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Strain-modulated piezoelectric and electrostrictive nonlinearity in ferroelectric thin films without active ferroelastic domain walls

Nazanin Bassiri-Gharb,[1,a)] Susan Trolier-McKinstry,[2] and Dragan Damjanovic[3]

[1]*G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*
[2]*Material Science and Engineering Department, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*Ceramics Laboratory, Swiss Federal Institute of Technology-EPFL, 1015 Lausanne, Switzerland*

In contrast to usual assumptions, it is shown that even when ferroelastic domain walls are inactive or absent, the motion of ferroelectrically active interfaces in ferroelectric materials contributes, at subcoercive electric fields, not only to the polarization but also to the strain. Specifically, in polycrystalline samples, strain coupling between adjacent grains, or mediated through the substrate in thin films, influences both the dielectric and piezoelectric response. The model developed explains the unexpected observation of piezoelectric nonlinearity in films even in cases in which the domain variants' projections are equivalent along the direction of the external driving field. © *2011 American Institute of Physics*. [doi:10.1063/1.3665410]

I. INTRODUCTION

Ferroelectric thin films with the perovskite structure have garnered considerable attention for piezoelectric applications as sensors and actuators in nano- and micro-electromechanical systems (NEMS/MEMS), because of their very high piezoelectric response. The dielectric and piezoelectric response in ferroelectric materials is a result of intrinsic (lattice) contributions, but also of extrinsic contributions, mainly from the motion of internal interfaces such as domain walls and phase boundaries.[1] Although low-field dielectric constants or piezoelectric coefficients are often used to characterize a ferroelectric material, it has been shown that the dielectric and piezoelectric coefficients are field dependent well below the coercive field. The weak-to-moderate field dielectric and piezoelectric nonlinear response of disordered ferroelectric materials can be approximated, in the simplest case, by the Rayleigh law.[2]

The Rayleigh law describes the nonlinear and hysteretic response of the dielectric polarization and strain as a function of ac field amplitude; the nonlinearity of the response is such that it produces a linear field dependence of the dielectric permittivity and piezoelectric coefficients as shown in Eqs. (1) and (2):

$$P(E_{ac}) = (\varepsilon_0 \chi_{init} + \alpha_\varepsilon E_0)E_{ac} \pm \frac{\alpha_\varepsilon}{2}\left(E_0^2 - E_{ac}^2\right) \quad \text{and}$$
$$\varepsilon_0 \chi(E_0) = \varepsilon_0 \chi_{init} + \alpha_\varepsilon E_0, \qquad (1)$$

and

$$S(E_{ac}) = (d_{init} + \alpha_d E_0)E_{ac} \pm \frac{\alpha_d}{2}\left(E_0^2 - E_{ac}^2\right) \quad \text{and}$$
$$d(E_0) = d_{init} + \alpha_d E_0, \qquad (2)$$

where P is the dielectric polarization induced by application of the electric field $E_{ac} = E_0 \sin(\omega t)$; S is the induced strain; χ_{init} and d_{init} are the reversible Rayleigh parameters for dielectric and piezoelectric response, respectively; α_ε and α_d are the irreversible Rayleigh parameters; ε_0 is the dielectric constant of free space, χ the dielectric susceptibility, and d the piezoelectric coefficient. The sign $\pm$ for the hysteresis expression denotes ascending (-) and descending (+) field cycles. The Rayleigh law is the simplest case demonstrating the connection between nonlinearity and hysteresis and is valid when motion of the internal interfaces occurs in a random potential energy landscape defined by the pinning centers.[1,2] The reversible Rayleigh parameters represent the sum of the intrinsic lattice contributions and the reversible motion of the interfaces. The irreversible Rayleigh parameters, as implied, are mostly a result of the irreversible, hysteretic motion of the internal interfaces. Equations (1) and (2) can be easily expanded to include the higher-order terms needed, for example, to describe non-random energy profiles.[3,4]

