahin1, J. Schultheiß3,4, J. E. Daniels5, A. Grünebohm2 and J. Koruza4

1Department of Materials and Earth Sciences, Technical University of Darmstadt, Otto-Berndt-Str. 3, 64287 Darmstadt, Germany

2Interdisciplinary Center for Advanced Materials Simulation, Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany

3Department of Materials and Earth Sciences, Technical University of Darmstadt, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

4Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, 7034 Trondheim, Norway

5School of Materials Science and Engineering, UNSW Sydney, NSW, 2052, Australia

Abstract

A stochastic model for the field-driven polarization reversal in rhombohedral ferroelectrics is developed, providing a description of their temporal electromechanical response. Application of the model to simultaneous measurements of polarization and strain kinetics in a rhombohedral Pb(Zr,Ti)O3 ceramic over a wide time window allows identification of preferable switching paths, fractions of individual switching processes, and their activation fields. Complementary, the phenomenological Landau-Ginzburg-Devenshire theory is used to analyze the impact of external field and stress on switching barriers showing that residual mechanical stress may promote the fast switching.

*Corresponding author: genenko@mm.tu-darmstadt.de
1. Introduction

Ferroelectrics are functional materials used for a wide range of important applications, ranging from actuators and sensors [1] to ferroelectric memories (FERAM) [2]. Relevant physical properties, such as permittivity [3], piezoresponse [4] and fracture toughness [5], strongly depend on the crystallographic structure and can be affected by composition [6,7], temperature, and application of mechanical stresses [8]. Furthermore, the appearance of a spontaneous polarization and the possibility to switch its direction by an electric field are key features for ferroelectric memories [2], especially for multi-bit data storage [9-12]. Thus, the manipulation and optimization of the switching kinetics is of high relevance. However, the understanding of the underlying mechanisms is still incomplete. In particular, the fact that most ferroelectrics are also ferroelastics with the second order parameter spontaneous strain [13], results in complex switching paths.

Macroscopic polarization switching kinetics is commonly described by stochastic models, such as the classical Kolmogorov-Avrami-Ishibashi (KAI) model originally developed to describe melt solidification [14]. The KAI model assumes random and statistically-independent nucleation and growth of reversed polarized domains in a uniform polarized medium [15,16]. Thereby individual random switching events are assumed to occur in parallel. Problematically, the KAI model involves only one polarization component, which makes it impossible to describe the electric-field induced switching of the spontaneous strain of ferroelectrics/ferroelastics.

Switching mechanisms in ferroelastic/ferroelectrics are subject to controversial discussion [17-24], and two successive non-180° events [17-19,22,23], predominantly 180° events [21], or exclusively single 180° events [24] have been predicted. Experimentally, consecutive 90°- or, generally, non-180°-switching events have been observed by in situ x-ray diffraction measurements [17] and ultrasonic investigations [18] and two characteristic times for sequential
polarization reorientation have been identified [19]. Some reports suggest that 180°- and non-180°-switching events might occur in parallel [20,21].

To get insight in the complicated switching mechanisms, the macroscopic strain of the ferroelectrics/ferroelastics can be measured simultaneously with the switched polarization. Recently such measurements supported by in situ X-ray diffraction experiments were performed on a polycrystalline ferroelectric lead zirconate titanate (PZT) with tetragonal symmetry [25]. Based on these experimental data, an original multistep stochastic mechanism (MSM) model was suggested [26], which allows describing the simultaneous polarization and strain responses of tetragonal ferroelectrics over a broad time range with high accuracy [27]. Particularly, the MSM model allows one to resolve the fraction of ferroelastically-active 90°-switching events. However, in ferroelectrics with rhombohedral and orthorhombic crystallographic symmetries, also 109°-, 71°-, 120°- and 60°-switching events become possible for which no stochastic model is available at the moment. Since in particular rhombohedral PZT has good prospects for single-phase electromechanical applications due to its low coercive fields, largest strain responses in thin film geometry [7], and fast switching [28,29], this is a severe shortcoming. Only a few other models for analysis of the electromechanical response of rhombohedral ferroelectrics have been advanced [30-33], which, however, do not account for the time-resolved response of strain and polarization. Chen and Lynch [30] studied the quasi-static field dependences of polarization and stress, using a computational micromechanics model. A combined switching assumption (CSA) model suggested by Li and Rajapakse, assuming that two or three types of non-180° switching occur simultaneously, exhibited good qualitative agreement with experimental polarization-field and stress-strain loops, but had no access to kinetics [31]. The analysis by Hall et al. demonstrated that stresses due to intergranular coupling play an important role during polarization reversal in polycrystalline rhombohedral ferroelectric/ferroelastic PZT ceramics [32]. Various domain structures were also studied in
rhombohedral barium titanate by means of molecular dynamics, but only in statics at zero-temperature conditions, thus excluding polarization switching processes [33].

The current work is devoted to the development of a stochastic model for the kynetics of multistep polarization switching processes in rhombohedral ferroelectrics/ferroelastics. The paper is organized as follows: In Section 2, the complexity of extending the MSM model to rhombohedral structures is explained and the possible switching paths are introduced. The classical KAI model is then extended by including all possible sequential non-180° polarization reorientation steps and parallel 180° switching events. To comprehend the simultaneous strain kinetics, a relation between the time-dependent strain and polarization is derived. In Section 3, the likelihood of the switching paths is evaluated by means of the phenomenological Landau-Ginzburg-Devonshire (LGD) model. In Section 4, the above models are applied to original polarization and strain switching experiments over a time domain from $10^{-6}$ s to $10^1$ s for a range of applied electric field values around the coercive field of the sample, and the fitting results are discussed based on the concepts from Sections 2 and 3. Finally, the results are concluded in Section 5.

2. Theory of consecutive stochastic polarization switching processes

In a rhombohedral ferroelectric, local polarization may adopt one of the eight possible directions along the body diagonals of the pseudo-cubic cell ($<111>$ directions). Application of an electric field opposite to the polarization direction induces reversal of the polarization, which may consist of different intermediate switching events. In this Section, we first define and display possible switching paths and then calculate their probabilities by an extension of the KAI approach. Finally, we derive the variation of strain according to the polarization variation.
A. Polarization rotations and switching channels

Consider a crystalline unit cell of a rhombohedral ferroelectric. Axes of a Cartesian frame are chosen to be collinear with main axes of a pseudo-cubic cell (Fig. 1(a)). The system is assumed to be initially in the polarization state $\frac{P}{\sqrt{3}}(-1,-1,-1)$ with spontaneous polarization $P$, and then it is driven to the final state $\frac{P}{\sqrt{3}}(1,1,1)$ by application of the electric field $E$ pointing into the [111] direction. Polarization reversal may proceed along different paths exemplarily shown in Fig. 1(a), namely, by a direct reversal path A-D, by two consecutive 109°- and 71°-polarization rotations A-E-D, by two consecutive 71°- and 109°-polarization rotations A-B-D and by a triple consecutive 71°-polarization rotation A-B-C-D. It should be noted that the term “rotation” is not in the same sense as in monoclinic ferroelectrics where the polar vector can freely rotate in

![Diagram](image_url)

Fig. 1. (a) Possible realizations of the field-driven polarization reversal in rhombohedral state: exemplary 71°-71°-71° polarization rotation path A-B-C-D, exemplary 71°-109° polarization rotation path A-B-D, exemplary 109°-71° polarization rotation path A-E-D and a direct 180° polarization reversal A-D. (b) Definition of fractions of different polarizations switching processes, indicated by the same colors as in (a).
given crystallographic plane, but instead a rotation path through a sequence of fixed polarization directions.

