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Piezoelectric Nonlinearity and Hysteresis Arising from Dynamics of Electrically Conducting Domain Walls

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Abstract

Macroscopic nonlinearity and hysteresis observed in the piezoelectric and dielectric responses of ferroelectric materials to external stimuli are commonly attributed to localized displacements of domain walls (DWs). The link between the macroscopic response and microscopic DW dynamics is provided by the well-known Rayleigh relations, extensively used to quantify the electrical and electromechanical behavior of ferroelectric ceramics and thin films under subswitching conditions. In this chapter, I will present an intriguing case where DWs exhibit enhanced electrical conductivity with respect to the bulk conductivity. By combining experimental data and modeling, it will be shown that the local conductivity, related to accumulation of charged points defect at DWs, does not only affect DW dynamics through DW-defect pinning interactions, as we may expect, but goes beyond it by affecting the macroscopic nonlinearity and hysteresis in a more complex manner. The major characteristics and implications of the underlying nonlinear Maxwell-Wagner piezoelectric relaxation, triggered by the presence and dynamics of conducting DWs, will be presented, reviewed and discussed in the framework of systematic multiscale analyses on BiFeO_3 ceramics. The result may have implications in the development of promising BiFeO_3 -based compositions for high-temperature piezoelectric applications.

Keywords: Piezoelectric, nonlinearity, hysteresis, domain wall, electrical conductivity, BiFeO_3

1. Introduction

Historically speaking, probably the most important examples of dielectric and piezoelectric nonlinearity and hysteresis in ferroelectrics can be found already in the initial lines of the introductory section of the paper by Joseph Valasek from 1921 [1], which we use today to celebrate the 100th anniversary of the discovery of ferroelectricity [2]. Despite struggling with moisture-sensitive Rochelle salt crystals, Valasek finally managed to publish the first ever case of a ferroelectric hysteresis loop. Today, such hysteresis of the polarization response to the external electric field, originating from ferroelectric domain switching, is essential in, e.g., ferroelectric random-access

memories (FeRAMs) [3]. Hysteretic and nonlinear responses to external fields, however, are not only observed at switching conditions. Deviations from simple linear relationship between polarization (P) and electric-field (E) (dielectric response), P and mechanical stress (Π) (direct piezoelectricity) and mechanical strain (x) and E (converse piezoelectricity), are very common at subswitching driving conditions at which many important devices operate, such as capacitors, sensors and actuators. Such responses are measured in both bulk and thin-film ferroelectrics [4–6].

The origins of subswitching macroscopic nonlinearity and hysteresis alongside the frequency dependence of the property coefficients, which are directly relevant for device performance, are difficult to assess due to complex interrelated mechanisms often operating simultaneously over a wide length-scale range of the material. By risking of being too general, one could say that the major players of these mechanisms are domain walls (DWs) and similar interfaces [7], charged point defects [8–11], grain boundaries [12], spontaneous ferroelastic strains [13, 14], oxygen octahedra tilts [15] and secondary phases [16], if only the widely discussed examples are listed. Most of these features are always present in polycrystalline ferroelectric materials and are capable of cross-interacting via electric and/or elastic fields (a classical example that every ferroelectrician should be aware of is the DW-defect electro-elastic interaction [17, 18]). Complicating the picture is the fact that many of these features are strongly dependent on the synthesis conditions. Despite playing a key role, some of them, such as point defects, could not be directly visualized until recently [19–22], meaning that the interpretations of their role in the macroscopic response are supported by either indirect analysis or other reasoning (see next section). Without extensive knowledge in the area and with just a little intuition, it is pretty easy to understand why dielectric and piezoelectric nonlinearity as well as hysteresis in ferroelectric and similar materials are so difficult to understand and predict. Based on my personal opinion, the results shown in this chapter are the perfect example to illustrate the difficulties in elucidating the mechanisms responsible for the piezoelectric nonlinearity and hysteresis in a complex material, such as BiFeO_3 (BFO). The results that I am going to present have been acquired over eight long years of multidisciplinary research focusing on theoretical and experimental studies and involving a large number of researchers from different fields.

One of the most important and widely-recognized origins of nonlinearity and hysteresis in the subswitching electrical and electromechanical response of ferroelectrics is the displacement of domain walls (DWs) [5, 23–26]. These are interfaces separating domain regions in which the spontaneous polarization is directed in one of the symmetry-allowed directions. Displacements of DWs are mechanistically treated via the interaction with charged points defects, which act as pinning sites and, depending on their type, mobility and location, affect the movement of DWs under applied fields (this issue will be thoroughly discussed in the next section). Reversible and irreversible motion of DWs in a ferroelectric with randomly distributed pinning sites (defects) is described by the Rayleigh law (RL), which is vastly used to quantify and cross-compare the subswitching responses of ferroelectric ceramics and thin films [6, 27]. For the converse piezoelectric effect (same is valid for the direct effect or dielectric response), the RL can be expressed by a set of two equations:

$$d'(E_0) = d_{init} + \alpha \cdot E_0 \quad (1)$$

$$x(E) = (d_{init} + \alpha \cdot E_0) \cdot E \pm \frac{\alpha}{2} (E_0^2 - E^2) \quad (2)$$

For simplicity, the subscripts of the piezoelectric coefficient are omitted. Eq. (1) describes the linear dependence of the real component of the piezoelectric coefficient (d') on the electric-field amplitude (E_0) with d_{init} and α representing the reversible and irreversible Rayleigh coefficients, respectively. Note that d_{init} corresponds to the coefficient extrapolated at zero field or $d_{init} = d'(E_0 = 0)$. Eq. (2) is a multivalued function and describes the strain (x) versus electric-field (E) relationship where the positive and negative signs, separating the first and the second term of the equation, are related to the strain branches defined by descending and ascending E , respectively. The second quadratic term of Eq. (2) thus defines the hysteresis. Note that *nonlinearity* refers here to the *nonlinear* relationship between strain (x) and electric field (E) (second quadratic term of Eq. (2)), in which case the proportionality coefficient, d' , is *linearly* dependent on the field amplitude (Eq. (1)).

By carefully inspecting the Rayleigh equations, it is not difficult to understand that the essence of this model is the intimate relationship between the nonlinearity and hysteresis. For example, in Eq. (1) the irreversible coefficient α defines the nonlinearity by the field dependence of the piezoelectric coefficient, however, α also appears in the second term of Eq. (2) describing the hysteresis (by the different up-field and down-field strain branches). Alternatively, one can easily realize the nonlinearity-hysteresis relation of RL in the second term of Eq. (2), which sets the nonlinear (quadratic) relation of strain to field while, at the same time, representing the hysteresis. In other words, hysteresis arises from nonlinearity and vice versa. A mathematical test is straightforward: in the absence of the irreversible contribution ($\alpha = 0$), there are two important consequences: (i) the coefficient d' becomes independent on E_0 (Eq. (1) reduced to $d'(E_0) = d_{init}$), meaning that the response is linear (i.e., the coefficient is constant), and (ii) the hysteresis vanishes (Eq. (2) reduces to the first anhysteretic term). Therefore, every irreversible DW displacement contributes to nonlinearity and hysteresis in a unique way set by the RL [27].

When mechanistically reasonable, the irreversible coefficient α , experimentally extracted from the measurements of, e.g., longitudinal converse piezoelectric coefficient d_{33} as a function of field amplitude E_0 (see Eq. (1)), is commonly used to quantify (irreversible) DW contribution to piezoelectric properties (an analogous approach is used to quantify DW contribution to dielectric permittivity). A rigorous test to find out whether the measured data can be approximated by RL is to at least validate the nonlinearity-hysteresis relationship implied by RL. This can be done by verifying whether the experimental hysteresis can be fitted by Eq. (2) using the coefficient α that is determined from the d_{33} versus E_0 slope [6, 27]. Importantly, other parameters of the measured response can be checked against the RL predictions. For example, using the Fourier-series analysis of Rayleigh equations (derivations can be found in Ref. [27]) and the hysteresis-area analysis in complex mathematical formalism (see, e.g., references [24, 28]), it can be shown that the ratio between the increment in the real piezoelectric coefficient ($\Delta d' = d'(E_0) - d_{init}$) and the increment of the imaginary piezoelectric coefficient ($\Delta d'' = d''(E_0) - d''(E_0 = 0)$) is constant (equal to $\frac{4}{3\pi}$) and does not depend on the external field amplitude. This can be easily verified if the experimental piezoelectric coefficients and piezoelectric phase angles (or dielectric permittivity and losses) are known for different driving fields [14]. Other response parameters that can be evaluated against the RL predictions are embedded in the third harmonic response; this is discussed in detail in Ref. [29].

It has been shown that the subswitching response of a number of ferroelectric materials well obey the RL. Examples include donor-doped soft $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)

ceramics [5, 27, 28, 30], coarse-grained undoped BaTiO₃ [31], high-Curie-temperature piezoceramics based on BiScO₃-PbTiO₃ [24], textured (K_{0.5}Na_{0.5})NbO₃ (KNN) ceramics [32], Aurivillius-type Nb-doped Bi₄Ti₃O₁₂ [31], some relaxor-ferroelectric Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ compositions [33, 34] and Pb-based thin films [35, 36]. It has to be pointed out, however, that even in these cases, strictly speaking, a good match between the Rayleigh model and the measured subswitching response is typically observed in a limited driving field range, sometimes referred to as the “Rayleigh range” [5, 27]. This is expected, considering that RL is an idealization and assumes DW motion in a perfectly random pinning potential. It is clear that real materials’ responses may come close to this situation; however, in most cases deviations from RL predictions are naturally observed and should not be surprising. It is legitimate to think that these deviations have microscopic origins different from DW motion. However, this is not necessarily the case. A nice supporting example can be found in soft PZT, which often exhibit sublinear, quasi-saturating field dependency of the piezoelectric coefficient at relatively weak fields, clearly deviating from the perfect linear behavior predicted by Eq. (1) [4]. In this case, Preisach approach becomes useful as it shows that such response can be understood by considering a non-uniform pinning potential where the concentration of weakly pinned DWs is higher than those that are strongly pinned (note that the two should be equal in a perfect Rayleigh random pinning potential, resulting in a flat Preisach distribution function) [37]. Therefore, while the experimental data deviates from the RL, in some cases this deviation can still be explained by DW motion without necessarily invoking other mechanisms unrelated to DWs.

