

Scaling Effects in Perovskite Ferroelectrics: Fundamental Limits and Process-Structure-Property Relations

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Ferroelectric materials are well-suited for a variety of applications because they can offer a combination of high performance and scaled integration. Examples of note include piezoelectrics to transform between electrical and mechanical energies, capacitors used to store charge, electro-optic devices, and nonvolatile memory storage. Accordingly, they are widely used as sensors, actuators, energy storage, and memory components, ultrasonic devices, and in consumer electronics products. Because these functional properties arise from a noncentrosymmetric crystal structure with spontaneous strain and a permanent electric dipole, the properties depend upon physical and electrical boundary conditions, and consequently, physical dimension. The change in properties with decreasing physical dimension is commonly referred to as a size effect. In thin films, size effects are widely observed, whereas in bulk ceramics, changes in properties from the values of large-grained specimens is most notable in samples with grain sizes below several micrometers. It is important to note that ferroelectricity typically persists to length scales of about 10 nm, but below this point is often absent. Despite the stability of ferroelectricity for dimensions greater than ~10 nm, the dielectric and piezoelectric coefficients of scaled ferroelectrics are suppressed relative to their bulk counterparts, in some cases by changes up to 80%. The loss of extrinsic contributions (domain and phase boundary motion) to the electromechanical response accounts for much of this suppression. In this article, the current understanding of the underlying mechanisms for this behavior in perovskite ferroelectrics is reviewed. We focus on the intrinsic limits of ferroelectric response, the roles of electrical and mechanical boundary conditions, grain size and thickness effects, and extraneous effects

related to processing. In many cases, multiple mechanisms combine to produce the observed scaling effects.

Keywords: *ferroelectricity/ferroelectric materials; thin films; grain size*

I. Introduction

SCALING effects in ferroelectric materials have received significant research interest for over five decades. In response to relentless demands for electronic devices with smaller package sizes, increased functionality, and higher operating frequencies, there has been a drive to decrease the size and increase the performance metrics of virtually every passive or active component. Many of these components utilize perovskite structure ferroelectric or paraelectric oxides. A few examples include: (1) multilayer ceramic capacitors (MLCCs) with modified barium titanate dielectric layers that provide power decoupling and smoothing; (2) tunable varactors used for frequency tuning of radio frequency (rf) and microwave antennae for mobile communications based on barium strontium titanate thin films; (3) nonvolatile memories utilizing ferroelectric lead zirconate titanate (PZT) thin films; and (4) sensors and actuators based on piezoelectric microelectromechanical systems (MEMS). In most cases, the dielectric layer thickness is on the order of 1 μm or less.

Consider MLCCs as an example technology; modern components have dielectric layer thicknesses substantially below 1 μm .^{1,2} Two decades ago, the state-of-the-art was 10 μm thick layers.³ This rapid decrease in layer thickness was driven by the technology roadmap where advancing performance goals necessitated increased volumetric capacitance (rather like a capacitor version of Moore's law). To illustrate this, Fig. 1 shows the dielectric layer thickness in MLCCs as a function of time.^{2,4} To improve long-term reliability under applied electric fields, it is preferable to have several grains (typically 5–6) spanning the thickness of the dielectric.⁵ The resulting grain boundaries act as interfaces that impede the transport of mobile species, such as oxygen vacancies.^{3,6–9} Thus, many capacitors have grain sizes $\ll 1 \mu\text{m}$ in diameter.

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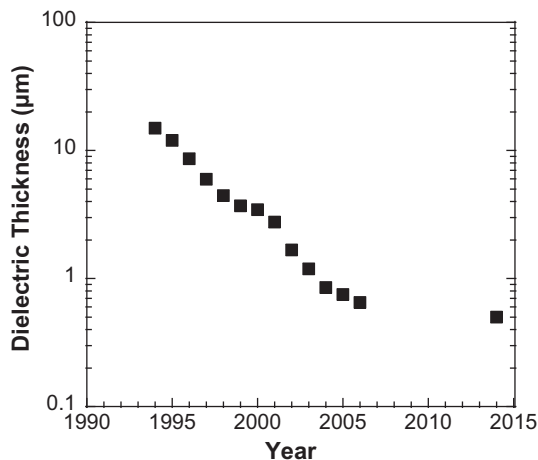


Fig. 1. Scaling of dielectric layer thickness in BaTiO₃-based multilayer ceramic capacitors as a function of time.^{2,4}

Other applications that utilize thin ferroelectric layers do not require multiple grains through the thickness, but still require submicrometer layer thickness to reduce operation voltage and increase device capacitance. In both cases, scaling effects are pronounced and are difficult to overcome.

In a limited number of cases, biaxial strains or internal electric fields in scaled ferroelectrics stabilize either ferroelectricity or improve the functional properties. More often though, decreasing the physical dimensions in ferroelectrics is associated with reduced phase transition temperatures, reduced ferroelectric distortions, diminished polarization, and reduced permittivities. These effects are intrinsic and result from the increasing relative fraction of surface/interface atoms to bulk atoms.^{10,11} For clarity, we refer to these changes as *fundamental size effects*. These fundamental size effects are common in ferroelectrics,^{12–14} and have also been reported in nanoparticle and ultrathin film studies of magnets¹⁵ and superconductors.^{16,17} The collection of experimental and theoretical reports on fundamental size effects teaches that they become important when at least one critical dimension is in the range of 10s of nanometers.

While size effects control the limits of thermodynamic stability for a ferroelectric phase, the properties typically begin to change over much longer length scales; in this article we define these changes as *scaling effects*. Scaling effects may also alter the relative stability of a ferroelectric phase, but they are not inherent to the host crystal. Scaling effects have numerous origins, which include finite electrode screening, external strain, interface mixing, finite grain-boundary thickness, point defects, crystallographic defects, and impurities. A cross-sectional transmission electron micrograph of a PZT thin film in Fig. 2 highlights several of the most important contributors to scaling effects.

Understanding the relative roles, importance, and interactions of scaling and size effects is a central challenge facing the oxide electronics community. Our goal in this article is to highlight the present understanding of scaling effects in the most compositionally broad class of ferroelectrics, perovskite structured oxides, and how they regulate the ferroelectric properties. Because size also affects phase stability, the size dependence of the stability of the ferroelectric phase is discussed briefly as well. Scaling effects are present regardless of the physical dimensions/embodyment of the material (i.e., thin films, bulk ceramics, and single-crystals), but the magnitude of the changes in the properties differs for each, due to the differences in mechanical and electrical boundary conditions). For that reason, this article focuses on the mechanisms leading to scaling of ferroelectric properties with specific examples highlighting their effect in systems of differing structure and size. This article is divided into the following sections: (1) Fundamental Limits, (2) Electrical and

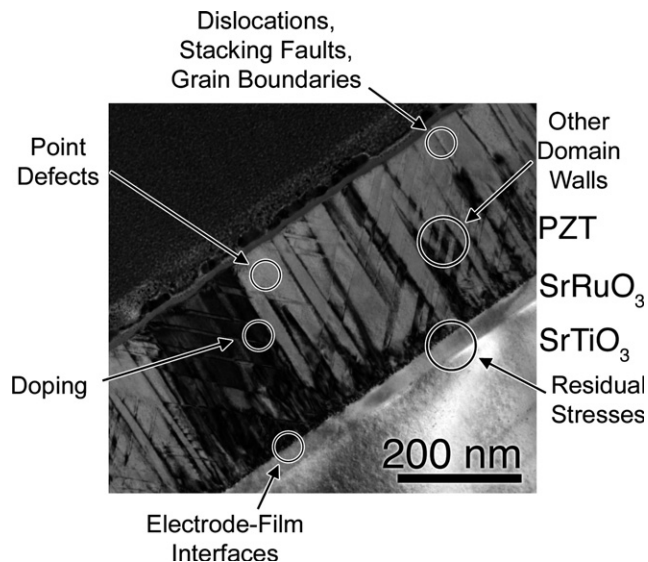


Fig. 2. Transmission electron micrograph of an epitaxial PZT film highlighting various features that lead to scaling effects in ferroelectrics: electrode-film electrical boundary conditions, substrate-induced strain and mechanical clamping, domain walls, point defects, and doping, among others.

Mechanical Boundary Conditions, (3) Domain, Grain Size, and Thickness Scaling Effects, and (4) Processing-Related Scaling Effects. While the phenomena leading to observed scaling effects are discussed separately, it is important to note that multiple mechanisms are often coupled. Furthermore, the focus of this review is on perovskite ferroelectrics. While scaling effects are observed across all ferroelectric material classes, the ubiquity of the phenomena leading to scaling in perovskites across all structural embodiments (i.e., single crystals, polycrystalline ceramics, and thin films) provides a landscape to discuss the important factors that lead to scaling. The scaling effects discussed will also be present in other ferroelectric material systems, but the degree to which they impact properties may vary.