We define the probabilities for the first switching event as $\eta_1$, $\eta_2$ and $\eta_3$ for switching starting with $71^\circ$, $109^\circ$ and $180^\circ$ rotations, respectively, and exclude all other more complex switching paths, i.e. $\eta_1+\eta_2+\eta_3 = 1$. After the first polarization rotation, the first switching channel splits up in two possible paths, single $109^\circ$-polarization rotation with a weight $\eta_{12}$ and double $71^\circ$-polarization rotation with weight $\eta_{11}$, satisfying $\eta_{11}+\eta_{12} = \eta_1$. In a ferroelectric, switching probabilities may depend on energy barriers between different polarization states, strength of applied field and/or mechanical stress, as well as electric and elastic interactions between domains and boundary conditions.

**B. Extension of the KAI model to consecutive switching events**

In the classical KAI approach [14-16], switching processes at all different locations and times are considered as statistically independent. This cannot be true when accounting consecutive switching events, whereby some polarization steps may only occur after previous ones are finished. The assumption of statistical independence of switching events at different locations is also questionable. In fact, piezoresponse force microscopy and transmission electron microscopy revealed clustering during polarization reversal ranging from a few grains [34] to agglomerations of $10^2$–$10^3$ grains [35,36] in polycrystalline thin films. On the other hand, the grain-resolved three-dimensional X-ray diffraction in bulk ceramics disclosed a collective dynamics correlated over about $10$–$20$ grains [37-39]. Analysis of polarization and field correlations, based on the self-consistent mesoscopic switching model [40-42], revealed that the electric field-mediated correlations in bulk ceramics remain short-range at the typical scale of the grain size. Physical background of the short-range correlations is an effective screening of depolarization fields by adapting surface charges at grain boundaries. The question of
correlations due to elastic interactions, however, remains open [25]. We retain here the simplified KAI assumption that switching processes at different locations are statistically independent, thus neglecting the electric and elastic interactions of domains during their switching, and focus on the sequential switching steps. Following the MSM approach [26], we derive the probabilities of different consecutive switching events.

Initially, we assume a monodomain single crystal with saturation polarization along $\{\bar{1}\bar{1}\bar{1}\}$. When an opposite field is applied, the local polarization may experience different switching events with different nucleation rates per unit time and unit volume and exhibit different geometries of growing switched domains. We first consider, in the spirit of the KAI model [14-16], the nucleation of reversed domains according to the single 180°-switching process A-D (Fig. 1(a)) by the application of electric field pulse starting at time $t_0 = 0$. The key conceptual element of this approach, introduced by Ishibashi and Takagi [16], is the probability $q_{180}(t,t_0)$ for an arbitrary point not to be comprised by a switched area of some domain,

$$q_{180}(t,t_0) = \exp\left[-\left(\frac{t-t_0}{\tau_3}\right)^{\beta_3}\right]$$

(1)

where $\tau_3$ is the characteristic time of 180°-switching process and $\beta_3$ is the so called Avrami index related to the dimensionality $D$ of the growing domain. Ishibashi and Takagi [16] considered two alternative regimes of the reversed domain nucleation: (I) the nucleation rate is constant in space and time throughout the switching period when the constant uniform field is kept applied, and (II) there are only latent nuclei but no new nucleation. Under the prerequisite that the velocity of domain growth is constant (though field dependent), $\beta_3 = D+1$ applies for the regime I, and thus $\beta_3$ is larger than unity, while for the regime II, $\beta_3 = D$. This provides a
contribution to the total switched polarization proportional to the fraction \(1 - q_{180}(t, t_0)\) of the system volume and reads

\[
\Delta p_{180}(t) = \eta_3 2 P^* \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau_3} \right)^{\beta_3} \right] \right\}
\]  

(2)

The MSM model extended the KAI approach by application of the formula (1) to the first and the second switching events of the two-step switching processes with their specific characteristic times and Avrami indices. Similarly to the 90°-90° polarization rotation sequence in tetragonal ferroelectrics [26], for the 109°-71° polarization rotation path A-E-D (Fig. 1(a)) in rhombohedral counterparts, we introduce a probability \(q_{109}(t_1, t_0)\) not to switch according to the first switching mechanism by some intermediate time \(t_1\). Further, we introduce a probability \(q_{71}(t, t_1)\) not to switch according to the second switching mechanism by the time \(t\) after the first switching event occurred at time \(t_1\). When summarizing over all possible intermediate times \(t_1\) between 0 and \(t\), the total probability to switch once according to the first mechanism and not to switch anymore according to the second mechanism until time \(t\) is obtained,

\[
L_{20}(t) = \frac{\beta_2}{\tau_2} \int_0^t dt_1 \left( \frac{t_1}{\tau_2} \right)^{\beta_2-1} \exp \left[ - \left( \frac{t_1}{\tau_2} \right)^{\beta_2} \right] \exp \left[ - \left( \frac{t-t_1}{\tau_{21}} \right)^{\beta_{21}} \right]
\]  

(3)

where \(\tau_2\) and \(\tau_{21}\) are the characteristic times of the first 109°- and the second 71°-processes, respectively, and \(\beta_2\) and \(\beta_{21}\) are the respective Avrami indices. Accordingly, the total probability to switch firstly according to the first mechanism and secondly according to the second mechanism until time \(t\) reads as
This provides a contribution to the total switched polarization

\[ \Delta P_{109-71}(t) = \eta_2 \left[ \frac{4}{3} P_{L_20}(t) + 2P_{L_21}(t) \right] \]  

(5)

since each 109°-polarization rotation provides variation by 4\(P_s/3\) and each 71°-polarization rotation provides variation by 2\(P_s/3\) along the [111] direction (see Fig. 1(a)).

In the case of the first 71°-switching event, the description of polarization reversal becomes more complicated because it allows splitting in two channels as depicted in Fig. 1(b). The probabilities for the two-step 71°-109° channel are formally similar to the above considered 109°-71° process and can be described by formulas similar to Eqs. (3,4). Namely, the total probability to switch once according to the first 71°-mechanism and not to switch anymore by the second 109°-rotation reads

\[ L_{402}(t) = \frac{\beta_1}{\tau_1} \int_0^t \left( \frac{t}{\tau_1} \right)^{\beta_1-1} \exp \left[ -\left( \frac{t}{\tau_1} \right)^{\beta_1} \right] \left[ 1 - \exp \left[ -\left( \frac{t-t_1}{\tau_{12}} \right)^{\beta_{12}} \right] \right] \, dt \]  

(6)

where \(\tau_1\) and \(\tau_{12}\) are the characteristic times of the first 71°-and the second 109°- processes, respectively, and \(\beta_1\) and \(\beta_{12}\) are the respective Avrami indices. The total probability to switch firstly by 71° and secondly by 109° until time \(t\) reads as

\[ L_{22}(t) = \frac{\beta_2}{\tau_2} \int_0^t \left( \frac{t}{\tau_2} \right)^{\beta_2-1} \exp \left[ -\left( \frac{t}{\tau_2} \right)^{\beta_2} \right] \left[ 1 - \exp \left[ -\left( \frac{t-t_1}{\tau_{21}} \right)^{\beta_{21}} \right] \right] \, dt \]  