Another characteristic of ideal Rayleigh behavior is the appearance of only odd order harmonics as seen by developing the $P(E)$ and $S(E)$ equations into a Fourier series, shown below for $S(E)$:

$$S(E_{ac}) = (d_{init} + \alpha_d E_0)E_0 \sin(\omega t) + \frac{4}{3\pi}\alpha_d E_0^2 \cos(\omega t)$$
$$+ \frac{4}{15\pi}\alpha_d E_0^2 \cos(3\omega t) - \frac{4}{105\pi}\alpha_d E_0^2 \cos(\omega t) + \dots . \qquad (3)$$

Equation (3) directly correlates strain and electric field and, as confirmed by experimental studies,[5–9] holds for the contributions of ferroelastically active interfaces, such as 90° domain walls. It is not clear *a priori* that 180° domain walls, which separate domains with the same spontaneous strain, should contribute to the first-order piezoelectric response. And while a number of groups have reported on the ferroelectric (180°)

a)Electronic mail: nazanin.bassiri@gatech.edu.

domain wall contribution to the piezoelectric coefficient versus dc electric field hysteresis,[10–14] these studies have considered only high static (dc) electric fields (above global switching), which affect both the lattice response and volume fraction of domain variants. The field dependence of strain as expressed by the Rayleigh law in Eq. (3) refers instead to the low and intermediate dynamic (ac) fields and small motion of domain walls (bending and depinning) of interest for sensor and actuator devices rather than nucleation, growth, and large-scale displacement, as in global switching relevant for example for memory applications.

Although Rayleigh-like behavior has been reported for a wide range of ferroelectric single crystals, ceramics, and thin films, it fails to describe two major experimental observations. In systems where motion of non-180° domain walls is heavily clamped (such as ferroelectric thin films) and/or not available (for example, if the polarization projection on the field direction is the same for all domain variants, such as in domain-engineered (111)-oriented $Pb(Zr,Ti)O_3$ (PZT) films of tetragonal composition): (1) a Rayleigh law field dependence of strain has been nevertheless observed, and (2) a second-order harmonic in the strain dependence on applied electric field is evident, which is not allowed by Eq. (3).[6,15] Examples of such behavior are shown in Fig. (1) for a (111)-oriented tetragonal PZT film. We have previously shown in a simplified mathematical model[15] that a Rayleigh-like behavior of strain due to internal interfaces can be modified in terms of phase lag and amplitude dependence of the reversible term to account for these experimental observations. However, a formal physical description of the origin of the experimentally observed behavior has been, to date, lacking. As Rayleigh behavior is ubiquitous,[16,17] these results are relevant not only for purely ferroelectric but also for ferroelastic, ferromagnetic, and multiferroic materials.

II. MODELING AND DISCUSSION

To model such behavior, one may consider a one-dimensional ferroelectric crystal and assume that no external
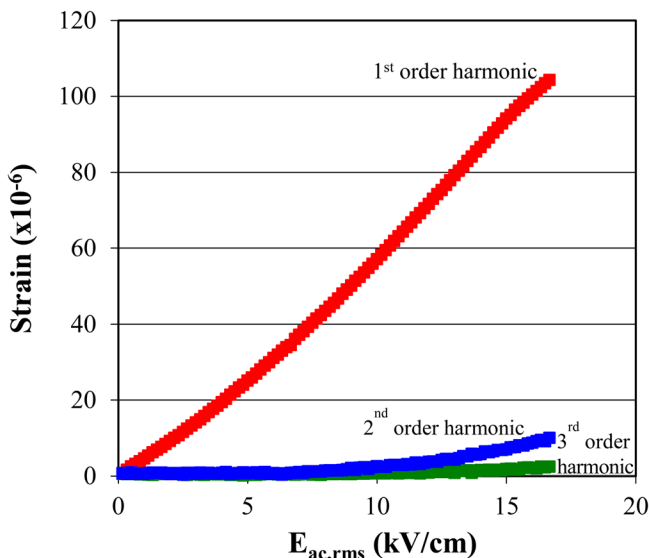
stress is applied. If the crystal is in a single domain state, the strain S as a result of the electrical polarization P is expressed as:

$$S = QP^2, \qquad (4)$$

where Q is the electrostriction coefficient, and P is the sum of the spontaneous polarization P_s and the electric field-induced polarization $P(E_{ac})$. Hence, the total strain is represented by:[18]