Some additional definitions are necessary to describe the contributions to the various physical properties of ferroelectrics that will be used throughout the remainder of this review. *Intrinsic* responses refer to those that arise from the crystalline lattice. These include the spontaneous polarization, permittivity, and piezoelectric coefficients, etc. that would be characteristic of a monodomain single crystal. Appropriate averaging is used to describe polycrystalline or oriented materials. *Extrinsic* responses are those that originate from domain wall and/or phase boundary motion in polydomain materials. Motion of these planar interfaces often makes a substantial contribution to the electromechanical and permittivity values in ferroelectrics.

It is also prudent at the outset of the paper to provide a cautionary note: ferroelectric responses are commonly measured using techniques that may be prone to artifacts that can mimic ferroelectricity. Polarization,^{18,19} capacitance,¹⁸ and piezoresponse²⁰ measurement and interpretation guidelines have been well addressed elsewhere.

II. Fundamental Limits

The spontaneous polarization in displacive ferroelectrics is the primary order parameter. The origin of this polarization is a phonon-mediated collective phenomenon. Therefore, in order for a stable ferroelectric dipole to exist, multiple unit cells are necessary to stabilize the characteristic reorientable, spontaneous polarization. The evolution of the polarization as a function of temperature can be ascribed to a ferroelectric soft mode.^{21,22} The soft mode is a transverse optical phonon mode that condenses to produce the dipole moment in a

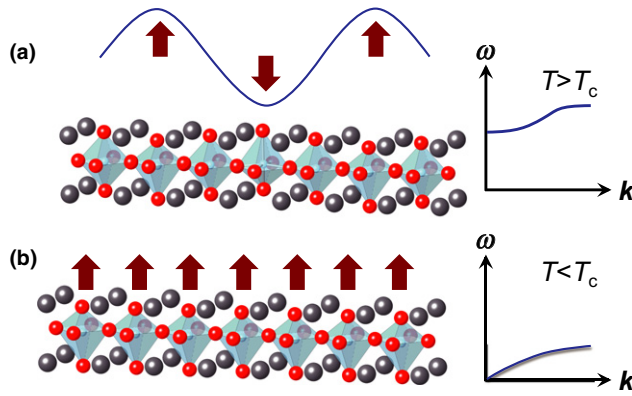


Fig. 3. Schematic of the polarization direction, titanium ion position, and ferroelectric soft mode phonon dispersion for a prototypical ferroelectric, PbTiO_3 . (a) Shows the optical phonon wavelength, the corresponding polarization magnitude for each unit cell, unit cells with titanium ions displaced differing amounts, and the soft mode dispersion with finite zero wavevector (k) frequency (ω). (b) Shows the condensed soft mode with uniform polarization magnitude for each unit cell with the titanium ions all displaced in the same direction with the same dipole moment, and the condensed soft mode dispersion with a zero frequency mode at the zone center. Shannon-Prewitt ionic radii scaled to 40% size were used in this representation.

ferroelectric (e.g., via the B -site titanium displacement in a prototypical ferroelectric such as PbTiO_3). As shown in Fig. 3(a), at temperatures above the Curie point, T_C , the soft mode exists at high frequencies and consequently has short wavelengths—the titanium ion is not necessarily in the same position for neighboring unit cells. As temperature is reduced, this soft mode frequency at the Brillouin zone center decreases and the wavelength of the mode increases until reaching the Curie point where it condenses to either a finite low frequency (long wavelength) mode or zero frequency (infinite wavelength) mode. Physically, this represents the wavelength of this mode approaching infinity and all neighboring unit cells have the titanium ion displaced in the same direction. This is shown schematically in Fig. 3(b), where all unit cells have equivalent polarization magnitudes and vectors. Using this soft mode model, one can clearly see that many unit cells are necessary to realize the optical phonon mode giving rise to the ferroelectric dipole moment. Thus, there are fundamental limits to the ensemble of unit cells needed to realize a ferroelectric material—a single unit cell cannot develop the necessary phonon dispersion spectrum to realize the collective response.

Experimentally observed limits to stable ferroelectricity can be divided into two categories: semi-infinite thin films and individual nanocrystals. For thin films, much of the work has focused on epitaxial layers. Ferroelectricity has been detected in 10 unit cell thick films (4 nm) using scanning probe techniques²³ and has been observed using synchrotron diffraction techniques in just 3 unit cell thick (1.2 nm) epitaxial PbTiO_3 films grown on (001)-oriented SrTiO_3 substrates where 180° domain walls form to stabilize against depolarization fields [discussed in Section III(1)].¹² Likewise, ferroelectricity has been verified in epitaxial BiFeO_3 films as thin as 5 unit cells (2 nm).²⁴ In BaTiO_3 films, the lower limit for ferroelectricity has been reported by various authors to range from 7 unit cells (2.8 nm)^{25,26} down to 4 unit cells (1.6 nm).^{27,28} Three unit cells likely represents the limit to observe ferroelectricity in a thin film, owing to the boundary conditions imposed by nonferroelectric interfaces²⁹ (i.e., the terminating unit cells would be chemically bound to nonferroelectric phases, which would alter the lattice distortions, phonon modes, and bond covalency^{30,31} necessary to realize the stable ferroelectric phase). These values are consistent with early computational predictions, where 3 unit cells of PbTiO_3 ³² and 6 unit cells of BaTiO_3 ³³ were suggested as limits for semi-infinite planes.

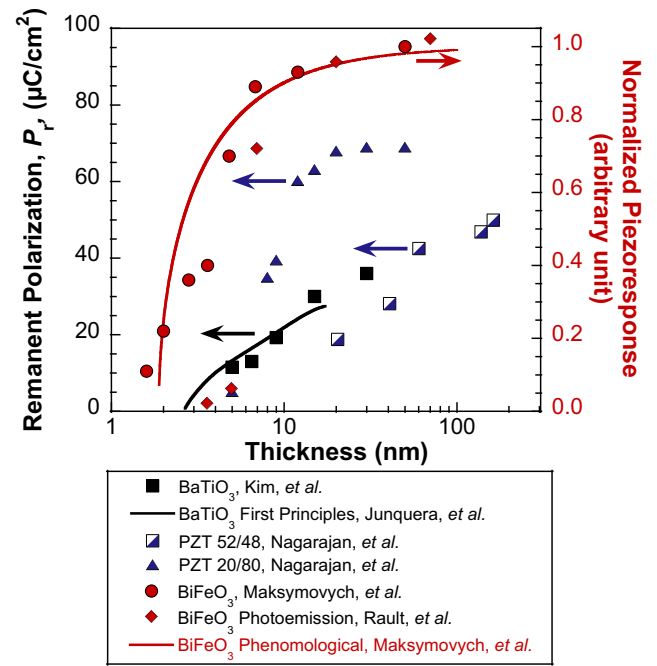


Fig. 4. Remanent polarization (left axis) for BaTiO_3 ⁴⁰ and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ^{41,42} and normalized piezoresponse⁴³ and polarization measured using photoemission⁴⁴ (right) for BiFeO_3 thin epitaxial films with decreasing film thickness. The lines are theoretical calculations of polarization for BaTiO_3 ³³ (from first principles) and BiFeO_3 (phenomenological model). All systems show similar response saturation at large thicknesses (>50 nm), with greatly reduced response at <10 nm. The lattice matched PZT 20/80 composition has fewer dislocations than the morphotropic PZT 52/48 film and exhibits saturation of response at smaller thicknesses.