(7)

\[ = 1 - \exp \left[ -\left( \frac{t_1}{\tau_1} \right)^{\beta_1} \right] - L_{402}(t) . \]
We note that the characteristic times and Avrami indices may differ between $71^\circ$-$109^\circ$ and $109^\circ$-$71^\circ$ switching since the energy barrier for both rotation angles depends on initial polarization and strain configuration. The $71^\circ$-$109^\circ$ switching path provides a contribution to the total switched polarization

$$\Delta P_{71-109}(t) = \eta_{12} \left[ \frac{2}{3} P_i L_{302}(t) + 2 P_i L_{12}(t) \right].$$

A succession of three $71^\circ$-switching processes (such as the A-B-C-D path in Fig. 1(a)) can be considered in a similar way with intermediate times $t_1$ and $t_2$ for the second and the third event, respectively. When integrating over all possible intermediate times, the probability to switch first time on the $71^\circ$-$71^\circ$-$71^\circ$ path and not to switch anymore reads

$$L_{401}(t) = \frac{\beta_1}{\tau_1} \int_0^t dt_1 \left( \frac{t_1}{\tau_1} \right)^{\beta_1-1} \exp \left[ -\left( \frac{t_1}{\tau_1} \right)^{\beta_1} \right] \exp \left[ -\left( \frac{t-t_1}{\tau_1} \right)^{\beta_1} \right],$$

where $\tau_1$ and $\tau_{11}$ are the characteristic times of the first $71^\circ$- and the second $71^\circ$-processes, respectively, and $\beta_1$ and $\beta_{11}$ are the respective Avrami indices. Similarly, the probability to switch the first and the second time on the $71^\circ$-$71^\circ$-$71^\circ$ path and not to switch anymore is

$$L_{310}(t) = \frac{\beta_1}{\tau_1} \int_0^t dt_1 \left( \frac{t_1}{\tau_1} \right)^{\beta_1-1} \exp \left[ -\left( \frac{t_1}{\tau_1} \right)^{\beta_1} \right] \int_0^{t_1} dt_2 \frac{\beta_{11}}{\tau_{11}} \left( \frac{t_2-t_1}{\tau_{11}} \right)^{\beta_{11}-1} \exp \left[ -\left( \frac{t_2-t_1}{\tau_{11}} \right)^{\beta_{11}} \right] \exp \left[ -\left( \frac{t-t_2}{\tau_{111}} \right)^{\beta_{111}} \right],$$

where $\tau_{11}$ and $\beta_{11}$ are the characteristic time and the respective Avrami index of the third $71^\circ$-switching event. Finally, the probability to consequently switch three times by $71^\circ$ equals...
\[ L_{111}(t) = \frac{\beta_1}{\tau_1} \left[ \int_0^t \left( \frac{t_1}{\tau_1} \right)^{\beta_1-1} \exp \left[ -\left( \frac{t_1}{\tau_1} \right)^{\beta_1} \right] dt_1 \right] \times \left[ \int_0^t \frac{\beta_{11}}{\tau_{11}} \left( \frac{t_2 - t_1}{\tau_{11}} \right)^{\beta_{11}-1} \exp \left[ -\left( \frac{t_2 - t_1}{\tau_{11}} \right)^{\beta_{11}} \right] \right] \times \left[ 1 - \exp \left[ -\left( \frac{\tau_{11}}{t_{111}} \right)^{\beta_{11}} \right] \right]. \] (11)

The contribution to the total switched polarization for the path 71°-71°-71° is thus

\[ \Delta P_{71\rightarrow71\rightarrow71}(t) = \eta_{11} \left[ \frac{2}{3} P_s L_{101}(t) + \frac{4}{3} P_s L_{110}(t) + 2 P_s L_{111}(t) \right]. \] (12)

Taken together, the contributions of all switching channels sum up to a total polarization variation of

\[ \Delta P(t) = \eta_3 2 P_s \left[ 1 - \exp \left[ -\left( \frac{t}{\tau_3} \right)^{\beta_3} \right] \right] + \eta_2 \left[ \frac{4}{3} P_s L_{20}(t) + 2 P_s L_{21}(t) \right] + \eta_{12} \left[ \frac{2}{3} P_s L_{102}(t) + 2 P_s L_{112}(t) \right] + \eta_{11} \left[ \frac{2}{3} P_s L_{401}(t) + \frac{4}{3} P_s L_{410}(t) + 2 P_s L_{411}(t) \right]. \] (13)

Being a direct extension of the KAI approach to the case of double and triple switching events, the formula (13) includes additional integrations over intermediate time steps and cannot be solved in a closed form. In order to illustrate qualitative trends, it is convenient to set all beta values to unity. In this case the involved event probabilities become

\[ L_{20}(t) = \frac{\tau_{21}}{\tau_2 - \tau_{21}} \left( e^{-it_{21}} - e^{-i\tau_{21}} \right), \] (14a)

\[ L_{21}(t) = 1 - e^{-i\tau_{21}} - \frac{\tau_{21}}{\tau_2 - \tau_{21}} \left( e^{-i\tau_{21}} - e^{-i\tau_{21}} \right), \] (14b)

\[ L_{102}(t) = \frac{\tau_{12}}{\tau_1 - \tau_{12}} \left( e^{-i\tau_{12}} - e^{-i\tau_{12}} \right), \] (14c)

\[ L_{12}(t) = 1 - e^{-i\tau_{12}} - \frac{\tau_{12}}{\tau_1 - \tau_{12}} \left( e^{-i\tau_{12}} - e^{-i\tau_{12}} \right), \] (14d)

\[ L_{101}(t) = \frac{\tau_{11}}{\tau_1 - \tau_{11}} \left( e^{-i\tau_{11}} - e^{-i\tau_{11}} \right), \] (14e)
\[ L_{110}(t) = \frac{\tau_{111}}{\tau_{11} - \tau_{111}} \left[ \frac{\tau_{11}}{\tau_{11} - \tau_1} (e^{-it\tau_{111}} - e^{-it\tau_1}) - \frac{\tau_{111}}{\tau_{111} - \tau_1} (e^{-it\tau_{111}} - e^{-it\tau_1}) \right], \]  
\[ L_{111}(t) = 1 - e^{-it\tau_1} - \frac{\tau_{11}^2}{(\tau_{11} - \tau_{111})(\tau_{111} - \tau_1)} (e^{-it\tau_{111}} - e^{-it\tau_1}) + \frac{\tau_{111}^2}{(\tau_{11} - \tau_{111})(\tau_{111} - \tau_1)} (e^{-it\tau_{111}} - e^{-it\tau_1}). \]

In the following, we do not use any assumptions for beta or the other fitting parameters and use Eq. (13) together with expressions (3,4,6,7,9-11) to describe experimental data.