Apart from those cases where the response is close to RL predictions, the subswitching response can be clearly non-Rayleigh. Acceptor-doped hard PZT [30, 38], Sm-doped PbTiO₃ [27] or monoclinic Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) ceramic compositions with relaxor features [34] are just few of such examples. In this chapter, I am going to present another case that has attracted particular attention in recent times. The case is on BFO, a perovskite that is unique for at least two reasons: (i) because it contains electrically conducting DWs that are formed spontaneously and are attractive for applications in nanoelectronics [39] and (ii) due its high Curie temperature ($\sim 835^\circ\text{C}$) [40, 41], which makes it the key perovskite in the development of novel compositions for high-temperature piezoelectric applications [42]. As it will be shown in the next section, enhanced conductivity at DWs completely alters the DW dynamics under applied subswitching fields. I will give evidence of a very large nonlinear contribution to the total piezoelectricity in BFO arising from irreversible DW dynamics, which is strongly dependent on the frequency of the external driving field. Along with a peculiar hysteretic behavior, characterized by a negative piezoelectric phase angle, and an unusual clock-wise rotational sense, I will strive to demonstrate how complex the dynamic response of electrically conducting DWs can be and how careful should we be in analyzing and treating materials that show unique behaviors. Somewhat surprisingly, I will show that despite the charged point defects, which are accumulated at DWs and are responsible for the local conductivity, act as pinning sites (as explained in Section 2), they can even increase the DW mobility and largely contribute to the enhanced nonlinear converse piezoelectric response. This may happen because the local conductive paths through the grains, set by the conductive DWs, lead to a redistribution of internal fields, effectively resulting in grains or grain families inside which the electric field is largely enhanced with respect to the field applied externally. The mechanism, called nonlinear Maxwell-Wagner piezoelectric effect (explained in Section 3), can be supported by simple

analytical modeling (Section 4) and should be more seriously considered when engineering BFO-based materials for high-temperature piezoelectric applications.

2. Dynamic interactions between charged point defects and domain walls: a microscopic view

In this section, we will take a look at idealized microscopic pictures describing the interactions between DWs and charged point defects, which have profound implications in the DW dynamics and play a key role in the macroscopic dielectric and piezoelectric nonlinearity and hysteresis. Before discussing these interactions, however, it is timely to emphasize few important points. First, the reader should be aware that DW dynamics is not the only mechanism giving rise to electrical and electromechanical hysteresis. An example that should be familiar to every scientist and engineer working in the field of dielectrics or capacitors, is the DC electrical conductivity, which can directly contribute to the imaginary dielectric coefficient and thus dielectric losses and P-E hysteresis. In ionic compounds, electron and holes tend to be trapped at local sites in the lattice; they locally polarize and deform the lattice, creating the so-called polarons. Being self-trapped, these charges can move via an activated hopping process, similar to ionic conductivity [43]. Interestingly, in both physical and mathematical sense, hopping charge transitions are indistinguishable from pure dipole reorientations, meaning that hopping conductivity can contribute not only to losses (imaginary dielectric permittivity) but also to polarization (real dielectric permittivity). Mathematical descriptions of these problems are given in the book by Jonscher, which is highly recommended for learning conductivity phenomena in dielectrics [44].

Second, the effect of the electrical conductivity can go beyond a simple contribution to the complex dielectric permittivity and can strongly affect piezoelectricity, too. This case, which is less trivial and somewhat difficult to digest (even for experts in the field), is the Maxwell-Wagner (M-W) piezoelectric relaxation [45–49]. As an analogue of the well-known dielectric M-W relaxation [50], it originates, generally speaking, from electrically conductive paths present locally inside the material, which lead to internal electric-field redistribution as a function of the driving field frequency and, consequently, to electromechanical relaxation phenomena. The effect was predicted for the direct [4, 48] and converse piezoelectric response [51], and even for purely elastic response [52]. It was experimentally observed in heterogeneous ceramic materials [48], two-phase polymer systems [53] and piezoelectric-polymer composites [47]. The piezoelectric M-W effect is described in detail in an older book on hysteresis [4], to which the reader should refer to as a support to the data presented in this chapter where the focus is on BFO ceramics.

To explain the dielectric M-W effect, either grain boundaries or sample-electrode interfaces are commonly considered, as these are the regions where depletion layers are likely to be formed, giving rise to inhomogeneous field distribution inside the material and, consequently, to M-W relaxation [50]. In this chapter, I will present a different case where local conductive paths originate from charges concentrated at DWs. It is intuitively understood that this case must be unique because, unlike grain boundaries or sample-electrode interfaces, the conductive paths provided by the DWs are dynamic: they can move and locally displace under external fields. One may simplistically view this scenario as a local conductivity that is not spatially confined.

The third point to consider is rather general. While the discussion in this chapter is mostly about DWs, the reader should understand that also the dynamics of other types of interfaces may lead to the same macroscopic effects associated with subswitching nonlinearity and hysteresis. As an example, those other interfaces may be represented by boundaries separating regions consisting of phases with different crystallographic symmetries, which are present in morphotropic compositions [7]. The role of interface boundary motion during subcoercive loading of morphotropic $\text{BiScO}_3\text{-PbTiO}_3$ ceramics was recently demonstrated by in situ X-ray diffraction (XRD) analysis [54].

We come back now to our case on DWs. In analogy to the well-known pinning of DWs in ferromagnetic materials [55], the same concept is used for ferroelectrics [56]. An important difference is that, on average, ferroelectric DWs are an order of magnitude thinner than ferromagnetic DWs [39, 57–59]. While it is clear that the subject is complex and cannot be reduced to few (over)simplified pictures, like those shown in **Figure 1**, it is surprising to realize that the behavior of many ferroelectric materials under applied fields can be qualitatively interpreted by considering relatively simple interactions between DWs and charged point defects. This is particularly true for high-field P-E (switching) hysteresis (see, e.g., reference [18]) and, to some degree, for subswitching responses (see, e.g., reference [4]). Precaution is, however, necessary because there are various parameters to consider, such as type, concentration, location and mobility of defects along with their binding state, as well as the presence of other pinning centers, including grain boundaries [12] or oxygen octahedra tilts [15]. Nevertheless, a simple exercise linking possible DW-defect interactions with the macroscopic response, which will be explained next, is very useful to assess the behavior of a given ferroelectric material.

Early studies identified three microscopic scenarios to describe the strong pinning and DW stabilization effects observed macroscopically by pinched and/or biased high-field P-E hysteresis loops of acceptor-doped PZT and BaTiO_3 [8–11, 17]. The three scenarios are illustrated in **Figure 1a** and assume different locations of the pinning centers: (i) inside the domains (called “volume” or, sometimes, “bulk” effect), (ii) in DW regions (“domain wall” effect) and (iii) in or close grain boundary regions (“grain boundary” effect). The common feature of all these scenarios is that defects are arranged in a somewhat ordered manner and, by that, they stabilize the domain configuration via electric and elastic coupling [11, 18], inhibiting domain wall motion. Ordered defects are a characteristic of the so-called “hard” ferroelectrics, exemplified by acceptor-doped PZT. In contrast, “soft”

Figure 1.

Simplified microscopic pictures of interactions between charged point defects and domain walls in (a) hard and (b) soft ferroelectrics. P_s and P_d are spontaneous and defect polarization, respectively. Thick black lines denote DWs and circles noted with + and – signs represent individual charged point defects (see also legend on the right-hand side of the schematics). To be further noted is that P_d represents the well-known acceptor–oxygen–vacancy defect complexes (see text for details). The pictures shown in panel (a) were adapted according to the pioneering studies by Jonker [10], Carl and Hardtl [9], Lambeck and Jonker [8] and Robels and Arlt [11]. The scenario in panel (b) assumes disordered defects in soft materials as discussed in, e.g., reference [4].

ferroelectrics, represented by donor-doped PZT, are usually described by assuming disordered defects as shown in **Figure 1b**. Hard-soft transitions, induced in hard-type compositions by disordering the otherwise ordered defects, can be achieved by either electric-field cycling [9, 60] or quenching [30, 61, 62].

The “volume scenario” shown in **Figure 1a** (left schematic), which assumes binding of defects into complexes (see black arrows), is probably the only DW-pinning mechanism that is highly accepted in our research community and is widely used to explain hardening and aging in acceptor-doped PZT, BaTiO₃ and similar perovskites (an excellent review on this topic can be found in the paper by Genenko et al. [63]). DW pinning effects mediated by orientation of defect complexes have been put in a theoretical framework more than 30 years ago [17]. More recent studies confirmed the formation of defect complexes and their orientation kinetics both theoretically (by first principles, [64]) and experimentally. In particular, electron paramagnetic resonance (EPR) spectroscopy was found to be a powerful tool due to its high sensitivity, not only to the binding state of certain defects (for details see [65]), but also to the orientation of the defect complexes in the material [65, 66], allowing thus to directly monitor the alignment kinetics of the complexes under the applied field [67]. In most cases, the identified complexes are of the acceptor–oxygen-vacancy type. The literature contains many examples of lead-based and lead-free ferroelectric compositions where such complexes have been identified by EPR; the list includes (but is probably not limited to) PbTiO₃, PbZrO₃, PZT, BaTiO₃, KNN and (Bi,Na)TiO₃ (BNT). The dopants in those cases are typical B-site acceptors, such as Fe, Cu and Mn [65, 66, 68–71].