For nanocrystals, ferroelectric phase stability is lost at dimensions that are comparatively larger than in semi-infinite thin films. This loss of phase stability likely stems from the challenge of preparing high-quality nanoparticles, combined with complicating factors such as the substantial difficulty in characterizing discrete particles. Early experiments investigating particles via Raman spectroscopy suggested a critical limit of ~12.6 nm for PbTiO_3 ,³⁴ whereas early X-ray diffraction studies of BaTiO_3 particles indicated a much larger critical size of ~100 nm.³⁵ The critical limit for PbTiO_3 was further refined to 10.7 nm by Ishikawa et al. for individual particles.³⁶ More recent studies on BaTiO_3 have shown that tetragonal symmetry and ferroelectricity exists in much smaller sizes than originally reported, including confirmation for 40 nm¹⁴ and 26 nm¹³ diameter particles and, most recently, ferroelectric polarization and polarization switching has been measured in BaTiO_3 nanocubes that are 10 nm on edge.³⁷ Combined, these results suggest that the lower *intrinsic* limit for room-temperature-stable ferroelectricity is less than 10 nm for three-dimensionally scaled particles and may be stable in volumes as small as 600 nm³,³⁸ and potentially to 10–100 nm³.³⁹

It is critical to note, however, that while ferroelectricity itself persists to extremely small sizes in displacive ferroelectrics, the magnitude of the polarization is suppressed as the critical thickness is approached. The decrease in ferroelectric response with decreasing thickness is shown in Fig. 4, which plots the remanent polarization (or half of the switching polarization) for epitaxial BaTiO_3 ,⁴⁰ $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT 52/48),⁴¹ and $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT 20/80)⁴² metal-insulator-metal structures. For BiFeO_3 , high electrical leakage currents in ultrathin films prevents traditional electrical-based characterization using metal-insulator-metal devices, so instead the normalized piezoresponse⁴³ [measured via piezoresponse force microscopy (PFM)] and polarization⁴⁴ (measured via photoemission) are shown. All films show similar trends with thickness: saturation of the polarization response at thicknesses

above 20–30 nm with severe depression of the polarization below 10 nm.

The impact of reduced ferroelectric response extends to properties that depend on ferroelectricity, including the dielectric and piezoelectric responses. Consider one observation of note: several authors have demonstrated room-temperature properties, such as permittivity, in scaled BaTiO_3 that are close to bulk values, but at temperatures near the Curie point, the differences remain pronounced, that is, sharp transitions with permittivities $>10^4$ have not been seen in films even when grain sizes are large. The remainder of the article focuses on *scaling effects* in bulk and thin film systems, which are in part responsible for this property contrast.

III. Electrical and Mechanical Boundary Conditions

As described by Aizu,⁴⁵ in many displacive ferroelectrics, the noncentrosymmetric ferroelectric phase develops on cooling from a high-temperature parent phase. This transformation occurs with a reduction in at least one symmetry element. For example, transitions from cubic to tetragonal or rhombohedral phases are often observed. Accompanying the spontaneous polarization is a spontaneous strain. Altering the strain state results in a change in polarization magnitude and vice-versa—that is, the strain and electrical polarization are coupled phenomena. As such, ferroelectrics are sensitive to both electrical and mechanical boundary conditions. In this section, the primary scaling effects associated with electrical and mechanical boundary conditions are discussed.

(1) Electrical Boundary Conditions: Depolarization Fields and Electrode Screening

Terminating the spontaneous polarization in ferroelectrics by introducing a surface or interface, by definition creates a depolarization field. For example, in a single domain single crystal an electric field develops as a result of surface charges that compensate the normal component of the polarization. This electric field will oppose the polarization and destabilize the ferroelectric phase.⁴⁶ Four suggested mechanisms that sustain the polar nature of the lattice in response to the depolarization field are summarized in Fig. 5. These include: (1) electrode screening, resulting in a compensating surface charge, (2) electrical conduction through the crystal, (3) polarization gradients within the crystal, and (4) domain formation.^{47,48}

Electrode screening, in particular, has been shown to dramatically influence the stability of the ferroelectric phase and the resulting properties. In a ferroelectric capacitor, polarization induces a surface charge that must be balanced with an accumulated counter charge in the electrodes. For real metals, the charge occupies a finite physical thickness, resulting

in a finite screening length and thus incomplete screening of the ferroelectric polarization and a depolarization field. The magnitude of the depolarization field is strongly crystal-size dependent. Consider an ideal single-domain crystal with a thickness-independent spontaneous polarization that is uncompensated at the surfaces. As the crystal thickness decreases, the surface charge remains constant. Thus, the electric field increases substantially as the thickness drops. As a result, depolarization-field-induced scaling effects are most prominently observed in thin films. When present, this depolarization field can lead to domain formation, reduced spontaneous polarization, or destabilization of the ferroelectric phase.⁴⁹

Starting with stability of the ferroelectric phase, first principle calculations have quantified the impact of such electrical boundary conditions on ferroelectric properties. For example, a SrRuO_3 - BaTiO_3 - SrRuO_3 film stack on a SrTiO_3 substrate was investigated and the magnitude of the depolarization field increased as the film thickness decreased.³³ A critical thickness for ferroelectric stability was predicted to be 2.4 nm (6 unit cells). This destabilization was driven by the electrostatics of the depolarization field resulting from incomplete charge screening in the SrRuO_3 metallic electrodes. The first principles calculations showed that polarization is suppressed in the ferroelectric phase to thicknesses in excess of 15 nm—all as a result of incomplete charge screening. It was found that models with “perfect” metal electrodes with “perfect” screening resulted in films with polarization values equivalent to the bulk, demonstrating the strong effect that incomplete screening has on polarization magnitude. The model used, however, ignored interface bonding effects, which will be discussed later. Experimentally, ultra-thin films of BaTiO_3 with SrRuO_3 electrodes grown by Kim, et al.⁴⁰ showed remarkable agreement with first principles calculations,³³ as seen in Fig. 4. In addition to ferroelectric polarization stability changes owing to depolarization fields, substantial changes in lattice distortion are common. Epitaxial PbTiO_3 films grown on conducting niobium-doped SrTiO_3 substrates were observed to have decreasing tetragonality as a result of incomplete charge screening.⁵⁰ The tetragonality decreased with film thicknesses below 20 nm. The decreased c/a ratio was consistent with the expected trend for incomplete charge screening and demonstrates that this effect can be a dominant scaling effect for very thin layers.

Building on the early first principles studies of the effects of electrode charge screening, more recent first principle studies compared the effect of different metallic contacts, platinum and SrRuO_3 , on the properties of the incipient ferroelectric, SrTiO_3 .⁵¹ It was found that regions of decreasing polarization and permittivity extended into the SrTiO_3 at the electrode/ SrTiO_3 interfaces owing to incomplete screening. These calculations predicted more complete screening

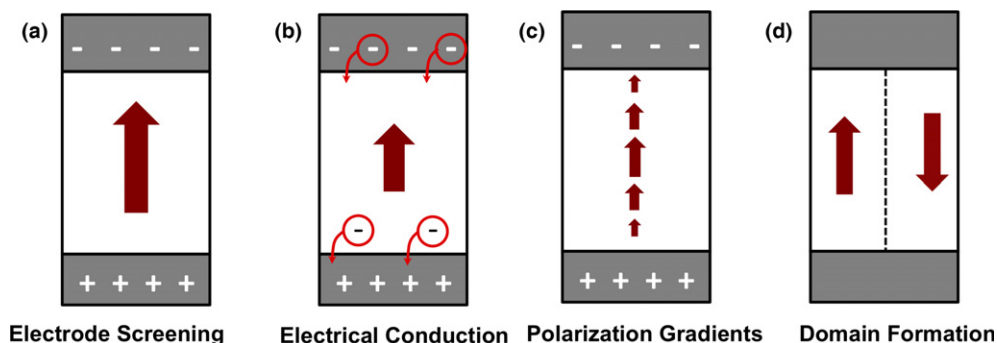


Fig. 5. Compensating mechanisms for ferroelectric polarization. Red arrows indicate the polarization vector. (a) Shows charge accumulation in electrodes adjacent to the surfaces of the ferroelectric. These charges compensate for the polarization charge of the ferroelectric. (b) Shows electrical charges leaking into and through the ferroelectric material. (c) Shows polarization gradients forming with lower polarization near the surfaces/interfaces of the ferroelectric. (d) Shows a 180° domain wall (dashed line) separating regions of equivalent polarization. In actuality, the domain wall would have a finite width, typically single to several unit cells.

with platinum electrodes and showed that the incomplete screening at the contact interface should lead to noticeable reductions (~15%) in permittivity for 75 nm thick SrTiO₃ films with SrRuO₃ electrodes, in stark contrast to behavior of BaTiO₃ with SrRuO₃ electrodes discussed above, where depolarization effects were not observed until sub-30 nm thicknesses.⁴⁰ This computational result was obtained even for the fully relaxed state of a freestanding single crystal (i.e., no epitaxial strain was present to stabilize or/destabilize polarization).

Although first principles calculations predicted that platinum would provide more complete screening compared to conducting oxides, experimental results reveal inconsistent behavior for Ba_{1-x}Sr_xTiO₃ with metal and conducting oxide electrodes, with many experiments showing smaller thickness effects with conducting oxide electrodes.^{52–56} Unfortunately, differences in Ba:Sr ratio and contact symmetry in these studies complicate analysis and understanding of electrode effects. The data above demonstrate the great challenge of understanding scaling effects. Consider that making an epitaxial ferroelectric thin film very thin enables one to observe screening effects, but that thinness also promotes coherent growth, which imparts a strong mechanical boundary condition, and the two effects confound each other. In addition, as will be discussed next, the differing bonding environments between electrodes and SrTiO₃ or BaTiO₃ leads to unanticipated differences in screening and explains some of the challenges in understanding ferroelectric screening.