C. Relation between polarization and strain

To establish a relation between the macroscopic strain, \( S \), and the macroscopic polarization, \( p \), during the polarization reversal a general relation can be used [43,44],

\[ S_{ij} = Q_{ijmn} p_m p_n \]  
(15)

with the electrostriction tensor \( Q_{ijmn} \) and summation over the repeated indices implied, if no stress is applied to the system. For ferroelectrics with a cubic parent phase, the piezoelectric contribution can be derived from Eq. (15) when the spontaneous polarization \( P \) is singled out as

\[ p_n = P_n + \varepsilon_0 \varepsilon_{nm} E_m \]  
(16)

with the permittivity of vacuum \( \varepsilon_0 \) and the relative permittivity of the ferroelectric \( \varepsilon_{nm} \). By substitution of Eq. (16) into Eq. (15) one obtains in linear order of the field

\[ S_{ij} = Q_{ijmn} P_m P_n + d_{ijk} E_k \]  
(17)

and an expression for the piezoelectric coefficient [43]

\[ d_{ijk} = 2\varepsilon_0 \varepsilon_{kam} Q_{ijmn} P_l. \]  
(18)
Experimental measurements of polarization and strain performed on a polycrystalline ferroelectric in the direction of the applied field will be approximated by the presented single crystal model with the field applied in the [111]-direction. Nevertheless, it makes sense to specify the relations (15,17,18) in the “parent” coordinate frame of Fig. 1(a) collinear with the cubic parent phase, where the tensor of electrostriction has a particularly simple form [44]. This way all coefficients depending on electrostriction can be expressed by the matrix elements $Q_{11}, Q_{12},$ and $Q_{44}$ [44] (Voigt notation). The strain variation along the field direction $\Delta S'_{33}(t)$ in the new coordinate frame $(x', y', z')$, such that the $z'$ axis points in the field direction, may then be determined as

$$\Delta S' = T \Delta S T^{-1}$$

with

$$T = \begin{pmatrix} 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ -2/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{pmatrix}.$$

This reveals the time dependent strain variation along the field direction

$$\Delta S(t) = \Delta S'_s(t) + \Delta S'_{\pi}(t),$$

where the first term presents a contribution of the spontaneous polarization variation to the strain (the first term in Eq. (17)) and the second one a contribution of the piezoelectric effect (the second term in Eq. (17)). Since each 71°- and each 109°- rotation of the polarization of the amplitude $P_s$ contributes the maximum strain variation,

$$\Delta S_{\text{max}} = -\frac{16}{9} Q_{44} P_s^2,$$

the total variation of strain due to the spontaneous polarization equals

$$\Delta S'_s(t) = \Delta S_{\text{max}} \left[ \eta_{12} L_{20}(t) + \eta_{12} L_{102}(t) + \eta_{11} (L_{101}(t) + L_{410}(t)) \right].$$

According to Eq. (17) the piezoelectric strain is coupled to the spontaneous polarization by the
piezoelectric coefficient \((18)\), proportional itself to the spontaneous polarization, that results in

\[
\Delta S_p(t) = \frac{2\varepsilon_0\varepsilon_c}{3} \left( Q_{11} + 2Q_{12} + 4Q_{44} \right) \left( \Delta P(t) - P_i \right) E, \tag{23}
\]

where \(E\) is the electric field applied in the \(z'\) direction, \(\varepsilon_c = \varepsilon_{33}'\) is the permittivity in the new coordinate frame and \(\Delta P(t)\) is the time dependent polarization variation along the applied field direction given by Eq. \((13)\).

The 180°-switching processes only change the strain by the second term in Eq. \((20)\), which is linear in polarization. In contrast, the non-180° switching events rotate polarization by either 71° or 109°, thus contributing to the variation of the strain by both terms in Eq. \((20)\). It is also important to note that consequent rotations along all paths cause no variation of the strain in the final state by the term quadratic in polarization, Eq. \((22)\), but by the term linear in polarization, Eq. \((23)\). Notice that both formulas for polarization, \((13)\), and strain, \((20)\), present averaging over the whole system and neglect electric and elastic interactions \([45]\) between different switching regions during the polarization reversal, as discussed above in section 2B.

### 3. Model evaluation of polarization switching barriers

In order to interpret the switching rates, obtained by application of our model to experiments, the Landau-Ginzburg-Devonshire approach was used, which allows estimation of barriers for different switching paths. The Gibbs free energy has spontaneous polarization \(P\) as an order parameter for the electric subsystem and mechanical stress \(\sigma\) as an order parameter for the mechanical subsystem. Using a simplified approach for estimations, the expression for Gibbs free energy density consists of the Landau and elastic parts (as \(\Delta G = G_{\text{Land}} + G_{\text{elast}}\)) \([46]\):

\[
\Delta G = \alpha_{ik}P_iP_k + \beta_{ijkl}P_iP_jP_kP_l + \gamma_{ijklmn}P_iP_jP_kP_mP_n - P_iE_i - \frac{s_{ijkl}}{2} \sigma_{ij} \sigma_{kl} - Q_{ijkl} \sigma_{ij} P_kP_l - \sigma_{ij} S_{ij}, \tag{24}
\]
where $\alpha_{ik}$, $\beta_{ijkl}$ and $\gamma_{ijklmn}$ are the Landau expansion coefficients describing the properties of the ferroelectric phase at room temperature, $E_i$ is a component of the applied electric field, $s_{ijkl}$ is the elastic compliance tensor, $Q_{ijkl}$ is the electrostriction tensor, and $S_{ij}$ is the imposed strain. Since gradient terms are omitted in Eq. (24), it describes a monodomain single crystal. Values of the aforementioned coefficients were taken from [47,48] for the PZT 60/40 composition; the applied electric field and strain were considered as variable parameters.

A series of polarization-dependent double-well potentials is obtained from the evaluation of the Gibbs free energy density with minima located at amplitudes $\pm P_i^r = \pm 0.354$ C/m² when external field and strain are absent (Fig. 2(a)). Those values of the polarization amplitudes are applicable to each polarization component. We calculate the energy barriers for 71°, 109° and 180° switching, starting from the state of $P_1 = -P_1^r$, $P_2 = -P_2^r$, $P_3 = -P_3^r$. These barriers can determine which path the system will choose from the beginning. In the absence of external electric field and strain, we find the smallest barrier for 71° switching on path A-B in Fig. 1(a), followed by 109°-switching along the path A-E and 180°-switching along the path A-D, which is by factors of 2.70 and 2.16 higher than the first and the second barriers, respectively. This relative height of the barriers is related to the direction of the polarization deviating from the favourable [111] direction in one, two and three components. If an electric field is applied in the [111] direction, the linear $P$-$E$ coupling in (24) distorts the energy wells and stabilizes the state with $+P_i^r$. Since no domain nucleation is considered, the coercive electric fields in the classical Landau theory, i.e. the field values necessary to switch polarization, are an order of magnitude higher than the experimentally observed ones [49]. However, the overall tendency can be anticipated. Most important is that the energy barriers for polarization rotation are modified differently by an external field for the considered switching paths, see Fig. 3 (a). The change of the barrier is largest for 180° switching and smallest for 71° switching as either all or only one component of the polarization can align with the field direction. Thus, although the
71°-leap has initially the lowest potential barrier, also its coupling to the applied field is the weakest. When the applied field reaches 29.4 kV/mm (Fig. 2(b)) the barrier for the 109°-switching disappears, making it the most favourable one among the first switching steps. In the same fashion the potential barrier vanishes for the 180°-switching at the applied field of 41.6 kV/mm. As the last one, the barrier for the first 71°-switching disappears at 45 kV/mm, making this switching path the least likely of all.