The “DW scenario”, which assumes defects accumulated in DW regions (**Figure 1a**, middle schematic), was first predicted by Postnikov more than 50 years ago [72]. Note that the original model does not assume defects bound into complexes. Interestingly, despite being seriously discussed in studies on fatigue mechanisms [73], the DW scenario received strong criticism (to be even labeled as “a well-known speculation”) from those that were strictly in favor of the volume scenario [74]. Nevertheless, very recent studies on BFO ceramics using atomic-resolution electron microscopy, which will be discussed later, support the idea of this scenario and indeed suggest that is active in this material [75].

The “grain-boundary scenario” (**Figure 1a**, right schematic), often referred to as the space-charge mechanism, was extensively discussed in a combined theoretical and experimental frame against the volume scenario originally proposed by Arlt et al. [17]. Key hardening characteristics of acceptor (Fe) doped PZT, such as the dopant-concentration dependent aging time, were shown to be well predicted by the space charge model [76, 77]. A perhaps interesting observation is that phenomenological calculations revealed that the electrostatic pinning effects on DWs from the space charges can be two orders of magnitude stronger than the pinning effects provided by the aligned defect complexes (for the same charge-carrier concentration) [76]. Considering that grain boundaries are strained areas and sources of polarization discontinuities where point defects may be attracted due to electrostatic and elastic driving forces, the grain boundary scenario should probably be always considered when interpreting the macroscopic responses of ceramics to external driving fields, particularly if the ceramics are fine-grained.

It is clear that more than one of the three domain-stabilizing effects shown in **Figure 1a** may be active in a given material. Actually, the reason for considering only a single scenario is in the human nature seeking for the simplest explanation. A number of arguments supports the idea of multiple pinning mechanisms. I give two examples. In hard PZT, it was predicted by first principles that the acceptor–oxygen-vacancy defect complexes should energetically prefer to be situated closer to DWs (as shown

schematically with black arrows in **Figure 1a**, left schematic) [78]. This means that the pinning mechanism may consist of a combination of volume and DW effects. In another study based on conductive atomic-force microscopy (c-AFM) analyses, it has been shown that in BFO ceramics both DWs and grain boundaries exhibit enhanced electrical conductivity with respect to the bulk conductivity measured in the grain interiors [79]. This suggests the presence of mobile charges at both locations, which may act as pinning centers. In this same material, defect complexes based on oxygen vacancies have been also identified by EPR [80]. The overall data, therefore, point to an extremely complex situation where all three pinning scenarios shown in **Figure 1a** may be active. The challenge is to find whether and which mechanism is dominant. At present, conductive DWs appear to be the key features affecting the piezoelectric response of BFO, which will be discussed in detail in the next section.

In contrast to ordered defects in hard ferroelectrics, disordered defects in soft counterparts, as shown schematically in **Figure 1b**, are more difficult to be directly identified. Nevertheless, in the case of PZT, for example, the presence of disorder in donor-doped samples (in a pragmatic sense) is supported by the fact that the measured macroscopic subswitching nonlinearity and hysteresis are well consistent with the major predictions from the Rayleigh model [27]. Another argument is that EPR data on Gd-doped PbTiO_3 indicate no binding of the donor (Gd) dopant with the expected compensating Pb vacancies [81], supporting the results of first-principles studies on the same perovskite [78]. In addition, none of the two defects (donor dopants and Pb vacancies) are mobile below the Curie temperature of the material, where the defects can in principle be ordered because they are provided by electric and elastic driving forces originating from the spontaneous polarization and strain, respectively (see, e.g., the graphic explanations by Ren [18]). If the two defects are not mobile nor they show tendency of binding, then a “frozen-in” defect disorder state in donor-doped PT or PZT can be envisioned. It is not unusual, however, that the dopants segregate at the grain boundaries (a nice recent example is shown for Ti-doped BFO in Ref. [82]). The issue of defect segregation at or close to grain boundary regions should be more seriously considered, as recently pointed out by Slouka et al. [83].

Other discussions related to the nature of defects in soft PZT point to the likely possibility that the donor dopant reduces the concentration of oxygen vacancies in PZT (due to charge compensation), leading to a progressive transition from a state characterized by ordered defects (undoped PZT) to a state governed by disordered defects, as the donor dopant is added to PZT [29]. In this sense, experimental data even indicate that the dominant pinning centers affecting DW displacements and, consequently, nonlinearity, in both hard and soft PZT, could be oxygen vacancies. The lesson that can be learned from all these data is that the defect arrangements shown in **Figure 1** should not be treated individually; as a matter of fact, all of them may be present, to some degree, in a given ferroelectric. Finally, it has to be emphasized that the situation in soft materials is more complex, and the true origins of softening are still not clear (if the reader is interested in these issues, it is recommended to consult the work of Dragan Damjanovic [29, 78]).

3. Piezoelectric nonlinearity and hysteretic response of BFO ceramics: low-frequency nonlinearity and negative piezoelectric phase angle

One of the distinct characteristics of the piezoelectric response of BFO is the strong dependence of the nonlinearity on the frequency of the driving field. This is illustrated

in **Figure 2**, which compares the converse piezoelectric response of BFO with that of hard and soft PZT. The PZT compositions correspond to the rhombohedral symmetry and were selected exactly to enable a comparison with the isostructural rhombohedral BFO, although symmetry is probably the only common aspect of these two perovskites. In the first place, it should be mentioned that the increasing tendency of d_{33} with the electric-field amplitude E_0 observed in **Figure 2a–c** for the two PZTs (at all measured frequencies) and BFO (mostly at 1 and 0.2 Hz) is accompanied by an increase in the piezoelectric $\tan\delta$ (not shown here). This suggests irreversibility in the response as implied by the intimate nonlinearity-hysteresis relationship predicted by RL (see Eqs. (1) and (2)). The nonlinear behavior in these samples can be thus related to irreversible domain wall contribution. This is supported by in situ XRD analysis on BFO [84] and similar PZT samples to those shown here [26].

As expected and described in the previous section, due to stronger DW pinning effects, hard PZT shows a lower absolute d_{33} value, which is less dependent on the field magnitude (**Figure 2a**) than that of soft PZT (**Figure 2b**). Also, the d_{33} field

Figure 2. Converse piezoelectric d_{33} coefficient as a function of electric-field amplitude E_0 measured at different frequencies for (a) 1% Fe doped $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ (hard PZT), (b) 1% Nb doped $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ (soft PZT) and (c) BFO ceramics. (d) Comparison of the fraction of the piezoelectric d_{33} coefficient related to the irreversible contribution (X_{IR} ; see Eq. (3)) among the three samples. The response is in this case shown for two limited frequencies (90 or 100 Hz and 0.2 Hz) and as a function of relative electric field, i.e., E_0/E_C (E_C is the coercive field determined by standard P-E hysteresis measurements, which are not shown here). For clarity, color coding of the curves is the same in all panels. The green arrow in panel (d) illustrates the strong effect of the driving electric-field frequency on the nonlinearity in BFO, which is absent in hard and soft PZT. The data correspond to fine-grained BFO sample (average grain size 1.8 μm) as reported in Ref. [79].

dependency in soft PZT is sublinear with respect to the rather linear dependency in hard PZT. This behavior is retained at all frequencies used in the measurements. The sublinear trend in soft PZT has been discussed to some degree in the introduction of this chapter in relation to non-uniform pinning potential.

The next information can be obtained by quantifying the data. The slope of the d_{33} -vs- E_0 curves is for hard PZT $\sim 0.2 \cdot 10^{-16} \text{ m}^2 \text{ V}^{-2}$ and is practically independent on the frequency. By contrast, in soft PZT, the slope (in this case calculated for 1 kV cm^{-1} , which corresponds to 10% of coercive field E_C , i.e., $E/E_C = 0.1$) is an order of magnitude higher, i.e., $8.1 \cdot 10^{-16} \text{ m}^2 \text{ V}^{-2}$ at 90 Hz, and further increases to $9.9 \cdot 10^{-16} \text{ m}^2 \text{ V}^{-2}$ at 0.2 Hz. The frequency dependence of the irreversible coefficient of soft PZT has been reported earlier and correlated with interface pinning in a disordered medium [85].

As easily assessed from **Figure 2c**, the nonlinearity and the associated irreversible contribution to piezoelectricity in BFO is completely different than in PZT. Here, the nonlinear behavior is strongly dependent on frequency: the d_{33} -vs- E_0 slope is nearly zero at 100 Hz, precisely $0.003 \cdot 10^{-16} \text{ m}^2 \text{ V}^{-2}$, and increases to $0.27 \cdot 10^{-16} \text{ m}^2 \text{ V}^{-2}$ when the frequency is reduced to 0.2 Hz (as in the previous case on PZT, the slope was calculated for the relative field $E/E_C = 0.1$). Such a dramatic two-orders-of-magnitude increase in the nonlinearity coefficient with reduced frequency is obviously absent in the two PZT variants.