An experiment to decouple film growth related strain and processing parameters on scaling effects was performed via dielectric characterization of a free-standing BaTiO₃ capacitor prepared by ion milling a 75-nm-thick sheet from a single crystal and depositing gold electrodes.⁵⁷ Dielectric measurements showed a sharp transition at the expected Curie temperature, with typical Curie-Weiss behavior above the transition. The high permittivity (greater than 25 000 at the transition temperature) and lack of T_C shifts or broadening observed in this experiment support the hypothesis that many of the size effects reported in the literature are not intrinsic. This result contrasted sharply with the theoretical prediction of incomplete screening in the SrTiO₃ system and suppressed properties even in 75-nm-thick SrTiO₃, strain free layers.⁵¹ Additional first principles evaluations were conducted to expand on the early SrTiO₃ models to include the ferroelectrics BaTiO₃ and PbTiO₃.⁵⁸ These calculations showed that insufficient screening by the metal electrode is not the only determining factor for ferroelectric instabilities in these ultrathin films. Despite the more effective screening of platinum on PbTiO₃ than on BaTiO₃, it was predicted that BaTiO₃ with platinum electrodes had significantly thinner “dead layers” (where dead layers correspond to regions with differing polarization or permittivity from that of the bulk, including polarization gradients), and had stable ferroelectricity down to one unit cell. The difference in this account with prior work stemmed from allowing the film surfaces to rumple/buckle in the simulations, which stabilizes ferroelectricity to a lower critical thickness. Models suggest that the buckling mechanism originates from weak bonding of an *A*-site/O-terminated perovskite ferroelectric to the metal that can actually enhance the spontaneous polarization. Furthermore, due to differences in screening capability, it was shown that platinum electrodes should yield thinner dead layers than SrRuO₃ electrodes. This result shows that the chemical environment at the interface is a crucial factor in scaling of ferroelectric properties.

Chang et al. added experimental evidence to this prediction by comparing the temperature dependent dielectric response of 300-nm-thick lamellae capacitor structures prepared from BaTiO₃ and SrTiO₃ bulk single crystals.⁵⁹ Using platinum contacts, no signature of a dead layer was observed for BaTiO₃, whereas equivalent SrTiO₃ structures exhibited a decreased response, as predicted by first principle

simulations. Additional simulations and experiments confirm that the interfaces of various ferroelectrics can indeed be engineered to avoid or minimize these so-called dead-layer effects, which can lead to depression of ferroelectric properties in the complete capacitor structure.^{60–63} For example, by engineering the BaO-RuO₂ termination through the addition of a SrTiO₃ layer at the electrode interface, the polarization can be de-pinned and ferroelectricity enhanced.⁶² Although interface engineering shows promise for increasing the stabilized spontaneous polarization, the addition of SrTiO₃ leads to less effective screening and faster relaxation.⁶⁴ Combined, these computational and experimental studies demonstrate the care that must be taken when investigating materials and attributing thickness effects to electrode interface features, such as dead layers—the atomic structure and terminating layers play an important role.

Finally, the effectiveness of screening by electrodes and the resulting depolarization field can also strongly influence the formation of ferroelectric domains.^{65,66} For instance, PbTiO₃ on conducting Nb-doped SrTiO₃ shows suppressed tetragonality with decreasing thickness, consistent with an increasing depolarization field. However, a polydomain structure appears for thinner PbTiO₃ films grown on conducting La_{0.67}Sr_{0.33}MnO₃ electrodes, which compensates for the depolarization field and results in an *increased* PbTiO₃ tetragonality.⁶⁷ The domain's relative orientation (e.g., poled-up, down, or in-plane) can also influence the depolarization field by changing the relative thermodynamic stability of defects or interacting with step-edges.^{68–70} Insertion of dielectric spacers at ferroelectric-electrode interfaces reduces the screening efficacy of the electrode and leads to the formation of a polydomain structure to compensate the depolarization field.⁶³ Compensation at interfaces can also be affected by adsorbates, such as hydroxide, that can compensate exposed ferroelectric surfaces and stabilize monodomain material.⁷¹

Incomplete screening effects, seen in epitaxial and free-standing single crystal experiments and simulations, serve as a limiting case for metallized devices with thin ferroelectric layers. However, many applications require thicker (>100 nm) polycrystalline layers, well above the reported intrinsic and depolarization-field-induced critical sizes. In contrast to the demonstration of bulk, single-crystal-like properties in 75-nm-thick BaTiO₃,⁵⁷ polycrystalline films, ceramics, and even many epitaxial films with thickness and grain size less than several micrometers exhibit broadened/depressed phase transitions and significantly lower permittivities. This fact points to the complication of isolating scaling effects and that many effects often contribute to measured thickness dependence in the properties. The role of grain boundaries, domain structure, and material processing conditions on functional properties will be discussed in Sections IV and V.

(2) Mechanical Boundary Conditions

In addition to electrical boundary conditions, mechanical boundary conditions, such as substrate-induced strains, contribute strongly to the behavior of ferroelectrics. Stress/strain effects can be generally classified into two types: (1) hydrostatic compressive strain, which tends to decrease the unit cell volume and the ferroelectric phase transition temperature⁷² and (2) biaxial strain, which can either increase^{73–76} or decrease the phase transition temperature and can promote a preferred polarization orientation.⁷⁷ Biaxial strain effects on ferroelectric polarization and domain structure are illustrated in Fig. 6. In an ideal uniaxial ferroelectric, biaxial compression normal to the polar axis will stabilize the polarization vector against thermal fluctuations, thus increasing the polarization magnitude and raising T_C , as shown in Fig. 6(b). Biaxial tension imparts the opposite trend, Fig. 6(c).

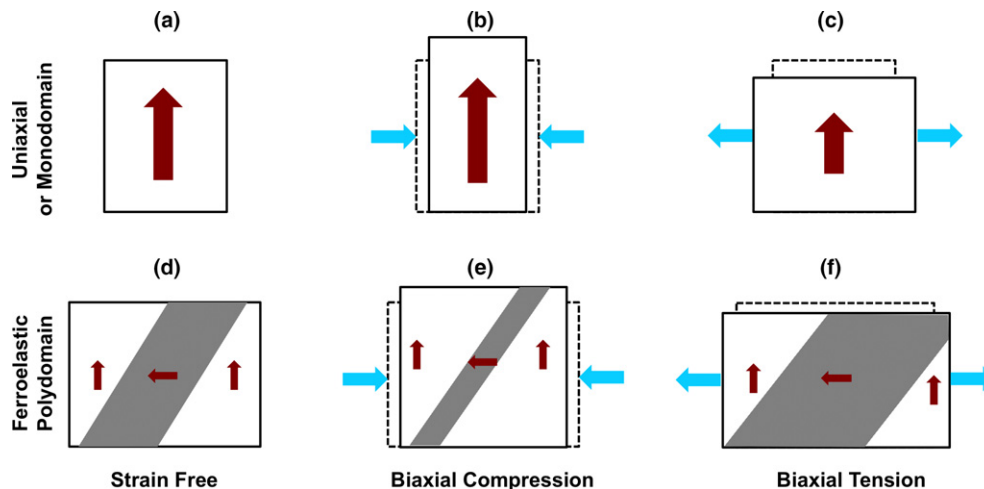


Fig. 6. Biaxial strain effects on polarization in (a–c) uniaxial ferroelectrics and (e–f) biaxial ferroelectrics with more than one stable polarization direction. Red arrows indicate the polarization direction and blue arrows indicate the direction of applied stress. The shaded regions in (e–f) represent domains with in-plane polarization vectors. The polarization state in the unstrained condition is represented (a) and (d) and the superposition of that condition is represented by the dashed lines in (b, c, e, and f). Biaxial tension in a uniaxial ferroelectric with polarization out-of-plane will result in a reduced polarization vector (b). Biaxial compression in a uniaxial ferroelectric with polarization out-of-plane will result in an increased polarization vector (c). Biaxial tension in a polydomain ferroelectric with polarization out-of-plane will result in increased volume fractions in in-plane oriented polarization domain (e) and biaxial compression in a polydomain ferroelastic material will result in increased volume fractions of out-of-plane oriented polarization domains (f).