![Fig. 2. Free energy density profiles showing potential barriers of the first 71° switching (solid red), the first 109° switching (dotted blue) and the 180° switching (dashed green) processes (a) at no applied electric field (E = 0) and strain field (S = 0), (b) at applied electric field E = 29.4 kV/mm, (c) at no applied electric field (E = 0) but with a strain equal to -25% of the spontaneous one, and (d) at applied electric field E = 11.95 kV/mm and the strain equal to -25% of the spontaneous one. The energy density range is adjusted to its variation in different plots.](image)

The situation changes if we account for residual stresses, which are introduced into polycrystalline system through intergranular coupling by setting the polarization to the [111]
direction through electrical poling [45,50]. The tensor of these stresses in one grain should be related to the spontaneous strain experienced by the considered grain. In the context of our single-crystalline formulation, Eq. (24), the residual stresses can be introduced as follows. First a spontaneous strain \( S_r \) in the polarized \([\overline{1}\overline{1}\overline{1}]\) state is evaluated and appears to be about \(2 \times 10^{-3}\). Since the surrounding grains in the polycrystalline matrix are expected to oppose the development of this strain, a negative strain of the same tensorial structure is imposed on the model system through the last term in Eq. (24). In calculations presented in Fig. 2 (c,d) the external strain \( S \) is exemplarily taken to be -25% of \( S_r \). Though the simplified LGD model used here cannot be directly applied to real polycrystalline materials, the considered strain amplitude seems to be of a reasonable order of magnitude [19].

These stresses are believed to help pull the polarization from the initial \([\overline{1}\overline{1}\overline{1}]\) state [19,25,45,51]. For \( E=0 \), the impact of the residual stress on the energy landscape (Eq. (24)) is illustrated in Fig. 2(c). All well depths and switching barriers are reduced by the stress. Though these modifications are the largest for 180° switching, this path remains least favourable with and without stress. Although the relative height of barriers for 71°- or 109° switching depends on the value of stress, for the choice of the strain \( S \) exemplarily adopted in (Fig. 2(c)), the change compared to the stress free material is about two times smaller. However, the residual stress modifies the coupling of the switching paths to the field as is seen from a comparison of Fig. 3(a) and 3(b). In the absence of the strain, the switching barrier for 109° switching vanishes as the first one with the field increase (cf. Figs. 2(b) and 3(a)). For \( S=-0.25 \ S_r \) the coupling is reduced for all switching paths and the switching barrier for 71° vanishes as the first one. Thus, the chosen residual stress promotes the first 71° switching step.
Fig. 3. Field dependence of the energy barrier heights for the first 71° switching (solid red), the first 109° switching (dotted blue) and the 180° switching (dashed green) processes at (a) no applied strain ($S = 0$) and (b) a strain equal to -25% of the spontaneous one.

4. Analysis and discussion of experimental results

A. Experimental details and sample characterization

Bulk, polycrystalline Pb$_{0.985}$La$_{0.01}$(Zr$_{0.6}$Ti$_{0.4}$)O$_3$ ceramics of rhombohedral symmetry were prepared by a mixed-oxide route [52]. Standard electromechanical characterization of the sample combining large-signal and small-signal measurements is presented in Fig. 4.

Moreover, the switched polarization and the macroscopic strain were measured simultaneously as a function of time. The samples were poled in the downward direction with an electric field...
of 3 kV/mm for 20 s. After a waiting time of 100 s, a 10 s pulse switching field of an amplitude $E$ was applied opposite to the poling direction. In order to realize a sharp high voltage (HV) pulse with a rise time of 115 ns, a buffer capacitor, which was charged by a high voltage source (Trek Model 20/20C, Lockport, NY, USA), was combined with a commercial fast HV transistor switch (HTS 41-06-GSM, Behlke GmbH, Kronberg, Germany) [53]. The charge was monitored by measuring the voltage drop across a reference capacitor (WIMA MKS4, Wima, Mannheim, Germany), while the macroscopic displacement of the sample was simultaneously measured by an optical displacement sensor (D63, Philtec Inc., Annapolis, MD, USA), which allows a time resolution of $10^{-4}$ s. Further details on the measurement procedures and on the crystallographic and electromechanical characterization of the sample may be found in Refs. [25] and [29], respectively.

B. Fitting dynamic polarization and strain data

Fig. 5 displays the time-dependent data of polarization and strain for exemplary switching field values $E$ in the range 0.900-1.230 kV/mm for which the switching processes were completed. For the field values outside this range, only initial or final stages of the polarization and strain reversal are observed (displayed in Ref. [29]), which do not allow reliable evaluation of fitting parameters. Note that the leakage current and the reversible dielectric displacement were subtracted in the presented polarization $\Delta P$ data in Fig. 5. The variation of the strain starts in all measurements from zero (poled reference state), which is not explicitly seen in the plot since the data below $10^{-4}$ s are not experimentally accessible.

Application of the models for single crystalline materials, presented in Sections 2 and 3, to the polycrystalline material, experimentally studied here, is possible with some reservations. In polycrystalline materials, the orientations of crystalline grains are randomly distributed and the
Fig. 5. Variation of the polarization (a,c,e,g) and strain (b,d,f,h) with time during field-induced polarization reversal at different applied field values in kV/mm, as indicated in the plots. Experimental curves are shown by red symbols and fitting curves by black solid lines.

non-180° domain switching fraction strongly depends on the orientation angle of the grain with respect to the electric field [25]. This leads, on the one hand, to a reduction of the maximum possible polarization of rhombohedral ceramics to the value of 0.866$P_s$ [54] and, on the other hand, to the deviation of local polarization directions from directions of local electric fields, which is one of the reasons for the statistical distribution of local switching times [55]. Account of these circumstances allows a much more precise description of polarization kinetics, but makes the theory substantially more complicated [27] and is thus not applied here for reasons of transparency. At the same time, application of single crystalline concepts to polycrystalline ceramics of tetragonal symmetry proved to properly capture key features of polarization and strain responses [26]. Hence, in the present study, we restrict ourselves to the direct extension of the KAI model to single crystalline rhombohedral systems subject to a uniform electric field, as presented in Section 2, and recognize its limited ability to describe polycrystalline materials, which can be improved in further work.
For fitting the experimental data in Fig. 5 using Eqs. (13) and (20), some weakly field-dependent material parameters, namely, the total polarization variation $2P_s$, the maximum strain value $\Delta S_{\text{max}}$, and the asymptotic value of the macroscopic piezoelectric coefficient $S_x = 2\varepsilon_0\varepsilon_r (Q_{11} + 2Q_{12} + 4Q_{44}) P_s / 3$ in Eq. (23), which can be called a normalized strain, are derived from the experimental data presented in Fig. 4. The fractions of switching processes $\eta_i$, their Avrami indices $\beta_i$ and switching times $\tau_i$ are used as field-dependent fitting parameters. Based on available results for rhombohedral ferroelectrics [29], we implement a similar fitting procedure as developed for tetragonal PZT [26] and assume the Merz law [56] for the field dependence of the switching times: $\tau_i = \tau_0 \exp(E_{\lambda}^{(i)} / E)$ with the same characteristic time $\tau_0$ and different activation fields $E_{\lambda}^{(i)}$ for different switching events. The fitting parameters are obtained from a least squares regression with implementation of “A Python Library for Optimizing the Hyperparameters of Machine Learning Algorithms” (Hyperopt) [57], which allows approximation of polarization and strain curves with relative inaccuracy of about 3%. Experimental data are displayed in Fig. 5 by red symbols, while black solid lines highlight the theoretical fitting curves. All parameters used for fitting are presented in Table I. The inaccuracy of the determination of activation fields is below 3%; the inaccuracy of the other field-dependent parameters is characterized by error bars in Fig. 6.