A direct comparison between the nonlinearity of BFO and PZT is shown in **Figure 2d**. As a quantitative measure, we use the fraction of the total piezoelectric coefficient that is due to irreversible DW displacements (X_{IR}). This parameter is essentially represented by the fraction of the field-dependent coefficient and can be derived from Eq. (1) as:

$$X_{IR}(E_0) = \frac{d_{33}(E_0) - d_{33}(E_0 = 0)}{d(E_0)} \quad (3)$$

where $d_{33}(E_0)$ and $d_{33}(E_0 = 0)$ is the coefficient at a given field amplitude E_0 and at zero field amplitude, respectively. As anticipated, the irreversible contribution in hard and soft PZT is practically independent on the frequency (**Figure 2d**, blue and red data). X_{IR} reaches a maximum of 10% and 55% in hard and soft PZT, respectively. Interestingly, the irreversible contribution in BFO at 100 Hz is smaller than that of hard PZT and becomes higher at 0.2 Hz than that of soft PZT (for the same relative field E/E_C ; see green data in **Figure 2d**). Note that the large contribution from the displacements of non-180° domain walls at sub-Hz driving frequencies in BFO was recently confirmed by in situ XRD stroboscopic analysis [84]. One could imagine BFO as very hard material at high frequencies and very soft at low frequencies. The data, therefore, present a distinct hard-to-soft transition in BFO induced by the driving frequency. As will be explained throughout the rest of the chapter, this transition originates from the presence and dynamics of conductive DWs.

Another distinct feature of the piezoelectric response of BFO is the negative piezoelectric phase angle (here and in subsequent discussion, the phase is represented as the tangent of the piezoelectric phase angle, $\tan \delta_p$). This rather unusual response is particularly strong in coarse-grained BFO and is presented in **Figure 3**. From these data it is clear that the piezoelectric response of BFO is rather complex and show strong frequency dependence (**Figure 3a**). When inspected from high to low frequencies (right to left), the response can be described as a sequence of increasing and decreasing d_{33} in the frequency range 1–200 Hz and 0.1–1 Hz, respectively, giving

Figure 3. (a) Piezoelectric coefficient (d_{33}) and tangent of the piezoelectric phase angle ($\tan\delta_p$) as a function of driving field frequency for coarse-grained BFO. The data were obtained at 11.9 kV/cm of driving field amplitude. Error bars represent measurement error. These errors alongside the details of the annealing procedure of the coarse-grained BFO sample (average grain size 16 μm), its microstructure, domain structure and local electrical conductivity are reported in Ref. [79]. The two insets show the time-domain driving field E signal (black sinusoidal curves) with overlaid mechanical displacement ΔL signals (blue or green sinusoidal curves) together with the corresponding ΔL - E piezoelectric hysteresis loops for the case of (b) positive (10 Hz; blue data) and (c) negative (1 Hz; green data) piezoelectric phase angle. The bigger arrows in panels (b) and (c) indicate the lagging and leading ΔL signal with respect to the driving field signal for the case of positive and negative phase angle, respectively. The corresponding counter-clockwise and clock-wise rotational sense of the hysteresis, which is set by the lagging and leading output signals, respectively, is also noted on the respective loops. Numbered points on the time-domain plots and hysteresis are drawn to help identifying the rotational sense of the hysteresis.

rise to a d_{33} maximum at 1.5 Hz (**Figure 3a**, black points). These two d_{33} -vs-frequency behaviors are accompanied by a broad $+\tan\delta_p$ maximum at ~ 10 Hz and a rather narrow $-\tan\delta_p$ minimum at 0.4 Hz, respectively (**Figure 3a**, red points). The overall behavior can be thus simplified to a sequence of retardation process (d_{33} increasing with decreasing frequency accompanied by $+\tan\delta_p$ peak) and relaxation process (d_{33} decreasing with decreasing frequency accompanied by $-\tan\delta_p$ peak) [4, 46]. As it will be shown in the next section, this is consistent with the distinct features of M-W piezoelectric effect, which can be easily predicted by simple analytical modeling.

As it has been done in the case described here, the sign of the piezoelectric phase is very often determined by measurements performed using lock-in technique, which is capable of extracting the amplitude and phase of individual harmonic responses to external sinusoidal excitations [29]. For less experienced, this may be sometimes non-trivial as several instruments may reverse (by 180°) or somewhat affect the phase of the output signal. While the sign of $\tan\delta_p$ can be checked by, e.g., measurements of a sample with known response, such as, e.g., a donor-doped soft PZT where $\tan\delta_p$ should be positive (and, ideally, related to Eqs. (1) and (2)), it is useful to acquire the total signal containing all information by conventional oscilloscope imaging. Two examples of such acquired signals displayed either in time domain or as piezoelectric

hysteresis loop (mechanical displacement ΔL versus electric field E plots) are shown in **Figure 3b** and **c**. The case in **Figure 3b** is shown for 10 Hz where a positive $\tan\delta_p$ was measured using the lock-in method. As expected, the output displacement ΔL signal lags behind the input driving field E signal (see arrow in **Figure 3b**), corresponding to counter-clockwise rotational sense of the piezoelectric hysteresis. In terms of hysteresis, this is a common situation observed during, e.g., conventional measurements of ferroelectric P-E hysteresis loop at switching fields (to give a popular example). The case that is less common is when $\tan\delta_p$ is negative as shown in **Figure 3c**. Here, instead of *lagging*, the output ΔL signal *leads* the input E signal, effectively resulting in a clock-wise rotation of the piezoelectric hysteresis.

Very often (and not to be blamed) the negative piezoelectric phase is misinterpreted because it gives a wrong impression that it violates the basic law of energy conservation. This is also the reason why is so often interpreted as a measurement artifact. An example is the clockwise hysteresis measured in the response of ferroelectric field-effect transistor thin-film structures, which arise due to charge injection during measurements [86, 87].

It is not within the scope of this contribution to provide a deep and detailed physical analysis of the negative piezoelectric phase, neither is such analysis within the main expertise of the author of this chapter. The reader is strongly advised to follow the discussion provided in the chapter on hysteresis by Damjanovic [4]. Nevertheless, one can envision a very simple reasoning based on the classical power dissipation principles in dielectrics (found in general textbooks, such as [88]) where the power loss is defined by the positive dielectric $\tan\delta$ (considering that all other parameters in the equation for the dissipated power density, i.e., electric-field amplitude, frequency and real part of the dielectric permittivity, are positive by definition). Similarly, the area of the charge density (D) – electric field (E) hysteresis represents the energy loss of a dielectric during an electric field cycle per unit volume of the material (units of D-E hysteresis is J m^{-3}) [89]. In this analogy, one could understand a negative piezoelectric phase angle corresponding to energy gain that is represented by the piezoelectric hysteresis area. The simplest and perhaps strongest argument against this claim is that, unlike the dielectric D-E hysteresis area, the piezoelectric hysteresis area (either converse x-E or direct D- Π) does not have units of energy density. Therefore, the hysteresis shown in **Figure 3c**, where the phase is negative, does not *directly* represent an energy gain because the hysteresis area does not reflect energy density. This problem has been extensively elaborated by Holland [90]. The rigorous mathematical treatment therein shows that the necessary restriction of positive total power loss, which is represented by the sum of dielectric, elastic and mix piezoelectric components (proportional to respective imaginary coefficients), results into dielectric and elastic loss terms being always positive and bigger than the piezoelectric term. The latter was shown to not be restricted in its sign. Therefore, taking the longitudinal piezoelectric response of poled ferroelectric ceramics as an example, the imaginary piezoelectric coefficient d_{33}'' is permitted to be either positive or negative; for a positive real longitudinal coefficient d_{33}' , as is the case of ferroelectric ceramics, the piezoelectric $\tan\delta_p$ (defined as $\tan\delta_p = \frac{d_{33}''}{d_{33}'}$) can thus be either positive or negative. While not restricted in its sign, the piezoelectric term in the total power dissipation function is, however, restricted in magnitude. This essentially means that a negative piezoelectric phase angle measured in poled ceramics indicates a partial reduction of the total power loss. To avoid confusion, it should be noticed that in the power dissipation equation, reported in the paper by

Holland, the term related to the piezoelectric coupling is proportional to $E \cdot \Pi \cdot d''$, which must obviously possess units of energy density (subscripts are omitted for simplicity). In contrast, the piezoelectric hysteresis area is proportional to either the product of $x \cdot E$ (converse effect) or $D \cdot \Pi$ (direct effect), none of which possess energy density units. A very nice experimental example of the reduction of the total power dissipation due to piezoelectric coupling was shown for Sm-doped PbTiO_3 [4].

Coming back to our case on BFO, it must be emphasized at this point that the negative converse piezoelectric phase angle has also been confirmed in the direct piezoelectric response of BFO [91]. In addition, a negative phase has also been detected in the lattice microstrain response of BFO ceramics to external electric field,

Figure 4.
(a) Scanning electron microscopy (SEM) image of the surface of BFO ceramics with visible grains and domains. At the lower part of the image, a grain was highlighted for clarity with the thick white line indicating the grain boundary and the thin red dashed lines indicating DWs. Note that the domains, which are separated by these DWs, are clearly seen as alternating dark/bright bands in the SEM image. The other two regions highlighted with blue circles were further analyzed by means of EBSD analysis. In each of the two regions, the type of DW (either 180° or non- 180°) was determined based on the orientation of $[111]$ polar axis of the rhombohedral lattice (with respect to the surface sample plane) in domains adjacent to the analyzed DW (for details, see text and reference [79]). (b) c-AFM maps of the same regions which are in panel (a) highlighted with blue circles. I_{rel} on the scale bar signifies relative current, displayed with respect to the average background current signal. The bright lines observed at DWs (see blue arrows on the maps), which correspond to an increased local electric current signal, confirm the enhanced conductivity at both 180° (bottom c-AFM image) and non- 180° DWs (top c-AFM image). Adjacent to the c-AFM maps are the electric current profiles measured by scanning the AFM tip on the surface along the white dashed lines noted on respective c-AFM maps. The peaks noted by blue arrows clearly emerge from the electric-current background, supporting the idea of electrically conducting 180° and non- 180° DWs in BFO ceramics. Parts of the figure are reprinted from reference [79] with the permission of John Wiley and Sons.

which was characterized by in situ XRD stroboscopic analysis [84]. This is perhaps the most important evidence of a negative piezoelectric phase angle measured in any piezoelectric so far because, prior to that work, such response (to the best of the author's knowledge) was demonstrated only on the level of macroscopic measurements.