Biaxial strain will also strongly influence the arrangement of ferroelastic domains, if present. If one considers a ferroelectric where the polarization vector can switch ferroelastically between orthogonal [001] and [100] directions, then biaxial compression perpendicular to the polar axis will stabilize that orientation and increase T_C , as shown in Fig. 6(e). For a large enough biaxial tension perpendicular to the polar axis, the polar direction will switch into the tensile plane, and T_C will increase, as shown in Fig. 6(f). These strain effects, however, become more complicated when superimposed upon scaling effects. Consider that below a certain dimension, it is possible to lose or perhaps immobilize ferroelastic domains in a biaxial ferroelectric.⁷⁸ In such a situation, the strain-dependence of T_C can, in principle, reverse. It is possible that such effects contribute to the T_C depression seen many times in very fine-grained $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films, as will be discussed in more detail in Section IV. Ultimately, it is most important to recognize that mechanical boundary conditions act in combination with intrinsic scaling effects producing a complex size and strain-dependent response that can be very difficult to separate.

There can be many origins of strain in ferroelectric materials depending on the geometry and embodiment of the device. In thin films, there are three primary origins of strain: (1) lattice mismatch strain that is present in epitaxial systems, (2) growth-related strain common to physical vapor deposition methods, and (3) coefficient of thermal expansion mismatch between the ferroelectric film and the substrate. In bulk ceramics, strain can exist in individual grains owing to mechanical boundary conditions present at grain boundaries as the material passes through the paraelectric/ferroelectric phase transition and develops a spontaneous dipole.

The wide range of perovskite single crystals with varying lattice parameters lends itself to coherent epitaxial growth of ferroelectrics.⁷⁹ In many cases, extremely thin films are grown on substrates that do not perfectly lattice match to control biaxial strain, altering phase stability and phase transition temperatures. Importantly, strain effects can be interlinked with other scaling effects, with changes to the stable polarization direction and the phase transition temperature dependent on the depolarization field.^{65,66} Some examples of utilizing strain to alter phase stability and ferroelectric response include the demonstration of ferroelectric response

in SrTiO_3 at room temperature when grown on DyScO_3 substrates⁸⁰ with a +1% lattice mismatch; the increase in phase transition temperature and remanent polarization of BaTiO_3 to 540°C and 70 $\mu\text{C}/\text{cm}^2$, respectively, grown on DyScO_3 (–1.7% lattice mismatch),⁷⁵ and stabilization of a tetragonal-like phase^{81,82} and strain-induced morphotropic phase boundary in BiFeO_3 .⁸³ The utility of strain engineering with ferroelectric films has generated significant theoretical and experimental attention with dedicated reviews.^{79,84,85}

However, growth of films beyond the critical thickness for strain relaxation results in formation of dislocations. These dislocations have been predicted^{86–93} and shown^{41,94–99} to affect the ferroelectric and dielectric properties. In epitaxial $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ films, a suppression of the permittivity was reported and explained by a concentration of misfit dislocations ($\sim 10^{11} \text{ cm}^{-2}$) altering the dielectric stiffness.⁹⁹ Dislocations in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films have been shown to strongly affect the polarization response. The dislocation effect is shown in Fig. 4 in comparing PZT 20/80 films,⁴² which are grown on lattice matched substrates, with the PZT 52/48 films,⁴¹ which are fully relaxed with dislocation densities of $\sim 10^{12} \text{ cm}^{-2}$. The critical thickness for the dramatic decrease in polarization is much higher for the PZT 52/48 films than the PZT 20/80 films. The strain fields surrounding the dislocations have been proposed to enhance depolarization fields and result in the greater thicknesses necessary to observe polarization saturation.⁴¹ This enhancement of depolarization field by dislocations illustrates clearly how different mechanisms can combine to magnify scaling effects.

For nonepitaxial films, the mechanical boundary conditions can include thermal expansion mismatch and mechanical compliance of the substrate. To illustrate the various mechanical boundary condition effects acting on nonepitaxial BaTiO_3 systems, Fig. 7 shows permittivity measurements from room temperature to 200°C from several different reports. The systems shown were selected on the basis of high material density and overall quality and to illustrate the differences between a 75-nm-thick strain-free single crystal,⁵⁷ a 70 nm grain size bulk ceramic,¹⁰⁰ a 55 nm grain size film (~ 180 nm thick) on platinized silicon,¹⁰¹ a 130 nm grain size film (~ 500 nm thick) on rigid α -sapphire (with top interdigitated contacts),¹⁰² and a 157 nm grain size film (~ 650 nm thick) on flexible copper foil.¹⁰³ The latter two example thin films were processed with added $\text{BaO-B}_2\text{O}_3$ (869°C eutectic

composition) to enhance densification and grain growth at lower temperatures.

The fine-grained bulk ceramic and the film processed on copper foil may be expected to possess reduced levels of biaxial strain, whereas the films on the rigid substrates will be subjected to strains associated with thermal expansion mismatch with the substrate. The free-standing 75-nm-thick single crystal exhibits bulk-like behavior with a pronounced permittivity peak at T_C nearing a value of 25 000. The 70 nm grain size ceramic and 157 nm grain size film on the flexible substrate samples, however, show significantly depressed permittivities at the ferroelectric-paraelectric transition temperature, but generally show bulk-like properties at room temperature (permittivity greater than 2000), and a bulk-like temperature of the permittivity maximum ($\sim 125^\circ\text{C}$). The flattening of the temperature dependence of permittivity is beneficial for many applications where stable properties over a wide operating range are desirable. However, the films deposited on rigid substrates exhibit suppressed permittivity (<1500) below and at T_C . The sample on sapphire is characterized using surface interdigitated capacitors, probing the in-plane dielectric properties and resulting in an increase to T_C to $\sim 175^\circ\text{C}$.¹⁰⁴ In contrast, the sample on silicon has a finer grain size, often correlated with T_C suppression, and is measured using the typical metal-insulator-metal geometry, which probes the out-of-plane permittivity. Since the film is under tensile stress with a preferred polarization lying in the plane, the applied fields interact with the in-plane polarization only indirectly and is less sensitive to ferroelectric transitions.^{74,80,105–109} As can clearly be seen, the final dielectric properties are heavily dependent on not just the presence of strain, but also differences in the grain size, as will be discussed in more detail in Section IV.

Comparing films prepared on the rigid sapphire substrate and copper substrates provides insight into strain-mediated properties. In this particular comparison, grain sizes are similar, processing temperatures are identical (900°C), and the liquid forming sintering aide is added to each. However, for films on sapphire the final dielectric constant is roughly 67% lower than for films on flexible substrates.^{102,103} Ferroelectric films on flexible substrates are one of few examples where

bulk-like permittivities, dielectric tuning, and piezoelectric coefficients are present at room temperature. In addition to the data shown in Fig. 7, these high value properties have been observed^{103,110–118} and predicted¹¹⁹ using a number of different deposition techniques, substrates, and other processing modifications. The high thermal expansion coefficient of the metallic substrates would be expected to place the films into a compressive stress, resulting in reduced cross-plane permittivity, however, the possibility for plastic deformation upon cooling due to metal annealing and a very low shear modulus minimizes residual strains.¹²⁰ In addition, because the foil substrate is thin and flexible, as compared to conventional rigid substrates such as sapphire and silicon, in-plane stresses can be reduced substantially through substrate bending.

The observation of a strong strain effect on dielectric and ferroelectric properties was previously quantified in polycrystalline $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST)¹²¹ and $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ ¹²² and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ ¹²³ thin films on silicon substrates using wafer flexure tests. The application of tensile stress in addition to the tensile film stress from thermal expansion mismatch with the silicon substrate led to large decreases (up to 25%) in the capacitance of metal-insulator-metal BST devices. By extrapolation, these results indicated that the stress imposed by the mechanical boundary conditions with the silicon substrate decrease the film permittivity by nearly 25%. Applying a compressive stress to PZT films that were already under tensile stress, post-processing, resulted in increases in permittivity (2%¹²²) and remanent polarization ($\sim 11\%$ ¹²² and 8% ¹²³) through lowering the overall film stress by $\sim 30\%$ ¹²² and transitioning from tensile to compressive stress.¹²³ Several other studies have confirmed that appropriately selected thermal expansion mismatch can increase the measured permittivity.^{107,108,124–128}

Mechanical boundary conditions affect all ferroelectrics and for ferroelastic ferroelectrics the mechanical constraints strongly affect the extrinsic properties. These mechanical boundary conditions can be a function of size, and hence can contribute to scaling effects. For example, the elastic interaction between thin films and their substrates can both change the intrinsic properties (e.g., by moving closer to constant strain rather than constant stress conditions) and reduce the domain wall mobility via substrate clamping.^{48,129,130} Furthermore, stress can affect the orientation of the polar axis with respect to the substrate plane and measurement direction, resulting in vastly differing polarizations and permittivities, depending on the substrate used.^{77,131} In tetragonal PZT compositions, for example, a substrate that places a film in compressive stress will result in high (001) domain orientations and large polarizations, but low measured permittivities.¹³² Substrates that place the film in tensile stress will, in many cases, have the opposite effect. In both instances, the ferroelastic domain wall mobility is reduced.