Table I. Parameters used for fitting the experimental curves in Fig. 5 by implementing formulas (13) and (20). Exemplary processes are indicated as in Fig. 1(a). For the field-dependent parameters $\eta_i$ and $\beta_i$ the ranges of their variation with the electric field are displayed.

| Process/parameter | A-B | B-C | C-D | E-D | A-E | B-D | A-D |
|-------------------|-----|-----|-----|-----|-----|-----|-----|
|                   | 71° | 2nd | 3rd | 2nd | 109°| 2nd | 180°|
| $\eta_i$          | 0.28-0.33 | 0.11-0.16 | 0.11-0.16 | 0.01 | 0.01 | 0.14-0.19 | 0.67-0.71 |
| $\beta_i$         | 0.18-0.21 | 0.66-0.83 | 1.28-1.75 | 1.28-1.75 | 0.69-0.97 | 2.85-2.88 | 2.88-2.98 |
| $E_{\lambda}^{(i)}$ (kV/mm) | 19.4 | 20.3 | 22.0 | 22.0 | 21.4 | 22.2 | 22.2 |

$2P_s = 0.8 \text{ C/m}^2$, $\Delta S_{\text{max}} = -0.795\%$, $S_x = 6.6 \times 10^{-10} \text{ C/N}$, $\tau_0 = 0.7 \times 10^{-11} \text{ s}$
The theory, in principle, properly captures the time dependence of both the polarization and strain responses for all considered field values. Fair quality of the polarization and strain description at lower fields may be related to the violation of the Merz law, which was established before for some ceramics in certain field regions [26,58,59]. A quasi-linear behavior of polarization and strain on the logarithmic scale at the final switching stage, not captured by the present theory, is known to originate from the statistical distribution of switching times [55,58] and can, in principle, be described by accounting of the latter [27].

Analysis of the field dependence of the fitting parameters reveals the following traits. Within the accuracy of determination, the fractions of different switching processes are approximately constant, see Fig. 6(a). The largest fraction corresponds to 180° processes (0.7), while the first 71°-switching process is characterized by the fraction \( \eta_1 \) of about 0.3. In contrast, fraction of the first 109°-events, \( \eta_2 < 0.01 \), remains virtually negligible. After the first step, the switching 71° process splits up in two – 71°- and 109°– possible events, characterized, respectively, by the fractions \( \eta_{11} \) and \( \eta_{12} \), making together \( \eta_1 \).

The activation field for the first 71°- process, \( A_{E1}^{(1)} \), is the smallest of all and, particularly, smaller than that of the first 109°-process, \( A_{E1}^{(2)} \). As discussed in Section 3, this may be related to residual stress favouring 71° over 109° switching. The final 71° switching events over paths C-D and E-D in Fig. 1(a) are thermodynamically equivalent and thus the activation fields \( A_{E11}^{(111)} \) and \( A_{E21}^{(21)} \) coincide.

The Avrami indices of the first and the second 71°, second 109° and 180° switching are almost constant for all field values and correspond to \( \beta_1 \approx 0.19 \), \( \beta_{11} \approx 0.7 \), \( \beta_{12} \approx 3 \) and \( \beta_3 \approx 3 \), respectively (Fig. 6(b)). The indices of both equivalent final 71°switching events (\( \beta_{21}, \beta_{111} \)) are identical and increase with the field gradually from 1.28 to 1.75; however, this variation may be apparent considering the inaccuracy of their determination. In terms of the Ishibashi
and Takagi classification [16], the switching events with $\beta_i < 1$ may only proceed according to the regime II from a number of latent nucleation sites being exhausted in the fast initial switching phase. This switching process seems to be facilitated by residual stresses in the initial highly polarized state, as was proposed in Ref. [19]. This hypothesis is confirmed by the analysis of energy profiles in Fig. 2 (c-d), which show that residual stresses mostly favour the first $71^\circ$-switching process.

![Energy profiles for different processes](image)

Fig. 6. Variation of (a) the fractions $\eta_i$ of the switching processes, depicted in Fig. 1(a), and (b) of the respective Avrami indices $\beta_i$ with the increasing applied field. Note the pairwise coincidence, within the inaccuracy of fitting, of the indices $\beta_{12}$ and $\beta_3$, $\beta_{21}$ and $\beta_{111}$, $\beta_2$ and $\beta_{11}$.

The most meaningful feature, revealed by a comparison of parameters of different processes, is the coincidence of the activation fields, $E_A^{(3)} = E_A^{(12)} = 22.2$ kV/mm, (and, thus of the respective switching times) and the respective Avrami indices, $\beta_3 = \beta_{12} \equiv 3$, for the $180^\circ$ (path A-D)- and the second $109^\circ$-processes (path B-D) in the $71^\circ$-$109^\circ$ succession. This is reminiscent of the recent results for the tetragonal PZT ceramics [26,27], where the kinetic switching characteristics for the second $90^\circ$- and the $180^\circ$-processes appeared to be identical. In the tetragonal case, a hypothetical coherent $90^\circ$-switching process suggested by Arlt [60], which may mimic the $180^\circ$-switching, could be suggested as the explanation of this coincidence.

23
Though such coherent 109°-switching processes have not been directly observed in experiments, the similarities in switching behaviour of tetragonal and rhombohedral ceramics make it reasonable to look for such a phenomenon. In agreement with this hypothesis, the CSA model suggested by Li and Rajapakse [31] assumed that two or three types of non-180° switching events occur simultaneously. We note also that sequential 90°-processes were reported to dominate the response of tetragonal ferroelectrics [61].

C. Hypothetical coherent non-180° switching processes in rhombohedral ferroelectrics

How may a scenario of coherent 109°-processes in rhombohedral materials, similar to that suggested by Arlt for tetragonal ferroelectrics [60], look like? To answer this question let us consider possible orientations of 109°- and 71°-domain walls in a rhombohedral perovskite with a cubic parent phase [62]. Fig. 7 shows examples of mechanically compatible and electrically neutral 109°- and 71°-domain walls taking, respectively, {001} and {101} planes.

Fig. 7. Possible orientations of charge neutral and elastically compatible (a) 109°- and (b) 71°-domain walls in a rhombohedral ferroelectric [62].

Similarly to the proposal by Arlt [60], one can imagine a set of equally spaced parallel 71°-domain walls (Fig. 8(a)) separating domains whose polarizations are different only by the sign of the y-component, as in Fig. 7(b). The direction of the mean polarization of this domain
system [101] is normal to the domain planes. Applying an electric field perpendicular to the mean polarization, as is shown in Fig. 8(b), may create a domain wall in (y,z)-plane propagating in the negative x-direction. At this domain wall, two components of the polarization change their signs, thus it presents a 109°-domain wall. Propagation of this wall across the stack of domains provides coherent 90°-switching of the mean polarization to the field direction \([10\overline{1}]\), which does not change the macroscopic strain. Alternatively, application of the field opposite to the mean polarization direction, as is shown in Fig. 8(c), creates a 109°-domain wall parallel to the (x,y)-plane which propagates in the negative z-direction and provides a coherent

Fig. 8. (a) Array of equidistant 71°-domain walls (shown as solid lines) in a rhombohedral ferroelectric with a mean polarization in [101]-direction. (b) A field-driven 109°-domain wall (shown as a dashed line) sweeping through the domain system from right to left and switching the mean polarization to the \([10\overline{1}]\)-direction. (c) A field-driven 109°-domain wall sweeping through the domain system from top down and switching the mean polarization to the \([\overline{1}0\overline{1}]\)-direction, thus providing polarization reversal.
180°-switching of the mean polarization to the $[\bar{1}0\bar{1}]$-direction, which does not change the macroscopic strain. It is this process, which might mimic a 180°-switching of individual domains assumed by the formula (2).