$$S = QP_s^2 + 2QP_sP(E_{ac}) + QP(E_{ac})^2, \qquad (5)$$

where the three terms on the right side of the equation represent the spontaneous strain, piezoelectric strain, and electrostrictive strain, respectively. If the hypothetical crystal is in a partially poled state with only ferroelectric, 180° domain walls present (Fig. 2), the total strain may be calculated as the volume weighted sum of the strain contribution from each domain orientation:[12]

$$S_{tot} = v_+S_+ + v_-S_-, \qquad (6)$$

where v_+ and v_- are the volume fractions of the crystal with positive ("upward" P_+) and negative ("downward" P_-) polarization directions, respectively, and $S_+ = QP_+^2$ and $S_- = QP_-^2$.

Under an applied electric field, $E_{ac} = E_0\sin(\omega t)$, the field-induced polarization of lattice, $\varepsilon_0\chi_{lat}E_{ac}$ will appear in both domains. Note that we assume here that the magnitude of the spontaneous polarization and dielectric permittivity in oppositely oriented domains are equal. We shall come back to this assumption later on. Hence, Eq. (6) becomes:

$$S_{tot} = v_+Q(P_s + \varepsilon_0\chi_{lat}E_{ac})^2 + v_-Q(-P_s + \varepsilon_0\chi_{lat}E_{ac})^2. \quad (7)$$

To simplify the expression, we can use an effective volume $v_{eff} = 1 - 2v_- = 2v_+ - 1$, which describes polarization that is not "canceled" by the opposite polarizations of the two domains, Fig. 2. Equation (7) then can be rewritten as:

$$S_{tot} = Q\left[P_S^2 + 2v_{eff}P_s\varepsilon_0\chi_{lat}E_{ac} + (\varepsilon_0\chi_{lat}E_{ac})^2\right]. \qquad (8)$$

FIG. 1. (Color online) Field-dependent strain response of a 1.2-μm-thick, (111)-oriented $PbZr_{0.45}Ti_{0.55}O_3$ film at 220 Hz.
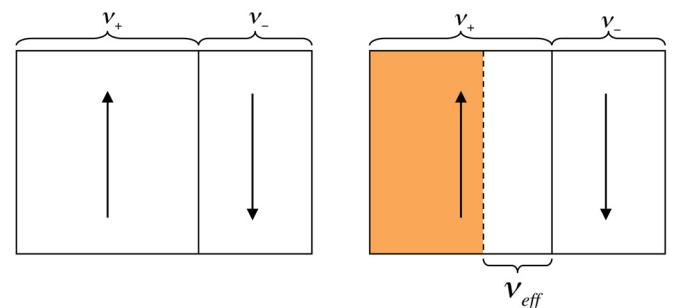

FIG. 2. (Color online) Schematic representation of a ferroelectric crystal with a single 180° domain wall present. ν_+ and ν_- represent the volume fraction of material with upward and downward polarization, respectively. ν_{eff} is the effective volume of the sample exhibiting polarization that is not canceled out by the opposite polarization of the two domains.

As v_{eff} must be field dependent (reflecting the motion of the domain walls), its variation with field represents also the modulation of the effective polarization, $v_{eff}(E_{ac})P_S$, which is responsible for the net piezoelectric effect (second term in Eq. (8)). Variation of the effective volume with field can be expressed as $v_{eff}(E_{ac}) = v_{eff}^0 + \Delta v_{eff}(E_{ac})$, where v_{eff}^0 is the initial effective volume and $\Delta v_{eff}(E_{ac})$ is its field modulation. Note that $v_{eff}^0 = \pm 1$ for a monodomain crystal and 0 for equal partitioning of "up" and "down" domains. In a system where the domain wall motion by the field consists of reversible and irreversible components and is governed by the Rayleigh law, it is possible to write:

$$v_{eff}(E_{ac}) = v_{eff}^0 + \left(v_{rev}^* + \alpha_v E_0\right)E_{ac} \pm \frac{\alpha_v}{2}\left(E_0^2 - E_{ac}^2\right), \quad (9)$$

where v_{rev}^* is the reversible change of Δv_{eff} per unit field and α_v describes the irreversible change of Δv_{eff}. Hence, $v_{eff}P_s$ in Eq. (8) can be rewritten as:

$$v_{eff}(E_{ac})P_s = v_{eff}^0 P_s + (\varepsilon_0\chi_{rev} + \alpha_\varepsilon E_0)E_{ac} \pm \frac{\alpha_\varepsilon}{2}\left(E_0^2 - E_{ac}^2\right). \quad (10)$$