The technological drive for MEMS with high piezoelectric response has led several groups to fabricate partially de-clamped structures from blanket films. Enhanced piezoelectric responses in tetragonal PZT films on silicon upon patterning has been demonstrated with explanations based on de-clamping¹³⁰ and increased c -domain volume fractions that emerge when residual thermal tensile strains are released.¹³³ Microfabrication of island¹³⁴ and antennae¹³⁵ structures have shown significant increases in domain wall mobility via field-dependent piezoelectric measurements and Rayleigh analysis of the dielectric response, respectively. De-clamping and subsequent increased domain wall mobility has also been found in released diaphragm structures by changes in dielectric response¹³⁶ and 002/200 Bragg reflection intensities as a function of electric field.¹³⁷ Ultimately, the intimate connection between strain and polarization in ferroelectric crystals makes their extrinsic properties particularly sensitive to mechanical constraints. Since mechanical boundary conditions are strongly dependent upon

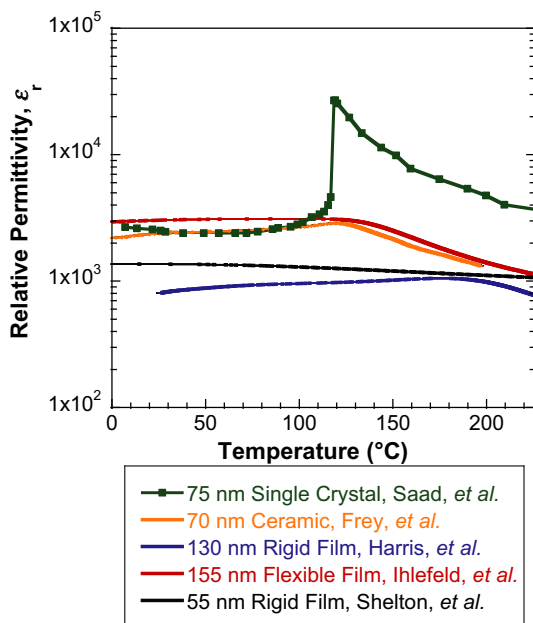


Fig. 7. Temperature dependence of permittivity for fine dimensioned BaTiO_3 materials: 75-nm-thick single crystal,⁵⁷ 70 nm grain size ceramic,¹⁰⁰ 130 nm grain size (500-nm thick) film on a rigid a -plane sapphire substrate,¹⁰² 157 nm grain size (650-nm thick) film on a flexible copper foil substrate,¹⁰³ and a 55 nm grain size (178-nm thick) film on a platinized silicon substrate.¹⁰¹

dimensions, their contributions to scaling effects can be pronounced.

Electrical and mechanical boundary conditions may affect the stability of ferroelectric phases. Electrical boundary conditions, such as the presence of depolarization fields can affect the stability of the ferroelectric phase and can be extremely sensitive to the chemical structure of the electrode/ferroelectric interface. Mechanical boundary conditions can result in changes of polarization magnitude, introduction of structural defects, such as dislocations, and clamping of domain walls affecting extrinsic contributions to electrical and electromechanical response. The relative magnitudes of the effects of electrical and mechanical boundary conditions on dielectric and electromechanical response changes with system size (thickness, lateral dimensions, etc.) and therefore constitute an important consideration in property scaling.

IV. Domain, Grain Size, and Thickness Scaling Effects

In addition to surfaces and electrode/ferroelectric interfaces, there are other interfaces that strongly affect ferroelectric properties. These include domain walls, grain boundaries, and their relative concentrations or volume fractions as the system size scales. These interfaces encompass many of the features already discussed in this review article: finite sizes and changing electrical and mechanical boundary conditions. The complex interactions between these conditions result in profound scaling effect dependencies. This section of the article describes how introduction of grain boundaries, domain boundaries, and decreasing material thickness affects properties of ferroelectrics.

(1) Grain and Domain Size Scaling in Ferroelectric Ceramics

Size dependent changes in the domain structures influence the grain size- and thickness-dependence of the properties of ferroelectric materials. Using BaTiO₃ ceramics as an example, the dielectric permittivity, ϵ_r , is a strong function of grain size over the range of 10 nm to 100 μm ,^{100,138–143} as is shown in Fig. 8. Typically, for dense materials, the room-temperature relative permittivity essentially saturates at ~ 1700 with grain sizes $>10 \mu\text{m}$.¹⁴⁰ There is a room-temperature peak in permittivity at BaTiO₃ grain sizes near 1 μm with values reaching ~ 5300 . Upon further grain size reduction, permittivity decreases. The observed trends can be divided into two categories using the grain-size-dependent permittivity peak as a demarcation point. For grain sizes larger than $\sim 1 \mu\text{m}$, Kinoshita¹³⁹ and Arlt¹⁴⁰ ascribed the observed grain size dependence of the dielectric properties of BaTiO₃ ceramics to changes in the domain configuration. In particular, Arlt reported that the domain size was dependent on grain size, where the domain size $\propto (\text{grain size})^m$. Experimentally, in both BaTiO₃ and Pb(Zr,Ti)O₃ ceramics with moderate grain sizes of ~ 1 – $10 \mu\text{m}$, the m value is consistently ~ 0.5 .^{140,144} An increasing density of mobile 90° domain walls with decreasing grain size increases the relative permittivity by increasing the extrinsic contribution to permittivity.^{140,145} This domain density trend has been confirmed in the piezoelectric response of BaTiO₃ single crystals with varying concentrations of domain walls.^{146,147}

While increasing domain wall density and subsequent increases in extrinsic contributions to permittivity with reducing grain size can explain the permittivity trend for BaTiO₃ ceramics with grain sizes larger than 1 μm , as grain sizes fall below $\sim 1 \mu\text{m}$, the measured permittivity is observed to decrease. There are several explanations for the decreasing dielectric response behavior; these include increased grain-boundary dilution of the dielectric response^{100,148} and changes in domain boundary density and their mobility.^{140,141} Focusing first on domain effects and grain size scaling, it was recently shown by Ghosh et al. using *in-situ*

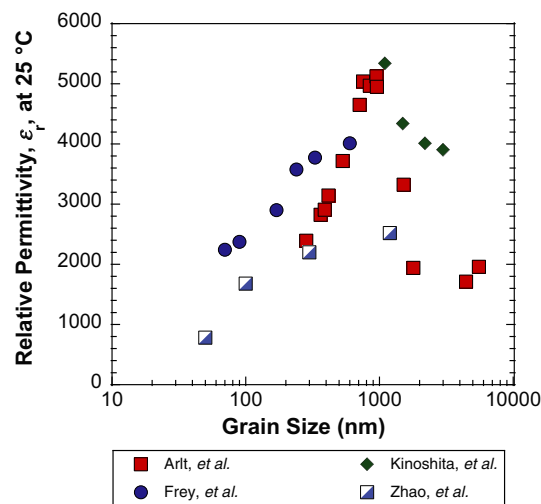


Fig. 8. Grain size dependence of room-temperature relative permittivity for bulk ceramic BaTiO₃.^{100,139,140,156}

high-energy X-ray diffraction that 90° domain wall reorientation is greatest at the intermediate grain sizes near 2 μm ; this correlates with the enhanced permittivity and piezoelectric properties observed in BaTiO₃¹⁴⁹ and is consistent with the observations of Arlt et al.¹⁴⁰ and Demartin et al.¹⁵⁰ Reduction in the grain size below 1 μm lowers the mobility and/or the density of 90° domain walls, and hence extrinsic contributions to the functional properties.^{149,151} In BaTiO₃ ceramics with submicrometer grains, the reduced mobility and/or density of 90° domain walls is often accompanied by a reduced unit cell tetragonality^{140,152} as well as decreased complexity of domain structures and their stable variants.^{144,153,154} In this case, because domain walls move collectively, limited twin configurations in a given grain could clamp the movement of domain walls in adjacent grains. In addition, nucleation of new domains becomes more difficult under application of electric fields as grain size is reduced toward the dimension of a single domain.^{149,155–157} In combination, these mechanisms erode extrinsic contributions to permittivity and produce scaling effects.