We note that also other coherent non-180° domain switching processes are conceivable in rhombohedral ferroelectrics, which do not change the macroscopic strain. As an example, a stack of domains separated by equidistant 109° domain walls, parallel to (x,y) planes, is shown in Fig. 9(a). Polarizations in neighbour domains differ in signs of the x- and y-components, as

Fig. 9. (a) Array of equidistant 109°-domain walls (shown as dashed lines) in a rhombohedral ferroelectric with a mean polarization in positive z-direction. (b) Field-driven 71°-domain wall (shown as a solid line) sweeping through the domain system from left to right and switching the mean polarization to the negative z-direction. (c) Field-driven 109°-domain wall sweeping through the domain system left to right and switching the mean polarization to the negative z-direction, thus providing polarization reversal.
in Fig. 7(a), making together a mean polarization in the positive z-direction. When an electric field is applied in the opposite direction, a 71°-domain wall may form, which propagates from left to right switching only the z-component of the polarization, resulting finally in the reversal of the mean polarization. Another possibility is a formation of the 109°-domain wall, parallel to (y,z)-plane, which propagates from right to left changing the signs of the y- and z-components of polarization. This also finally results in the reversal of the mean polarization from the positive to the negative z-direction.

To summarize, the multi-step stochastic mechanism model is able to satisfactory describe the time-dependent polarization and strain response of rhombohedral ferroelectrics and reveal the fractions of different switching processes and their characteristics. However, the interpretation of the apparent process fractions remains questionable. The fractions of ferroelastically-active processes, $\eta_{11}, \eta_{12}$ and $\eta_{2}$ seem to be reliable. However, the fraction $\eta_{3}$ representing ferroelastically inactive processes may include direct 180° polarization reversals as well as coherent collective non-180° processes, as exemplarily presented in Figs. 8-9. This may explain the dominating apparent fraction of 180°-switching events in contrast to the expected highest energy barrier and thus the least likelihood of 180°-switching from the LGD-analysis. This hypothesis is supported by the coincidence of activation energies for 180°- and the second 109°-switching events obtained from the fitting of experimental data.

5. Conclusions

Macroscopic electromechanical response of polycrystalline ferroelectric/ferroelastics can only be understood when the analysis includes sequential polarization rotation events. Consideration of consecutive switching events together with parallel ones opened for the first time a possibility to describe the dynamics of both electrical and mechanical response of ferroelectrics within one stochastic model. In the current work, the multi-step stochastic mechanism model of
polarization switching [26] was advanced to investigate rhombohedral ferroelectrics, which allow sequential and parallel 71°-, 109°- and 180°- switching events, important for both fundamental understanding of the behaviour of these materials and for their applications.

Successful application of the model to recent simultaneous measurements of polarization and strain response of rhombohedral ferroelectric PZT ceramics over a wide time window [29] allowed detangling the individual switching events and quantifying their fractions, activation fields and Avrami indices, related to the dimensionality of the nucleated reversed domains. The fraction of ferroelastically active processes was established to be about 0.3 and dominated by the processes starting with 71°-switching events. The analysis of the likelihood of different switching paths by means of the LGD theory revealed that the prevalence of the first 71°-polarization rotations over the first 109°-rotations might result from the residual stresses in the initial poled state. The dominating fraction of the ferroelastically inactive 180°-processes (about 0.7), however, appeared unexpectedly large, considering that the energy barrier for this process is the highest of all switching paths. In addition, the coincidence of the activation fields and the Avrami indices of the final 109°- and 180°- switching events raises a question on the genuine nature of the latter. These processes, contributing to the polarization variation but not contributing to the spontaneous strain variation, are reminiscent of the coherent processes in tetragonal materials, which do not develop macroscopically observable strain [60]. These observations suggest a hypothesis that the response of rhombohedral materials is dominated by coherent non-180°- switching events, which mimic the 180°- switching processes.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) Grants Nos. 270195408 (KO 5100/1-1) and GR 479/2. JED acknowledges financial support from the
Australian Research Council Discovery Projects DP120103968 and DP130100415. JS acknowledges the support of the Feodor Lynen Research Fellowship Program of the Alexander von Humboldt Foundation. Dr. H. Kungl is acknowledged for the preparation of the sample and Prof. K. Albe and Dr. Y. Lysogorskiy for fruitful discussions.

References

[1] A. J. Moulson and J. M. Herbert, J M, *Electroceramics: Materials, Properties, Applications*, 2nd edn., San Francisco, CA: Wiley (2003).

[2] J. F. Scott, *Ferroelectric Memories*, Springer (2000).

[3] D. Ghosh, A. Sakata, J. Carter, P. A. Thomas, H. Han, J. C. Nino, et al., Adv. Funct. Mater. 24, 885 (2014).

[4] B. Narayan, J. S. Malhotra, R. Pandey, K. Yaddanapudi, P. Nukala, B. Dkhil, et al., Nat. Mater. 17, 427 (2018).

[5] A. E. Glazounov, H. Kungl, J. T. Reszat, M. J. Hoffmann, A. Kolleck, G. A. Schneider, et al., J. Amer. Ceram. Soc. 84, 2921 (2001).

[6] B. Jaffee, W. R. Cook, and H. Jaffee, *Piezoelectric Ceramics*, R.A.N. Publishers, Marietta, OH (1971).

[7] P. Gerber, U. Böttger, and R. Waser, J. Appl. Phys. 100, 124105 (2006)[8] G. Catalan, A. Janssen, G. Rispens, S. Csiszar, O. Seeck, G. Rijnders, D. H. A. Blank, and B. Noheda, Phys. Rev. Lett. 96, 127602 (2006).

[9] V. Khikhlovskyi, A. V. Gorbunov, A. J. J. M. van Breemen, R. A. J. Janssen, G. H. Gelinck, and M. Kemerink, Org. Electron. 14, 3399 (2013).
[10] J. Lee, A. J. J. M. van Breemen, V. Khikhlovskyi, M. Kemerink, R. A. J. Janssen, and G. H. Gelinck, Sci. Rep. 6, 24407 (2016).

[11] D. Zhao, I. Katsouras, K. Asadi, W. A. Groen, P. W. M. Blom, and D. M. de Leeuw, Appl. Phys. Lett. 108, 232907 (2016).

[12] R. Xu, S. Liu, S. Saremi, R. Gao, J.J. Wang, Z. Hong, H. Lu, A. Ghosh, S. Pandya, E. Bonturim, Z.H. Chen, L.Q. Chen, A.M. Rappe, and L.W. Martin, Nat. Comm. 10, 1282 (2019).