Equation (10) can be used in Eq. (8), which, after expansion into Fourier series, gives:

$$S_{tot}(E_{ac}) = \frac{1}{2}\left\{2QP_S^2 + \varepsilon_0\chi_{lat}QE_0^2[2\alpha_\varepsilon E_0 + \varepsilon_0(\chi_{lat} + 2\chi_{rev})]\right\}$$

$$+ 2QP_S\varepsilon_0\chi_{lat}v_{eff}^0 E_0 \sin(\omega t) - \left\{\frac{1}{2}\varepsilon_0\chi_{lat}QE_0^2[2\alpha_\varepsilon E_0\right.$$

$$+\varepsilon_0(\chi_{lat} + 2\chi_{rev})]\cos(2\omega t) + \alpha\varepsilon_0\chi_{lat}QE_0^3$$

$$\left[-\frac{16}{15\pi}\sin(2\omega t) - \frac{32}{105\pi}sin(4\omega t)\right.$$

$$\left.\left.+\frac{16}{315\pi}\sin(6\omega t)...\right]\right\} \quad (11)$$

where the first, second, and the third terms represent the modified spontaneous, piezoelectric, and electrostrictive components of strain, respectively. Equation (11) shows clearly that the 180° domain wall motion may contribute to the strain mainly through a field-dependent electrostrictive-like response (second- and higher-order even harmonics). Thus, this approach explains the appearance of the second harmonic observed in films with only 180° domain walls, as well as previously observed weak-signal, field dependence of electrostrictive coefficients.[19] It is important also to note that the electrostrictive-like response of 180° domain walls has its origin in the second, essentially piezoelectric term of Eq. (8). Interestingly, Caspari and Mertz[18] have made a similar comment in their study of "butterfly" strain loops involving global 180° switching. Those loops also have an origin in the piezoelectric effect, whereas the quadratic appearance originates in the switching of polarization by 180°.

This approach, however, fails to account for the observed field dependence of the piezoelectric coefficient. The effective piezoelectric coefficient in Eq. (11), defined by the derivative with respect to the field of the first harmonic term,

$\partial\left[2QP_S\varepsilon_0\chi_{lat}v_{eff}^0 E_0 \sin(\omega t)\right]/\partial E_{ac}$, is equal to $2QP_S\varepsilon_0\chi_{lat}v_{eff}^0$. Therefore, a different approach is needed to explain the observed piezoelectric nonlinearity, $d = d(E_0)$.

To find a source for the observed piezoelectric nonlinearity, we note the assumption used in derivation of Eqs. (7)–(11) that spontaneous polarization and dielectric permittivity in oppositely oriented domains have equal magnitudes $|P_S|$ and χ_{lat}. As seen from Landau theory, this is strictly valid only in the absence of external electric fields and stresses and when domain walls are parallel to the polarization within the domains.[20–22] However, for a partially poled film, the amount of mechanical clamping on oppositely oriented domains might be different because of the overall net polarization. Similarly, in the case of thin films, the difference in response can be mediated through the overall substrate bending caused by the net polarization, i.e., substrate bending in one direction might hinder or mechanically clamp the deformation in the ill-oriented domains.

Additional polarization of the lattice by electric field is accounted for by introducing the term $\varepsilon_0\chi_{lat}E_{ac}$. As each domain is piezoelectric, application of an external electric field will cause tensile stress in one domain and compressive in the adjacent domain. If these stresses are not homogeneous, this will necessarily lead to differences in polarization, permittivities, and strains in the two domains.[13,23] We first explore how this symmetry breaking by external fields may affect strain response of the material and discuss its origins later.