As anticipated in the initial discussion of the results shown in **Figure 3**, the negative piezoelectric phase angle is a strong indication of M-W piezoelectric process that is very common in, e.g., piezoelectric composites [46, 47]. In analogy to the dielectric M-W relaxation, characterized by giant apparent dielectric permittivity [50], the modeling of Turik et al. showed the same effects in the piezoelectric M-W analogue [45]. As explained earlier, the M-W relaxation has origin in the internal electric field redistribution in a medium, where local regions exhibit different electrical conductivities; in the frame of modeling, such regions are often implemented in the form of M-W bilayer units, where the two layers are described by different conductivities [48, 51]. This is the reason behind a large piezoelectric M-W effect in some Aurivillius phases, such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [48]. These ceramics, in fact, tend to show anisotropic microstructure with elongated plate-like grains that are characterized by different electrical conductivities in the direction parallel or perpendicular to the plane of the plates. The piezoelectric M-W effect in heterogeneous $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics is thus easy to support using arguments of anisotropic conductivity.

Unlike in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the M-W features observed in the piezoelectric response of BFO (**Figure 3**) are more difficult to interpret because significant anisotropy in the conductivity in a homogeneous perovskite oxide, such as BFO, is not expected, at least not to a level as in layered Aurivillius-type structures. Also, BFO is characterized by a microstructure typically consisting of equiaxial grains (as it is illustrated in **Figure 4** in the next section). It should be recalled, however, that the piezoelectric M-W effect in BFO is particular in that it shows, in addition to the negative piezoelectric phase angle (**Figure 3**), a very strong DW contribution observed only at low (sub-Hz) driving frequencies (**Figure 2c**). The overall data thus suggest a piezoelectric M-W effect provoked by DWs. The idea becomes reasonable when DWs are electrically conducting as the conductivity is what triggers the M-W effect. As it will be shown in the next section, it is exactly the conducting DWs that likely cause large anisotropy in the conductivity from grain to grain or across cluster of grains. Obviously, in BFO the situation is more complex than in other known piezoelectric M-W cases, simply because the features that are triggering the M-W effects, i.e., the DWs, can also move inside the grains under applied fields.

4. Analytical modeling of nonlinear Maxwell-Wagner piezoelectric relaxation arising from electrically conducting DWs

While, pragmatically speaking, the idea of conducting DWs giving rise to macroscopic piezoelectric M-W effects does fit into a reasonable explanation, the details of the mechanism are rather complicated. The reason is the complex situation in a polycrystalline ceramic matrix containing randomly oriented grains, each characterized by a domain structure with different DWs and corresponding DW planes oriented in various directions with respect to the reference external field axis. The DW planes are assumed to provide conductive paths through individual grains or in local regions inside the grains, modifying the internal electric fields. If further grain-to-grain elastic interactions are considered, which have a significant effect in polycrystalline piezoceramics [26], modeling may become extremely difficult. In the first

approximation, therefore, the model can be simplified and reduced to a level that allows the major macroscopic parameters to be predicted and compared with experimental data. As demonstrated for the case of direct piezoelectric response of Aurivillius phases [48], analytical bilayer modeling is sometimes sufficient. A similar case study on BFO, but additionally elaborated to incorporate nonlinear effects, will be presented in this section.

In the first place, it is important to work out a physical picture onto which to construct the model. Following the original discovery of conducting DWs in epitaxial BFO thin films [92], conduction at DWs in BFO polycrystalline samples have been determined using the same c-AFM measurements, which make it possible to probe the local conductivity of the sample. In BFO films, the epitaxial growth determines the crystallographic orientation of the film with respect to the substrate plane, so that the determination of the type of DWs in rhombohedral (R) BFO (71° , 109° or 180°) is facilitated. In ceramics, this is more difficult as the orientation of the grains is random and it is thus not known when imaging the surface with microscopy techniques. A simple way to accomplish the task is to determine the orientation of the polar [111] axis of the BFO R symmetry in adjacent domains in a selected grain using, e.g., electron back-scattered diffraction (EBSD) analysis. By indexing the Kikuchi patterns obtained in individual domains, as those highlighted in blue circles in **Figure 4a**, with the available R BFO space group, the angle between the [111] vectors in adjacent domains can be determined. Once these angles are known and without going into detailed geometrical analyses, which may be non-trivial (see the example in the supplementary material 1 of the paper [93]), a separation between 180° and non- 180° DW-type is possible. In the former case, the angle should be zero ([111] vectors in adjacent domains are parallel), while in the second is non-zero. Note that further analysis is complicated by the fact that EBSD cannot determine the orientation of the ferroelectric spontaneous polarization, but only the ferroelastic distortion.

EBSD analysis was used to determine the 180° and non- 180° DWs in the example shown in **Figure 4a** (see also reference [79] for further details). In the next step, these same regions were analyzed by c-AFM (**Figure 4b**) to finally confirm that both 180° and non- 180° DWs in R BFO ceramics exhibit enhanced electrical conductivity with respect to that measured in the domains (see also the electric-current profiles in **Figure 4b** measured across DWs as indicated with the dashed white lines in respective c-AFM maps). The results are fully consistent with the atomic-scale microscopy analysis, which confirmed the presence of p-type charge carriers, identified as Fe^{4+} states, concentrated inside all three DW variants (71° , 109° and 180°) of BFO [19], resulting in the domains mostly likely depleted from the charges. The p-type conductive nature of the DWs is supported by annealing studies in controlled atmospheres, reported in the same paper, while the dynamic pinning effects of the p-type carriers is reported in Ref. [75].

The analysis of the effect of conductive DWs on the piezoelectric response can be reduced, in the first approximation, to a two-grain problem as shown in **Figure 5a** (left schematic). Since ceramics are composed of randomly oriented grains containing different type of DWs with various orientations, it is legitimate to analyze a hypothetical case of two grains oriented along [100] and [111] directions with respect to the externally applied electric field vector. The choice of these orientations will become evident in the subsequent discussion. If the two grains contain only 71° DWs percolating the grains, then the situation should closely resemble the left schematic shown in **Figure 5a** (detailed geometrical analysis of the DW angles in the two grains is reported elsewhere [84]). The key element of the model is the different orientation

Figure 5.

(a) Schematic of the two-grain model (left) representing a serial bilayer M-W unit (right). The two grains are assumed $[100]_{pc}$ and $[111]_{pc}$ oriented with respect to field axis E and are denoted as grain 1 (red) and grain 2 (blue), respectively. Notation “pc” indicates “pseudocubic”. The dashed lines inside the grains represent DWs. The DW orientation is assumed such that the DW planes in grain 1 are parallel to E , while those in grain 2 are not, forming an angle of $\sim 35^\circ$ with respect to E axis. These angles should correspond to those of 71° DWs present in the two grains (for detail geometrical analysis, see reference [84]). Due to the different orientation of the electrically conductive DW in the two grains, the conductivity measured along E axis will be higher in grain 1 than in grain 2 (see σ_1 and σ_2 notation with upward and downward arrow in grain 1 and grain 2, respectively). This will result in the drop of the electric field in grain 1 (noted by down-arrowed E_1) and rise of the electric field in grain 2 (up-arrowed E_2). The same difference in the orientation of the DW with respect to E will result in a lattice strain with no contribution from DW motion in grain 1 (see ΔL_1), while displacements of DWs is expected in grain 2, in addition to lattice strain (see larger ΔL_2). To incorporate DW contributions, the calculations were performed assuming RL relations in grain 2 as described in detail in Ref. [94]. The two grains may be viewed as a M-W bilayer unit where each layer is assumed as a leaky piezoelectric element, characterized by its own piezoelectric coefficient d_i , dielectric permittivity ϵ_i , specific DC electrical conductivity σ_i and volume fraction ν_i ($i = 100$ or 111 indicating the two grain orientations). Panels (b–d) show driving-frequency dependent (b) internal electric field distribution (E_1, E_2), (c) piezoelectric microstrains (x_1, x_2) and (d) tangent of the piezoelectric phase angle ($\tan \delta_1, \tan \delta_2$) of the two grains (layers) as calculated from the model. The different curves in panels (b,c,d) correspond to different anisotropic parameter, i.e., ratio of the conductivities $\frac{\sigma_1}{\sigma_2}$, which were set to 1.01, 1.5, 2.5, 4 and 5 (the increasing tendency of $\frac{\sigma_1}{\sigma_2}$ is shown by arrows on individual plots and the corresponding curves are drawn with different lines, each corresponding to specific $\frac{\sigma_1}{\sigma_2}$ ratio as noted in panel b). The data in panels (b,c) were calculated for 16 kV/cm of externally applied sinusoidal field amplitude, while those shown in panel (d) were calculated for zero-field amplitude (linear piezoelectric $\tan \delta_i^{init}$). (e) Effective (total) piezoelectric coefficient of the M-W bilayer unit normalized to the value at zero field ($d_{33}^{eff, norm}$) as a function of external (nominal) electric field amplitude calculated for different driving field frequencies (the anisotropic parameter $\frac{\sigma_1}{\sigma_2}$ was fixed to a value of 5). Parts of the figure are reprinted from Ref. [94] with the permission of AIP Publishing.

of conductive DWs in the two grains with respect to the external field axis, i.e., in the top grain 1 (red) the DWs are parallel to E , while in the bottom grain 2 (blue) they form a different angle. The net result is that the conductivity, measured along E , of grain 1 should be higher than that of grain 2 because in the former the charges may migrate along the vertical conductive DWs (see notations σ_1 and σ_2 in **Figure 5a** indicating the conductivity measured vertically in grain 1 and 2, respectively). Using the same reasoning, the conductivity of grain 2 should be higher when measured along a direction away from the E axis (not parallel). It is this anisotropy in the electric conductivity that it is assumed here to lead to M-W-like internal field redistribution (see down-arrowed E_1 and up-arrowed E_2 notations in **Figure 5a**, denoting the

internal fields). Note also that the bottom grain 2 is oriented in a way to give rise to a stronger DW contribution than the upper grain 1; in the ideal case, due to orientational constraints, grain 1 should exhibit only lattice strain as a response to the external E (in **Figure 5a** the microstrains arising from the two grains due to field application are noted as ΔL_1 and ΔL_2). Further details regarding the model and mathematical derivations can be found in the supplementary Section 5 of the paper by Makarovic et al. [94].