Similar to the well-studied BaTiO₃ system, polycrystalline Pb-based ferroelectrics, such as, morphotropic-composition PZT and 0.65Pb(Mg_{1/3}Nb_{2/3})O₃–0.35PbTiO₃ (PMN–PT), exhibit reduced piezoelectric coefficients and dielectric responses with decreasing grain size,^{158–162} though no property maximum has yet been observed as is present in BaTiO₃. Also similar to BaTiO₃, these more complex perovskite ferroelectrics and relaxors can display changes in crystal symmetry with decreasing grain size,^{162,163} which can further affect measured properties.

The inevitable increase in grain-boundary density that accompanies small grain sizes also affects the measured properties. For bulk ceramics, Frey et al.¹⁰⁰ used the “brick-wall” model¹⁴⁸ for a diphasic microstructure of high permittivity grains with disordered and thus low permittivity grain boundaries, as shown in Fig. 9 for the ideal system used in mathematical models and a realistic microstructure. The brick-wall model predicts a reduced net permittivity by a dilution effect from the grain-boundary volume. Using a grain-boundary thickness of 0.8 nm, which was determined by electron microscopy, the brick-wall model described the measured permittivities of a series of ceramics with grains sizes down to 40 nm for a grain core permittivity of ~ 4600 and a grain-boundary permittivity of ~ 130 in BaTiO₃. It should be noted that while this model fits experimental data well, it does not account for any changes in domain structure or domain wall mobility with grain size. Several groups have observed ferroelastic domain structure in fine-grained BaTiO₃,^{143,155} however the piezoelectric response of

fine-grained materials is suppressed,^{142,155} indicating that these domain walls are immobile. An ensemble of adjacent highly polarizable grains surrounded by defective grain boundaries can act as a source of charge that compensates the depolarization field within each grain to enable such high permittivities in the their cores. It should be noted, that Polotai et al. employed the brick-wall model for a similar set of dense fine-grained BaTiO₃ ceramics and found that the calculated grain boundary needed to be three to ten times thicker than the microscopy-measured grain boundary that pointed to a secondary mechanism for decreased permittivity near grain boundaries, which was attributed to depolarization fields.¹⁴³ A sample set of BaTiO₃ fine crystallites within a glass matrix, as described by McCauley et al., presents a situation where the depolarization field is less likely to be screened than in a sintered single-phase ceramic.^{164,165} It was shown that a decrease in both dielectric constant and phase transition temperature and an increase in the breadth of the phase transition occurred as crystallite size decreased from 80 to 25 nm. These three features: decreased permittivity, decreased T_C , and increased phase transition breadth, are characteristic of polarization gradients near the surfaces in incompletely screened ferroelectrics^{10,11} and again demonstrate the importance of the electrical boundary conditions at ferroelectric interfaces and how they affect the observed performance. Finally, Emelyanov et al. found a deviation of Curie–Weiss behavior in BaTiO₃, which was strongly dependent on grain size and that the Curie temperature in nanostructured ceramic systems are significantly lower than that in coarse ceramics.¹⁶⁶

Grain size scaling effects on permittivity in bulk ceramics result from a combination of mechanisms. (1) The grain size reduction results in a change in the numbers of domain boundaries within each grain, which tends to increase as the grain size decreases resulting in an increasing permittivity with decreasing grain size, particularly for BaTiO₃-based materials, reaching a peak at $\sim 1 \mu\text{m}$. Additional reduction in grain size results in a decrease in the numbers of stable domain configurations, a possible reduction in the numbers of domains within each grain, and a decrease in the mobility of these domain boundaries. The latter ultimately reduces extrinsic contributions to permittivity. (2) Decreasing grain size necessitates an increase in the volumetric fraction of material that is low permittivity grain boundaries, resulting in a decreasing permittivity for submicrometer grains due to dielectric mixing rules and is well fit by the brick-wall model.

(2) Thickness and Grain Size Scaling in Polycrystalline BaTiO₃-Based Thin Film Ferroelectrics

In polycrystalline thin films, property changes with decreasing thickness are one of the most commonly observed scaling effects. Like their bulk counterparts, these effects result from many interrelated microstructure and domain structure changes. Often these property changes with reduced thickness are attributed to the presence of a layer of suppressed ferroelectric activity at the film/electrode interface. As discussed in Section III, these layers may exist, but are highly dependent on the specific ferroelectric, electrode material, and interface structure, chemistry, and defects. Further complicating study of scaling effects in polycrystalline films is the common observation that grain size scales with thickness.^{167,168} The convolution of these two variables obscures the relative impact of grain size and film thickness. This discussion is confounded somewhat by inconsistent characterization within the community. Thin film microstructure, electrical properties, loss tangents, electrode properties, contacts, density, measurement frequency, and roughness are not always reported for sample sets with variable thickness. In the particular case of BST compositions with phase transitions near room temperature, characterization should include temperature-dependent measurements since shifts of T_C can cause large apparent changes to dielectric properties. Furthermore, processing conditions are commonly changed to modulate grain size, and the impact of those changes on the above parameters is not always elucidated,^{169–174} as will be discussed in Section V. The interlinked nature of processing conditions, microstructure, device geometry, contact material, substrate, and dielectric properties requires careful consideration of all these effects.

To simplify discussion of thickness scaling in films, we focus first on BaTiO₃-based compositions, including (Ba,Sr)TiO₃ (BST) where extensive research on thickness-dependent dielectric properties of columnar grained polycrystalline films has been conducted.^{56,167,168,170,175,176} Figure 10(a) shows thickness-dependent permittivity measurements¹⁷⁷ as well as the commonly applied series capacitance model that assumes reduced permittivity layers at the ferroelectric-electrode interfaces. This model usually makes the simplifying assumption that vertical grain boundaries (e.g., in columnar-structured films) run parallel to any applied fields and thus do not contribute significantly to the observed trends. In comparison to the epitaxial films discussed in Sections II and III and shown in Fig. 4, scaling effects in polycrystalline

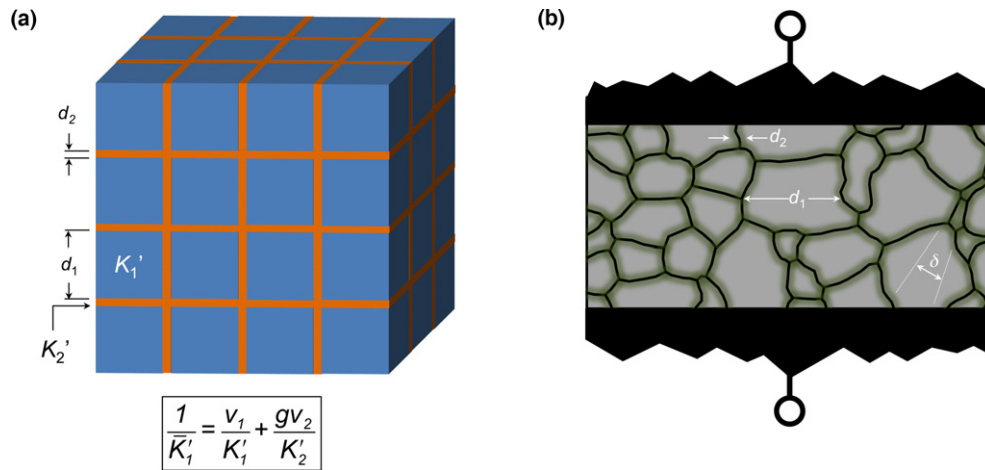


Fig. 9. Diphasic Brick-wall model used to describe the microstructure of polycrystalline ferroelectrics. (a) Cubic grains represent an ideal grain structure. d_1 , d_2 , K_1' , and K_2' represent the thicknesses of the grain core and boundary and permittivities of the grain cores and boundaries, respectively. The equation provides the model. v_1 and v_2 are the volume fractions of grain core and boundary respectively, and g represents a geometric factor describing the grain shape ($1 =$ perfect sphere, 0.8 is used in many real ferroelectrics).^{100,148} (b) A realistic grain structure showing grains with average sizes, d_1 , and grain boundaries of thickness d_2 . The dashed lines represent grain imperfections that yield smaller crystallite sizes than conventional physical grain sizes.

films play an important role at thicknesses an order of magnitude larger, as evidenced by the decreasing permittivity for films thinner than 150 nm. Figure 10(b) shows work by Sinnamon et al. exploring grain-boundary contributions as a possible explanation for the more pronounced thickness trend commonly seen in columnar films.¹⁶⁸ Although the grain boundaries run parallel to the applied field in these films, it was found that the thickness-dependent column diameter reproduces the series-like behavior commonly attributed to the presence of an interface layer, suggesting that the in-plane grain size can influence the observed scaling effects.