Let us consider again Eq. (7), but now take into account that the spontaneous polarization and permittivity in the "up" and "down" domains are no longer equal. Equation (7) now becomes:

$$S_{tot}(E_{ac}) = v_+ Q(P_S + \varepsilon_0\chi_{lat}E_{ac})^2 + v_- Q\left(-P_S' + \varepsilon_0\chi_{lat}'E_{ac}\right)^2, \quad (12)$$

where the prime symbol is used to distinguish polarization and susceptibility in oppositely oriented domains. Assuming that in the first approximation $P_S' = P_S + \Delta P_S$ and $\chi_{lat}' = \chi_{lat} + \Delta\chi_{lat}$, Eq. (12) becomes:

$$S_{tot}(E_{ac}) = Q\left[P_S^2 + \Delta P_S P_S - v_{eff}\Delta P_S P_S + \frac{1 - v_{eff}}{2}(\Delta P_S)^2\right]$$

$$+ 2\varepsilon_0 QE_{ac}\left[P_S\chi_{lat}v_{eff} - \frac{1 - v_{eff}}{2}(P_S\Delta\chi_{lat} + \Delta P_S\chi_{lat}\right.$$

$$+ \Delta P_S\Delta\chi_{lat})\right] + \varepsilon_0^2 QE_{ac}^2[\chi_{lat}^2 + \Delta\chi_{lat}\chi_{lat}$$

$$\left. - v_{eff}\Delta\chi_{lat}\chi_{lat} + \frac{1 - v_{eff}}{2}(\Delta\chi_{lat})^2\right] \quad (13)$$

Let us first analyze Eq. (13) and see which terms may give the experimentally observed Rayleigh-like response. In addition to Δv_{eff} (see Eq. (9)), ΔP_S and $\Delta\chi_{lat}$ may also be expressed in the form of Rayleigh equations (Eq. (1)). The reasons for this will be discussed below. Inspection of all terms in Eq. (13) shows that only the term $\Delta P_S P_S$ may give Rayleigh behavior as observed experimentally and as described by Eq. (2). Other terms give either even order

harmonics or dependence of the piezoelectric coefficient on E_0 with power >1.

We turn now to origins and reasons for the proposed Rayleigh-like dependence of ΔP_S and $\Delta \chi_{lat}$. Recent structural studies by high energy x-ray diffraction of piezoelectric nonlinearity in Pb(Zr,Ti)O$_3$ ceramics[9] have shown that the piezoelectric strain nonlinearity in tetragonal ceramics manifests itself on at least three levels: (1) macroscopic strain, detected by strain measurements on a sample with a volume above some critical value;[24] (2) motion of domain walls, detected by subcoercive field switching of (0 0 *l*)/ (*h* 0 0) peaks; and (3) lattice strain, detected by subcoercive field shifts of (*h k l*) peaks. This study demonstrates that all three nonlinear contributions can be described by the Rayleigh law. Of interest here is the nonlinear, Rayleigh-like field dependence of the lattice strain. In ceramics, its origin is in intergranular coupling, where deformation of one grain caused by electric-field-induced domain wall motion is transferred via elastic coupling into mechanical deformation of the adjacent grains. The Rayleigh-like mechanical deformation of a neighboring grain thus happens even if that grain itself has no ferroelastically active domain walls. Based on this experimental fact, we propose that in thin films without ferroelastically active domain walls, the adjacent regions of the opposite polarity interact in a Rayleigh-like fashion through piezoelectric coupling modifying spontaneous strain, polarization, and dielectric susceptibility and thus breaking the symmetry between the domains. In ceramics, this sort of intergrain coupling is responsible for considerable lattice Rayleigh-like nonlinearity. It needs to be mentioned here that the mechanical effect of a moving ferroelastic domain wall on its environment is larger than what can be expected of piezoelectric strain caused by motion of ferroelectric domain walls. However, the mechanical effects of displacement of 180° domain walls do not have to be confined to the piezoelectric strain difference between two oppositely oriented domains (e.g., it can in films cause substrate bending), and so the motion of 180° domain walls can also exhibit large lattice strain.