The assembly of the two grains represents a basic M-W bilayer unit. As in classical dielectric M-W modeling [50], the picture can be rationalized in terms of an equivalent circuit consisting of two leaky capacitors connected in series, where each leaky capacitor may be represented by an ideal capacitor and an ideal resistor connected in parallel (**Figure 5a**, right-hand schematic). Obviously, the piezoelectric effect is added to the two layers (grains). Due to the expected DW contribution in the bottom grain 2, the RL relations (Eqs. (1) and (2)) were used to calculate the piezoelectric response of this grain. In contrast, grain 1 is assumed to respond via intrinsic lattice piezoelectric effect, so its response can be modeled by the linear constitutive piezoelectric equation. For a set of dielectric, piezoelectric and conductivity parameters, which are within the margins reasonable for BFO (see reference [94]), the results of the modeling are shown in **Figure 5b–e**.

Driven by the anisotropy in the electrical conductivity, defined as the conductivity ratio of the two grains ($\frac{\sigma_1}{\sigma_2}$), the internal fields in the grains (E_1 , E_2) will be redistributed as a function of driving field frequency (**Figure 5b**). In accordance to the conductive behavior related to the different DW orientation in the two grains, the sinusoidal electric field applied externally to the bilayer serial structure will be redistributed at low driving frequencies (<10 Hz) such that the electric field in the top grain 1 (red color coding) will be reduced with respect to the nominal (external) field, while that of the bottom grain 2 (blue) will be increased instead (**Figure 5b**). In other words, due to leakage in grain 1 caused by the vertical orientation of conductive DWs, the field inside this grain will drop and will be thus transferred from the leaky grain 1 to the less-leaky grain 2 (see **Figure 5a**). This will happen at low driving frequencies as such driving conditions provide to the charges sufficient time to migrate along conductive DWs. Being proportional to the internal field, the microstrains of the two grains (**Figure 5c**) will show the same frequency behavior as that of respective internal fields, leading to either retardation and a peak in the positive piezoelectric phase angle (see $\tan\delta_2$ in **Figure 5d**), or relaxation and a peak in the negative piezoelectric phase angle (see $\tan\delta_1$ in **Figure 5d**). This M-W mechanism will ultimately lead to nonlinear effects: the increased internal electric field in grain 2 (E_2 in **Figure 5b**) will boost the DW motion in this grain, resulting in effective nonlinearity enhanced at low driving frequencies as shown in **Figure 5e** (compare also with experimental data, **Figure 2c**). The piezoelectric M-W effect has thus a nonlinear character or, in other words, the piezoelectric nonlinearity (i.e., DW motion) is boosted due to the electrical conductivity.

At this stage, I have to point out that the presented model used to understand the experimental data on BFO (as those shown in **Figures 2c** and **3**) is largely simplified: (i) it considers only two isolated and unconstrained grains connected in series, neglecting the true elastic and electric boundary conditions of the analyzed grains set by the presence of other surrounding grains, (ii) it does not consider elastic coupling of the two isolated grains and transverse piezoelectric effects (as was done in, e.g., reference [51]), (iii) it assumes very simple domain structure in the two grains and

only one type of DW (i.e., 71°), and (iv) the conductivity of the grains set by the conductive paths along DWs is assumed to be fixed, although a dynamic conductivity is not unreasonable considering that the conductive DWs may switch locally (through a RL-like irreversible jump, for example), resulting in a modified conductive path through the switched DW. Despite all these limitations, however, it is surprising to realize that the simple two-grain model predicts all the key experimental observations. First, the model predicts both retardation and relaxation processes (**Figure 5c and d**), which are likely convoluted in the experimental response (as discussed for **Figure 3a**). Second, the model shows that the lattice strain response should exhibit a negative phase with respect to sinusoidal external field, thus leading the field signal (**Figure 5d**). Not only is this consistent with macroscopically measured piezoelectric strain leading the field signal (**Figure 3c**), but this is also exactly the behavior of the lattice strain deconvoluted from the total converse piezoelectric response of BFO ceramics using synchrotron XRD measurements [84]. Third, the important outcome of the model related to the low-frequency nonlinearity is a natural consequence of introducing RL relations, lining up with the macroscopic experimental data (**Figure 2c**) and the low-frequency DW contribution determined by synchrotron XRD measurements [84].

The low-frequency nonlinearity has recently been shown to be a response parameter that can be controlled by designing the fraction of conductive DWs in BFO ceramics via doping [94]. The idea was triggered by the outcomes of the model itself, further reinforcing the value and importance of simple modeling. It is probably needless to say that controlling nonlinearity and hysteresis is very important for the development of high-temperature piezoceramics based on BFO. This is indeed supported by a study on BFO showing that the temperature dependent piezoelectric response of these ceramics is strictly controlled by the same M-W processes described in this chapter [95]. Importantly, it was shown that the strong temperature dependence of the piezoelectric nonlinearity and hysteresis, which is of a direct relevance for the device operation, has origin in the thermally activated nature of the local electrical conductivity in BFO ceramics.

Simple analytical modeling was found to be a promising first step toward understanding the complex piezoelectric behavior of BFO arising from conductive DWs. It could be interesting, however, to model a more complex situation to account for the many different parameters that are necessarily neglected in the simple analytical approach. As shown in **Figure 5b–d**, the effect of the anisotropic parameter is crucial as it determines the strength of the M-W effect. For more advanced modeling, this parameter could be viewed as varying from one M-W unit to another in a complex ceramic matrix composed of interacting grains forming units with different time constants (τ is proportional to the ratio of the weighted sum of permittivity and conductivity of the individual layers in the bilayer unit [48, 84]). This could eventually account for the different regions inside the ceramics exhibiting different levels of electric-field redistribution (as shown by the different curves in **Figure 5b**). 3-dimensional (3D) finite element modeling based on a phenomenological approach has been recently demonstrated to be a powerful tool in predicting local electric fields in 3D ceramic matrices with defined porosity [96]. For solving complex problems, such as those encountered in elastically and electrically coupled grains in ferroelectric ceramics, multiscale modeling approaches show great promises [97–99].

Another interesting point that could be considered in the future is to push the relaxation to higher frequencies (equal to decreasing the τ value). This would make it possible to use the large response in a higher frequency range that is more relevant for

piezoelectric applications (in the example shown in **Figure 5**, $\tau = 0.13$ s, corresponding to a relaxation frequency of $f_{\text{relax}} = 1.2$ Hz). As discussed in the preceding paragraph, the anisotropy in the conductivity is also an important factor in tailoring the usable frequency range. It is thus tempting to consider designing a matrix with charged DWs, which can possess metallic-like conductivity, as recently demonstrated for BaTiO₃ [100]. In this case, the DW conductivity may exceed the bulk conductivity for impressive 8–10 orders of magnitude, perhaps providing an opportunity in designing piezoelectric properties.

5. Summary and conclusions

In this chapter, I have reviewed and discussed a case study on BFO ceramics explaining how the presence and dynamics of DWs showing enhanced electrical conductivity with respect to bulk conductivity can have a crucial effect on the macroscopic piezoelectric response of BFO. The mechanism goes far beyond the expected DW-defects pinning interactions, described in Section 2 of this chapter, and reflect itself in the nonlinear and hysteretic piezoelectric response of BFO. The unusual features of the response, i.e., a hard-to-soft transition induced by lowering the driving electric-field frequency and negative piezoelectric phase angle, can be explained by nonlinear piezoelectric Maxwell-Wagner effects. Simple analytical modeling confirms these macroscopic-response features and show that the key entities leading to such effects are conductive DWs. I could envision few points that can be drawn from the presented results. First, the data clearly show that local conductive paths (such as those along DWs) should be considered more seriously in addition to conventional bulk conductivity, which is mostly discussed in the literature on BFO. This is particularly important for the development of next-generation BFO-based piezoceramics for high-temperature applications as the local conductivity is what makes the response of BFO unstable in terms of driving field parameters (amplitude and frequency) and, most importantly, temperature. Second, the key problem related to M-W effects is that the response is boosted only at quasi-static driving conditions, as shown earlier by modeling of ceramic-polymer composites [45]. While certainly limited in the frequency range, it could be interesting to test anisotropic effects and piezoelectric enhancements in engineered matrices containing highly conducting charged DWs. It seems reasonable, though, that one should first validate the idea by modeling.

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material, without which complex mechanisms, such as those discussed in this chapter, cannot be seriously studied and thus explained.

Conflict of interest

The author of this work declares no conflict of interest of any kind.

Notes/thanks/other declarations

This chapter is dedicated to my wife Mihaela and my kids Aleks and Jan. Without them, my love (in the broadest possible physical and metaphysical sense) would have no meaning.