[13] A. K. Tagantsev, L. E. Cross, and J. Fousek, *Domains in Ferroic Crystals and Thin Films*, Springer, Berlin (2010).

[14] A. N. Kolmogoroff, Izv. Akad. Nauk, Ser. Math. 1, 355 (1937).

[15] M. Avrami, J. Chem. Phys. 8, 212 (1940).

[16] Y. Ishibashi and Y. Takagi, J. Phys. Soc. Jap. 31, 506 (1971).

[17] S. P. Li, A. S. Bhalla, R. E. Newham, L. E. Cross, and C. Y. Huang, J. Mater. Sci. 29, 1290 (1994).

[18] J. Yin and W. Cao, Appl. Phys. Lett. 79, 4556 (2001).

[19] J. E. Daniels, C. Cozzan, S. Ukritnukun, G. Tutuncu, J. Andrieux, J. Glaum, C. Dosch, W. Jo, and J. L. Jones, J. Appl. Phys. 115, 224104 (2014).

[20] S. Gorfman, H. Simons, T. Iamsasri, S. Prasertpalichat, D. P. Cann, H. Choe, U. Pietsch, Y. Watier, and J. L. Jones, Sci. Rep. 6, 20829 (2016).

[21] C. M. Fancher, S. Brewer, C. C. Chung, S. Rohrig, T. Rojic, G. Esteves, M. Deluca, N. Bassiri-Gharb, and J. L. Jones, Acta Mater. 126, 36 (2017).

[22] S. P. Li, A. S. Bhalla, R. E. Newham, L. E. Cross, C. Y. Huang, J. Mater. Sci. 29, 1290 (1994).
[23] R. J. Xu, S. Liu, I. Grinberg, J. Karthik, A. R. Damodaran, A. M. Rappe, L. W. Martin, Nat. Mater. 14, 79 (2015).

[24] A. Roelofs, U. Böttger, R. Waser, F. Schlaphof, S. Trogisch, L.M. Eng, Appl. Phys. Lett. 77, 3444 (2000).

[25] J. Schultheiß, L. Liu, H. Kungl, M. Weber, L. K. Venkataraman, S. Checchia, D. Damjanovic, J. E. Daniels, J. Koruza, Acta. Mater. 157, 355 (2018).

[26] Y. A. Genenko, R. Khachaturyan, J. Schultheiß, A. Ossipov, J. E. Daniels, and J. Koruza, Phys. Rev. B 97, 144101 (2018).

[27] R. Khachaturyan, J. Schultheiß, J. Koruza, and Y. A. Genenko, Appl. Phys. Lett. 114, 222902 (2019).

[28] S. Zhukov, H. Kungl, Y. A. Genenko, and H. von Seggern, J. Appl. Phys. 115, 014103 (2014).

[29] J. Schultheiß, H. Kungl, and J. Koruza, J. Appl. Phys. 125, 174101 (2019).

[30] W. Chen and C. S. Lynch, Acta Mater. 46, 5303 (1998).

[31] F.X. Li, R. K. N. D. Rajapakse, Acta Mater. 55, 6481 (2007).

[32] D.A. Hall, A. Steuwer, B. Cherdhirunkorn, P.J. Withers, and T. Mori, Ceram. Intern. 34, 679 (2008).

[33] F. Endres and P. Steinmann, J. Appl. Phys. 119, 024105 (2016).

[34] I. Stolichnov, L. Malin, E. Colla, A. K. Tagantsev, and N. Setter, Appl. Phys. Lett. 86, 012902 (2005).

[35] P. Bintachitt, S. Trolier-McKinstry, K. Seal, S. Jesse, and S. V. Kalinin, Appl. Phys. Lett. 94, 042906 (2009).
[36] K. Seal, S. Jesse, M. P. Nikiforov, S. V. Kalinin, I. Fujii, P. Bintachitt, and S. Trolier-McKinstry, Phys. Rev. Lett. 103, 057601 (2009).

[37] J. E. Daniels, M. Majkut, Q. Cao, S. Schmidt, J. Wright, W. Jo, and J. Oddershede, Sci. Rep. 6, 22820 (2016).

[38] M. Majkut, J. E. Daniels, J. P. Wright, S. Schmidt, and J. Oddershede, J. Am. Ceram. Soc. 100, 393 (2017).

[39] S. Mantri, J. Oddershede, D. Damjanovic, and J. E. Daniels, Acta Mater. 128, 400 (2017).

[40] Y. A. Genenko, J. Wehner, and H. von Seggern, J. Appl. Phys. 114, 084101 (2013).

[41] R. Khachaturyan, J. Wehner, and Y. A. Genenko, Phys. Rev. B 96, 054113 (2017).

[42] R. Khachaturyan and Y. A. Genenko, Phys. Rev. B 98, 134106 (2018).

[43] A. L. Kholkin, E. K. Akdogan, A. Safari, P.-F. Chauvy and N. Setter, J. Appl. Phys. 89, 8066 (2001).

[44] R. E. Newnham, Properties of Materials. Anisotropy, Symmetry, Structure, Oxford University Press (2005).

[45] D. A. Hall, A. Steuwer, B. Cherdhirunkorn, T. Mori, and P. J. Withers, J. Appl. Phys. 96, 4245 (2004).

[46] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics, 99, 13 (1989).

[47] M.J. Haun, Z.Q. Zhuang, E. Furman, S.J. Zhang & L.E. Cross, Ferroelectrics 99, 45 (1989).

[48] D. Schrade, R. Müller, B.X. Xu, D. Gross, Comput. Methods Appl. Mech. Engrg. 196, 4365–4374 (2007).

[49] Y. W. Li, J. Wang, F. X. Li, Phys. Rev. B 94, 184108 (2016).
[50] A. Achuthan and C. T. Sun, J. Appl. Phys. 97, 114103 (2005).

[51] J. D. Eshelby, Proc. Royal Soc. A 241, 376 (1957).

[52] M. Hammer and M. J. Hoffmann, J. Amer. Ceram. Soc. 81, 3277 (1998).

[53] H. von Seggern and S. Fedosov, IEEE Trans. Dielectr. Electr. Insul. 7, 543 (2000).

[54] N. Uchida and T. Ikeda, Jap. J. Appl. Phys. 6, 1079 (1967).

[55] Y. A. Genenko, S. Zhukov, S. V. Yampolskii, J. Schütrumpf, R. Dittmer, W. Jo, H. Kungl, M. J. Hoffmann, and Heinz von Seggern, Adv. Funct. Mater. 22, 2058 (2012).

[56] W. J. Merz, J. Appl. Phys. 27, 938 (1956).

[57] J. Bergstra, D. Yamins, D. D. Cox, Proc. of the 12th PYTHON in Science Conf. (SCIPY 2013).

[58] S. Zhukov, Y. A. Genenko, M. Acosta, H. Humburg, W. Jo, J. Rödel, and H. von Seggern, Appl. Phys. Lett. 103, 152904 (2013).

[59] S. Zhukov, M. Acosta, Y. A. Genenko, and H. von Seggern, J. Appl. Phys. 118, 134104 (2015).

[60] G. Arlt, Integr. Ferroelectr. 16, 229 (1997).

[61] S. Liu, I. Grinberg, and A. M. Rappe, Nature 534, 360 (2016).

[62] P. Marton, I. Rychetsky, and J. Hlinka, Phys. Rev. B 81, 144125 (2010).