In support of this coupling between strain and polarization via Rayleigh-like processes, we note the experimental fact that when the modulation of the polarization response in a ferroelectric material follows a Rayleigh law, the strain modulation most often follows the same behavior. Such is the case even in systems without contributions to strain from ferroelastic domain wall motion.[6,15,24] For example, it has been shown that the decay with frequency of the Rayleigh coefficients follows a similar trend for both piezoelectric and dielectric response in (001)$_C$-oriented rhombohedral lead-ytterbium-niobate–lead-titanate (PYbN-PT) thin films of near morphotropic phase-boundary composition.[6]

Finally, recent work by Catalan *et al.*[23] on lead-titanate films has shown that strain mismatch between substrate and film and accommodation of the strain within the film may lead to a large variation of the strain (and, therefore, polarization) within one domain, over the distance of only a few tens of nanometers. The boundary conditions and domain structure in films investigated by Catalan *et al.* and ours are different, and we use their result as an illustration that strain and polarization may significantly vary over small distances even within a single domain.

Going back to Eq. (13), and assuming that ΔP_S can be described by Eq. (1), one obtains:

$$S_{tot}(E_{ac}) = QP_S^2 + Q\left[(\varepsilon_0 \chi_{init} + \alpha_\varepsilon E_0)E_{ac} \pm \frac{\alpha_\varepsilon}{2}\left(E_0^2 - E_{ac}^2\right)\right]P_S + \text{other terms}. \tag{14}$$

Developing (14) into a Fourier series yields the field dependence of the piezoelectric coefficient: $d(E_0) = \partial S_{tot}(E_{ac})/\partial E_{ac} = d_{init} + \alpha_d E_0$, where $d_{init} = \varepsilon_0 \chi_{init} Q P_S$ and $\alpha_d = \alpha_\varepsilon Q P_S$.

Equation (14) gives explicitly only the spontaneous strain and piezoelectric term of Eq. (13). The rest of the terms depend on higher-order harmonics, both even and odd, as well as on even and odd powers of E_0. Thus, Eq. (14) describes all experimentally observed features of the strain in films with only ferroelectric domain walls: linear dependence of strain on electric field amplitude, and second and third harmonics in strain. The equation also includes higher-order terms that describe the often-observed departure from Rayleigh relations at higher fields.

Equation (14) should be valid for all cases where the macroscopic polarization is modulated through the interaction with its environment. As well as strain-coupling, this can be, for example, the case of a domain wall interaction at a distance (or cluster motion) as recently reported by Bintachitt *et al.*[24] As observed in their work, polarization modulation can be an avalanche effect, where the "trigger" of motion by one or more domain walls can lead to motion of additional domain walls. The experimental observations suggesting the avalanche model indicate modulation of the strain by polarization coupling between adjacent ferroelectric domains/grains. This is a substantially different mechanism than a simple, field-induced, direct modulation of domain volumes (and corresponding motion of domain walls). It is also more complex than a polarization modulation because of strain coupling with surrounding grains/domains. However, the central concept is somewhat similar to what was reported by Comyn and Bell,[8] where any motion of 180° domain walls will lead to motion of 90° domain walls and vice versa: in fact, any change in the overall polarization, regardless if a result of applied electric or strain fields, will lead to a redistribution of 180° domain walls, without changing the total volume of 180° domains.

The model here presented is also valid for a system where all domains have degenerate polarization components along the probed axis. Such is the case of (001)-oriented rhombohedral, or (111)-oriented tetragonal perovskite-ferroelectric thin films. In such compositions and orientations, nonlinear and hysteretic motion of either ferroelectrically or ferroelastically active interfaces that result in a Rayleigh-like dielectric nonlinearity can lead to nonlinear strain. It is noteworthy that this piezoelectric strain nonlinearity, will add to the field-dependent electrostrictive response that will be always present (through Eq. (11)) in systems with internal interfaces that show Rayleigh-like behavior.

III. SUMMARY AND CONCLUSIONS

In conclusion, we demonstrate that any nonlinear and hysteretic motion of ferroelectrically active interfaces (such as $180°$ domain walls) that is manifested in a Rayleigh-like behavior of the dielectric polarization, may also lead to a Rayleigh-like nonlinear piezoelectric response. Furthermore, the analysis shows that electrostrictive response of the ferroelectric material is also nonlinear and field dependent. This mechanism is expected to be particularly important in ferroelectric thin films, where the motion of the ferroelastic domain walls is usually limited for submicron thickness, and in ferroelectric materials where ferroelastic domain walls are not allowed by the crystal system.