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References

- [1] Valasek J. Piezo-electric and allied phenomena in Rochelle salt. *Phys Rev* 1921; 17: 475–481.
- [2] Brennecka G, Sherbondy R, Schwartz R, et al. Ferroelectricity - A revolutionary century of discovery. *Am Ceram Soc Bull* 2020; 99: 24–30.
- [3] Scott JF, Paz De Araujo CA. Ferroelectric memories. *Science* (80-) 1989; 246: 1400–1405.
- [4] Damjanovic D. Hysteresis in piezoelectric and ferroelectric materials. In: Mayergoyz I, Bertotti G (eds) *The Science of Hysteresis*. Elsevier, 2006, pp. 337–465.
- [5] Hall DA. Nonlinearity in piezoelectric ceramics. *J Mater Sci* 2001; 36: 4575–4601.
- [6] Bassiri-Gharb N, Fujii I, Hong E, et al. Domain wall contributions to the properties of piezoelectric thin films. *J Electroceramics* 2007; 19: 47–65.
- [7] Cross LE. Ferroelectric ceramics: Tailoring properties for specific applications. In: Setter N, Colla EL (eds) *Ferroelectric ceramics*. Birkhäuser Basel, pp. 1–85.
- [8] Lambeck PV, Jonker GH. The nature of domain stabilization in ferroelectric perovskites. *J Phys Chem Solids* 1986; 47: 453–461.
- [9] Carl K, Hardtl KH. Electrical after-effects in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics. *Ferroelectrics* 1978; 17: 476–486.
- [10] Jonker GH. Nature of aging in ferroelectric ceramics. *J Am Ceram Soc* 1972; 55: 57–58.
- [11] Robels U, Arlt G. Domain wall clamping in ferroelectrics by orientation of defects. *J Appl Phys* 1993; 73: 3454–3460.
- [12] Marincel DM, Zhang H, Jesse S, et al. Domain wall motion across various grain boundaries in ferroelectric thin films. *J Am Ceram Soc* 2015; 98: 1848–1857.
- [13] Damjanovic D, Demartin M. Contribution of the irreversible displacement of domain walls to the piezoelectric effect in barium titanate and lead zirconate titanate ceramics. *J Phys Condens Matter* 1997; 9: 4943–4953.
- [14] García JE, Pérez R, Ochoa DA, et al. Evaluation of domain wall motion in lead zirconate titanate ceramics by nonlinear response measurements. *J Appl Phys* 2008; 103: 054108.
- [15] Eitel R, Randall CA. Octahedral tilt-suppression of ferroelectric domain wall dynamics and the associated piezoelectric activity in $\text{Pb}(\text{Zr,Ti})\text{O}_3$. *Phys Rev B* 2007; 75: 094106.
- [16] Lalitha K V., Riemer LM, Koruza J, et al. Hardening of electromechanical properties in piezoceramics using a composite approach. *Appl Phys Lett* 2017; 111: 022905.
- [17] Arlt G, Neumann H. Internal bias in ferroelectric ceramics: Origin and time dependence. *Ferroelectrics* 1988; 87: 109–120.
- [18] Ren X. Large electric-field-induced strain in ferroelectric crystals by point-defect-mediated reversible domain switching. *Nat Mater* 2004; 3: 91–94.
- [19] Rojac T, Bencan A, Drazic G, et al. Domain-wall conduction in ferroelectric BiFeO_3 controlled by accumulation of charged defects. *Nat Mater* 2017; 16: 322–327.

- [20] Mundy JA, Schaab J, Kumagai Y, et al. Functional electronic inversion layers at ferroelectric domain walls. *Nat Mater* 2017; 16: 622–627.
- [21] Campanini M, Gradauskaite E, Trassin M, et al. Imaging and quantification of charged domain walls in BiFeO₃. *Nanoscale* 2020; 12: 9186–9193.
- [22] Polking MJ. Deciphering the physics and chemistry of perovskites with transmission electron microscopy. *Nanoscale* 2016; 8: 6237–6248.
- [23] Zhang QM, Pan WY, Jang SJ, et al. Domain wall excitations and their contributions to the weak-signal response of doped lead zirconate titanate ceramics. *J Appl Phys* 1988; 64: 6445–6451.
- [24] Eitel RE, Shrout TR, Randall CA. Nonlinear contributions to the dielectric permittivity and converse piezoelectric coefficient in piezoelectric ceramics. *J Appl Phys* 2006; 99: 124110.
- [25] Damjanovic D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Reports Prog Phys* 1998; 61: 1267–1324.
- [26] Pramanick A, Damjanovic D, Daniels JE, et al. Origins of electro-mechanical coupling in polycrystalline ferroelectrics during subcoercive electrical loading. *J Am Ceram Soc* 2011; 94: 293–309.
- [27] Damjanovic D. Stress and frequency dependence of the direct piezoelectric effect in ferroelectric ceramics. *J Appl Phys* 1997; 82: 1788–1797.
- [28] Pramanick A, Damjanovic D, Nino JC, et al. Subcoercive cyclic electrical loading of lead zirconate titanate ceramics I: Nonlinearities and losses in the converse piezoelectric effect. *J Am Ceram Soc* 2009; 92: 2291–2299.
- [29] Riemer LM, Jin L, Uršič H, et al. Dielectric and electro-mechanic nonlinearities in perovskite oxide ferroelectrics, relaxors, and relaxor ferroelectrics. *J Appl Phys* 2021; 129: 054101.
- [30] Morozov M, Damjanovic D, Setter N. The nonlinearity and subswitching hysteresis in hard and soft PZT. *J Eur Ceram Soc* 2005; 25: 2483–2486.
- [31] Damjanovic D, Demartin M. The Rayleigh law in piezoelectric ceramics. *J Phys D Appl Phys* 1996; 29: 2057–2060.
- [32] Haugen AB, Morozov MI, Jones JL, et al. Rayleigh analysis of dielectric properties in textured K_{0.5}Na_{0.5}NbO₃ ceramics. *J Appl Phys* 2014; 116: 214101.
- [33] García JE, Guerra JDS, Arajo EB, et al. Domain wall contribution to dielectric and piezoelectric responses in 0.65Pb(Mg_{1/3}Nb_{2/3})O₃-0.35PbTiO₃ ferroelectric ceramics. *J Phys D Appl Phys* 2009; 42: 115421.
- [34] Otoničar M, Bradeško A, Fulanović L, et al. Connecting the multiscale structure with macroscopic response of relaxor ferroelectrics. *Adv Funct Mater* 2020; 30: 2006823.
- [35] Griggio F, Jesse S, Kumar A, et al. Substrate clamping effects on irreversible domain wall dynamics in lead zirconate titanate thin films. *Phys Rev Lett* 2012; 108: 157604.
- [36] Gharb NB, Trolier-McKinstry S, Damjanovic D. Piezoelectric nonlinearity in ferroelectric thin films. *J Appl Phys* 2006; 100: 044107.

- [37] Robert G, Damjanovic D, Setter N. Preisach distribution function approach to piezoelectric nonlinearity and hysteresis. *J Appl Phys* 2001; 90: 2459–2464.
- [38] García JE, Pérez R, Albareda A. Contribution of reversible processes to the non-linear dielectric response in hard lead zirconate titanate ceramics. *J Phys Condens Matter* 2005; 17: 7143–7150.
- [39] Catalan G, Seidel J, Ramesh R, et al. Domain wall nanoelectronics. *Rev Mod Phys* 2012; 84: 119–156.
- [40] Moreau JM, Michel C, Gerson R, et al. Ferroelectric BiFeO₃ x-ray and neutron diffraction study. *J Phys Chem Solids* 1971; 32: 1315–1320.
- [41] Selbach SM, Tybell T, Einarsrud MA, et al. Phase transitions, electrical conductivity and chemical stability of BiFeO₃ at high temperatures. *J Solid State Chem* 2010; 183: 1205–1208.
- [42] Stevenson T, Martin DG, Cowin PI, et al. Piezoelectric materials for high temperature transducers and actuators. *J Mater Sci Mater Electron* 2015; 26: 9256–9267.
- [43] Dyre JC. The random free-energy barrier model for ac conduction in disordered solids. *J Appl Phys* 1988; 64: 2456–2468.
- [44] Jonscher AK. *Dielectric relaxation in solids*. Chelsea Dielectric Press, 1983.
- [45] Turik A V., Chernobabov AI, Radchenko GS, et al. Giant piezoelectric and dielectric enhancement in disordered heterogeneous systems. *Phys Solid State* 2004; 46: 2213–2216.
- [46] Ueda H, Fukada E, Karasz FE. Piezoelectricity in three-phase systems: Effect of the boundary phase. *J Appl Phys* 1986; 60: 2672–2677.
- [47] Furukawa T, Ishida K, Fukada E. Piezoelectric properties in the composite systems of polymers and PZT ceramics. *J Appl Phys* 1979; 50: 4904–4912.
- [48] Damjanovic D, Demartin Maeder M, Duran Martin P, et al. Maxwell-Wagner piezoelectric relaxation in ferroelectric heterostructures. *J Appl Phys* 2001; 90: 5708–5712.
- [49] Nguyen BH, Zhuang X, Rabczuk T. Numerical model for the characterization of Maxwell-Wagner relaxation in piezoelectric and flexoelectric composite material. *Comput Struct* 2018; 208: 75–91.
- [50] Lunkenheimer P, Bobnar V, Bobnar V, et al. Origin of apparent colossal dielectric constants. *Phys Rev B* 2002; 66: 052105.
- [51] Turik A V., Radchenko GS. Maxwell-Wagner relaxation in piezoactive media. *J Phys D Appl Phys* 2002; 35: 1188–1192.
- [52] Turik A V., Radchenko GS. Maxwell-Wagner relaxation of elastic constants of layered polar dielectrics. *Phys Solid State* 2003; 45: 1060–1064.
- [53] Hamano K, Yamaguchi T. Piezoelectric relaxation in ferroelectrics and polymers. *Ferroelectrics* 1982; 42: 23–33.
- [54] Jones JL, Aksel E, Tutuncu G, et al. Domain wall and interphase boundary motion in a two-phase morphotropic phase boundary ferroelectric: Frequency dispersion and contribution to piezoelectric and dielectric properties. *Phys Rev B* 2012; 86: 024104.
- [55] Gaunt P. Ferromagnetic domain wall pinning by a random array of inhomogeneities. *Philos Mag B* 1983; 48: 261–276.

- [56] Lines ME, Glass MA. *Principles and applications of ferroelectric and related materials*. Clarendon Press, 1977.
- [57] Wade RH. The determination of domain wall thickness in ferromagnetic films by electron microscopy. *Proc Phys Soc* 1962; 79: 1237–1244.
- [58] Shilo D, Ravichandran G, Bhattacharya K. Investigation of twin-wall structure at the nanometre scale using atomic force microscopy. *Nat Mater* 2004; 3: 453–457.
- [59] Blank H, Amelinckx S. Direct observation of ferroelectric domains in barium titanate by means of the electron microscope. *Appl Phys Lett* 1963; 2: 140–142.
- [60] Morozov MI, Damjanovic D. Hardening-softening transition in Fe-doped $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ceramics and evolution of the third harmonic of the polarization response. *J Appl Phys* 2008; 104: 034107.
- [61] Rojac T, Kosec M, Budic B, et al. Strong ferroelectric domain-wall pinning in BiFeO_3 ceramics. *J Appl Phys* 2010; 108: 074107.
- [62] Rojac T, Drnovsek S, Bencan A, et al. Role of charged defects on the electrical and electromechanical properties of rhombohedral $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with oxygen octahedra tilts. *Phys Rev B* 2016; 93: 014102.
- [63] Genenko YA, Glaum J, Hoffmann MJ, et al. Mechanisms of aging and fatigue in ferroelectrics. *Mater Sci Eng B* 2015; 192: 52–82.
- [64] Erhart P, Träskelin P, Albe K. Formation and switching of defect dipoles in acceptor-doped lead titanate: A kinetic model based on first-principles calculations. *Phys Rev B* 2013; 88: 024107.
- [65] Eichel RA. Structural and dynamic properties of oxygen vacancies in perovskite oxides - Analysis of defect chemistry by modern multi-frequency and pulsed EPR techniques. *Phys Chem Chem Phys* 2011; 13: 368–384.
- [66] Zhang L, Erdem E, Ren X, et al. Reorientation of $(\text{Mn}_{\text{Ti}} - \text{V}_{\text{O}}^{\bullet\bullet}) \times$ defect dipoles in acceptor-modified BaTiO_3 single crystals: An electron paramagnetic resonance study. *Appl Phys Lett* 2008; 93: 202901.
- [67] Warren WL, Vanheusden K, Dimos D, et al. Oxygen vacancy motion in perovskite oxides. *Journal of the American Ceramic Society* 1996; 79: 536–538.
- [68] Eichel RA, Erhart P, Träskelin P, et al. Defect-dipole formation in copper-doped PbTiO_3 ferroelectrics. *Phys Rev Lett* 2008; 100: 095504.
- [69] Meštrić H, Eichel RA, Dinse KP, et al. Iron-oxygen vacancy defect association in polycrystalline iron-modified PbZrO_3 antiferroelectrics: Multifrequency electron paramagnetic resonance and Newman superposition model analysis. *Phys Rev B* 2006; 73: 184105.
- [70] Eichel RA, Erünel E, Jakes P, et al. Interactions of defect complexes and domain walls in CuO-doped ferroelectric $(\text{K},\text{Na})\text{NbO}_3$. *Appl Phys Lett* 2013; 102: 242908.
- [71] Aksel E, Erdem E, Jakes P, et al. Defect structure and materials ‘hardening’ in Fe_2O_3 -doped $[\text{Bi}_{0.5}\text{Na}_{0.5}]\text{TiO}_3$ ferroelectrics. *Appl Phys Lett* 2010; 97: 012903.
- [72] Postnikov VS, Pavlov VS, Turkov SK. Internal friction in ferroelectrics due to interaction of domain boundaries and point defects. *J Phys Chem Solids* 1970; 31: 1785–1791.

- [73] Warren WL, Dimos D, Tuttle BA, et al. Electronic domain pinning in Pb(Zr, Ti)O₃ thin films and its role in fatigue. *Appl Phys Lett* 1994; 65: 1018–1020.
- [74] Zhang L, Ren X. Aging behavior in single-domain Mn-doped BaTiO₃ crystals: Implication for a unified microscopic explanation of ferroelectric aging. *Phys Rev B* 2006; 73: 094121.
- [75] Bencan A, Drazic G, Ursic H, et al. Domain-wall pinning and defect ordering in BiFeO₃ probed on the atomic and nanoscale. *Nat Commun* 2020; 11: 1762.
- [76] Genenko YA, Lupascu DC. Drift of charged defects in local fields as aging mechanism in ferroelectrics. *Phys Rev B* 2007; 75: 184107.
- [77] Genenko YA, Glaum J, Hirsch O, et al. Aging of poled ferroelectric ceramics due to relaxation of random depolarization fields by space-charge accumulation near grain boundaries. *Phys Rev B* 2009; 80: 224109.
- [78] Chandrasekaran A, Damjanovic D, Setter N, et al. Defect ordering and defect-domain-wall interactions in PbTiO₃: A first-principles study. *Phys Rev B* 2013; 88: 214116.
- [79] Rojac T, Ursic H, Bencan A, et al. Mobile domain walls as a bridge between nanoscale conductivity and macroscopic electromechanical response. *Adv Funct Mater* 2015; 25: 2099–2108.
- [80] Makarovic M, Kanas N, Zorko A, et al. Tailoring the electrical conductivity and hardening in BiFeO₃ ceramics. *J Eur Ceram Soc* 2020; 40: 5483–5493.
- [81] Eichel RA, Meštrić H, Kungl H, et al. Multifrequency electron paramagnetic resonance analysis of polycrystalline gadolinium-doped PbTiO₃ - Charge compensation and site of incorporation. *Appl Phys Lett* 2006; 88: 122506.
- [82] Bernardo MS, Jardiel T, Peiteado M, et al. Intrinsic compositional inhomogeneities in bulk Ti-doped BiFeO₃: Microstructure development and multiferroic properties. *Chem Mater* 2013; 25: 1533–1541.
- [83] Slouka C, Kainz T, Navickas E, et al. The effect of acceptor and donor doping on oxygen vacancy concentrations in lead zirconate titanate (PZT). *Materials (Basel)* 2016; 9: 945.
- [84] Liu L, Rojac T, Damjanovic D, et al. Frequency-dependent decoupling of domain-wall motion and lattice strain in bismuth ferrite. *Nat Commun* 2018; 9: 4928.
- [85] Damjanovic D. Logarithmic frequency dependence of the piezoelectric effect due to pinning of ferroelectric-ferroelastic domain walls. *Phys Rev B* 1997; 55: R649–R652.
- [86] Georgiou V, Veksler D, Campbell JP, et al. Ferroelectricity in Polar Polymer-Based FETs: A Hysteresis Analysis. *Adv Funct Mater* 2018; 28: 1705250.
- [87] Hayashi T, Yoshihara M, Ohmi SI, et al. Electrical properties of ferroelectric BaMgF₄ films grown on GaAs substrates using AlGaAs buffer layer. *Appl Surf Sci* 1997; 117–118: 418–422.
- [88] Moulson AJ, Herbert JM. *Electroceramics*. Wiley & Sons, 2003.
- [89] Uchino K, Hirose S. Loss mechanisms in piezoelectrics: How to measure different losses separately. *IEEE Trans Ultrason Ferroelectr Freq Control* 2001; 48: 307–321.
- [90] Holland R. Representation of dielectric, elastic, and piezoelectric

losses by complex coefficients. *IEEE Trans Sonics Ultrason* 1967; 14: 18–20.

[91] Rojac T, Bencan A, Drazic G, et al. Piezoelectric nonlinearity and frequency dispersion of the direct piezoelectric response of BiFeO₃ ceramics. *J Appl Phys* 2012; 112: 064114.

[92] Seidel J, Martin LW, He Q, et al. Conduction at domain walls in oxide multiferroics. *Nat Mater* 2009; 8: 229–234.

[93] Condurache O, Dražić G, Sakamoto N, et al. Atomically resolved structure of step-like uncharged and charged domain walls in polycrystalline BiFeO₃. *J Appl Phys* 2021; 129: 054102.

[94] Makarovic M, Bayir MÇ, Ursic H, et al. Domain wall conductivity as the origin of enhanced domain wall dynamics in polycrystalline BiFeO₃. *J Appl Phys* 2020; 128: 064104.

[95] Rojac T, Makarovic M, Walker J, et al. Piezoelectric response of BiFeO₃ ceramics at elevated temperatures. *Appl Phys Lett* 2016; 109: 042904.

[96] Padurariu L, Curecheriu LP, Mitoseriu L. Nonlinear dielectric properties of paraelectric-dielectric composites described by a 3D Finite Element Method based on Landau-Devonshire theory. *Acta Mater* 2016; 103: 724–734.

[97] Daniel L, Hubert O, Billardon R. Homogenisation of magneto-elastic behaviour: From the grain to the macro scale. *Comput Appl Math* 2004; 23: 285–308.

[98] Daniel L, Rekik M, Hubert O. A multiscale model for magneto-elastic behaviour including hysteresis effects. *Arch Appl Mech* 2014; 84: 1307–1323.

[99] Labusch M, Keip MA, Shvartsman V V., et al. On the influence of ferroelectric polarization states on the magneto-electric coupling in two-phase composites. *Tech Mech* 2016; 36: 73–87.

[100] Sluka T, Tagantsev AK, Bednyakov P, et al. Free-electron gas at charged domain walls in insulating BaTiO₃. *Nat Commun* 2013; 4: 1808.