[1]D. Damjanovic and M. Demartin, J. Phys. D: Appl. Phys. **29**(7), 2057 (1996).

[2]D. A. Hall, J. Mater. Sci. **36**(19), 4575 (2001).

[3]L. Neel, Cah. Phys. **12**, 1 (1942).

[4]J. Ricote, M. Algueró, and D. Chateigner, "Tailoring of the Elastic Properties by Texture Control in Ferroelectric Thin Films for MEMS," Mater. Sci. Forum, vol. **426–432**, pp. 3433–3438, (2003).

[5]D. V. Taylor and D. Damjanovic, Appl. Phys. Lett. **76**(12), 1615 (2000).

[6]N. B. Gharb, S. Trolier-McKinstry, and D. Damjanovic, J. Appl. Phys. **100**(4), 044107 (2006).

[7]R. E. Eitel, T. R. Shrout, and C. A. Randall, J. Appl. Phys. **99**(12), 124110 (2006).

[8]T. P. Comyn and A. J. Bell, in "The 16th IEEE International Symposium on the Applications of Ferroelectrics," ISAF, Nara-city, Japan (2007).

[9]A. Pramanick, D. Damjanovic, J. E. Daniels, J. C. Nino, and J. L. Jones, J. Am. Ceram. Soc. **94**, 293 (2011).

[10]P. Gerber, C. Kugeler, U. Bottger, and R. Waser, J. Appl. Phys. **95**(9), 4976 (2004).

[11]C. Ding-Yuan and J. D. Phillips, J. Electroceram. **17**(2–4), 613 (2006).

[12]A. K. Tagantsev, P. Muralt, and J. Fousek, Mater. Res. Soc. Symp. Proc. **784**, 517 (2003).

[13]L. Chen and A. L. Roytburd, Appl. Phys. Lett. **90**, 102903 (2007).

[14]P. Mokry, Y. L. Wang, A. K. Tagantsev, D. Damjanovic, I. Stolichnov, and N. Setter, Phys. Rev. B **79**(5), 054104 (2009).

[15]S. Trolier-McKinstry, N. B. Gharb, and D. Damjanovic, Appl. Phys. Lett. **88**(20), 202901 (2006).

[16]F. Colaiori, A. Gabrielli, and S. Zapperi, Phys. Rev. B **65**, 224404 (2002).

[17]M. Alguero, B. Jimenez, and L. Pardo, Appl. Phys. Lett. **83**, 2641 (2003).

[18]P. Delobelle, E. Fribourg-Blanc, and D. Remiens, Thin Solid Films **515**, 1385 (2006).

[19]Q. M. Zhang, W. Y. Pan, S. J. Jang, and L. E. Cross, J. Appl. Phys. **64**(11), 6445 (1988).

[20]J. Shang, H. Zhang, Y. Li, X. Zhou, and P. Zhang, J. Cryst. Growth **312**, 1925 (2010).

[21]M. Budimir, D. Damjanovic, and N. Setter, Appl. Phys. Lett. **88**(8), 082903 (2006).

[22]J. Ouyang, R. Ramesh, and A. L. Roytburd, Appl. Phys. Lett. **86**(15), 152901 (2005).

[23]G. Catalan, A. Lubk, A. H. G. Vlooswijk, E. Snoeck, C. Magen, A. Janssens, G. Rispens, G. Rijnders, D. H. A. Blank, and B. Noheda, Nature Mater. **10**, 963 (2011).

[24]P. Bintachitt, S. Jesse, D. Damjanovic, Y. Han, I. M. Reaney, S. Trolier-McKinstry, and S. V. Kalinin, Proc. Natl. Acad. Sci. U.S.A. **107**(16), 7219 (2010).

[25]N. Bassiri-Gharb, I. Fujii, E. Hong, S. Trolier-Mckinstry, D. V. Taylor, and D. Damjanovic, J. Electroceram. **19**(1), 47 (2007).