The grain-size and thickness correlation required independent assessment of these two variables. Berge et al. varied column diameter from 10 to 60 nm while maintaining a constant film thickness of 500 nm in Pt/BaTiO₃/Pt stacks by changing the deposition temperature.¹⁷⁸ Decreasing the in-plane grain size led to a sharp drop in the measured dielectric properties and suppressed the transition temperature. Figure 10(c) shows work from Strukov et al. where grain size was decoupled from thickness in columnar films by varying annealing and deposition conditions.¹⁶⁷ Film thickness was varied from 20 to 1100 nm (150 nm grains) and grain size from 30 to 150 nm (500-nm-thick films), both showing strong independent contributions to transition-temperature suppression. Unfortunately, only structural/thermal measurements were reported, but this experiment illustrates the care needed in analyzing these systems and attributing the origins of observed trends to only an interfacial (dead) layer. The sharp decreases attributed by many to thickness effects are likely exaggerated by concomitant changes in microstructure.

While grain boundaries parallel to the applied electric field direction have been shown to affect scaling in BST and BaTiO₃ films, equiaxed grain morphologies that are more

similar to bulk ceramics have been shown to have a strong effect on properties. These effects have been studied in comparisons of equiaxed and columnar morphologies by multiple research groups.^{111,117,179} It has been shown that BaTiO₃ and BST films with columnar grain morphologies display much higher room-temperature permittivities (typically three to five times) compared to equiaxed counterparts processed at identical temperatures. Dielectric mixing rules and brick-wall models, identical to those employed for bulk ceramics, explain the differences between high permittivity columnar versus lower permittivity equiaxed grain morphology embodiments.

Finally, in assessing the effect of thickness on the temperature-dependent permittivity of columnar BST films Parker et al. observed that decreasing thickness resulted in decreases in permittivity and also shifts of the permittivity maximum to lower temperatures and broadening of the permittivity maximum.¹⁷⁰ These effects, shifts and broadening of the transition, were not consistent with the existence of a zero-polarization interface layer and could not be completely explained dielectric mixing with low permittivity columnar grain boundaries alone. Rather, these were more consistent with polarization gradients owing to depolarization fields,¹⁰ similar to observation of McCauley et al. in BaTiO₃ glass ceramics.¹⁶⁴

Combined, these studies shown that grain boundaries in columnar and equiaxed grain morphology thin films play a profound role on the property reductions observed in thin layers. In addition, the electrode effects discussed in Section III may also affect performance as features consistent with polarization gradients are commonly observed. These works serve to demonstrate that the introduction of grain boundaries in thin films, even when parallel to the applied field, can lead to a significant decrease in permittivity, consistent with the brick-wall model results for bulk ceramics.

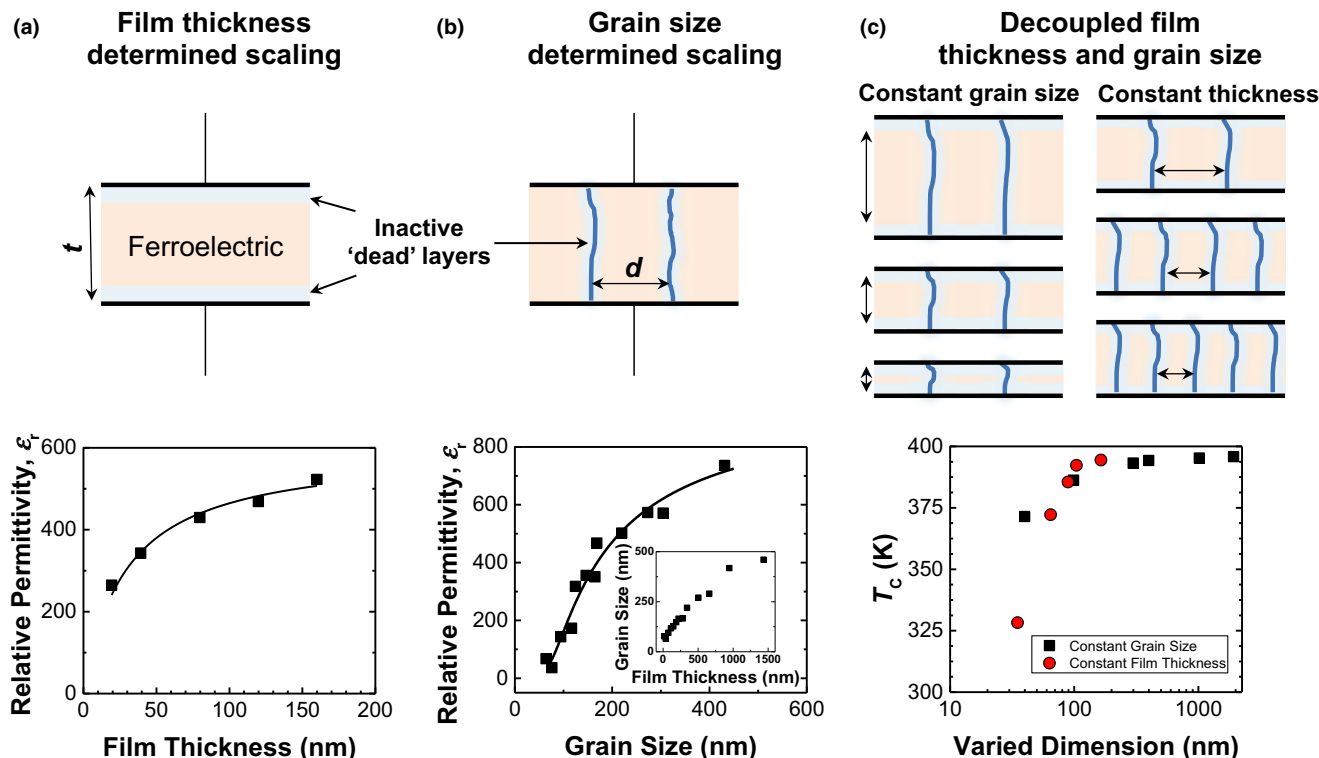


Fig. 10. Dependence of dielectric properties or ferroelectric phase transitions on film thickness or grain size for BaTiO₃ and (Ba,Sr)TiO₃. (a) Reduction in measured permittivity with decreasing ferroelectric thickness fit assuming interfacial “dead” layers at the ferroelectric-electrode interfaces using the series capacitor model.^{177,267} (b) Measured permittivity plotted against the diameter of columnar grains and fit using the series capacitor model with grain size as the controlling variable. The inset shows the commonly observed trend of grain size decreasing with film thickness.^{168,268} (c) Dependence of the ferroelectric-paraelectric transition temperature in two series of films: (■) Varied film thickness with constant grain diameter and (●) varied grain diameter with constant film thickness. Both series exhibit strong suppression of T_C below 100 nm.^{167,269}

(3) Thickness and Grain Size Scaling Effects in Thin Films with High Extrinsic Contributions

It is important to note that many of the studies on BaTiO₃-based films are for materials measured above T_C . As such, the roles of domain structure and extrinsic effects are not typically addressed. In Pb-based ferroelectric thin films, where studies of extrinsic versus intrinsic responses are more extensive, many groups have assessed the thickness dependence of properties. Thickness dependence of properties is apparent in the dielectric response and also in the piezoelectric properties.^{42,55,56,115,167–171,175,176,180–194} For several compositions of PZT (polycrystalline morphotropic phase boundary,^{180,183,185,187,188,191} polycrystalline PLaZT 12/50/50 and PLaZT 12/30/70,¹⁹⁰ polycrystalline PLaZT 5/30/70,¹⁸¹ epitaxial morphotropic phase boundary,¹⁸⁹ and epitaxial PbZr_{0.2}Ti_{0.8}O₃^{42,182}) and related materials (0.30BiScO₃–0.70PbTiO₃¹⁸⁴ and K_{0.5}Na_{0.5}NbO₃¹⁸⁶), representative properties for thin films as a function of thickness are compiled from the literature and are shown in Fig. 11. Regardless of composition, near thicknesses of ~100 nm, the permittivities change markedly as a function of film thickness. For the representative PZT compositions in this plot, the intrinsic lattice response is expected to have values spanning 200–250 and ~20–30 pm/V for permittivity and d_{33} , respectively.^{180,195,196} The higher values shown here, particularly for films thicker than 100 nm, suggest that the majority of the response can be attributed to extrinsic effects. As the film thickness decreases, contributors to extrinsic response are strongly affected by reduced thickness and approach the intrinsic lattice response. A relatively small contribution to this scaling effect is attributed to the metal-oxide interface capacitance (e.g., as described in Pintilie et al.¹⁸²), and an additional enhancement in dielectric permittivity is realized in films that contain a higher domain wall density.¹⁸²

It is generally accepted that the largest extrinsic contributions to permittivity and piezoelectric response are due to domain wall motion, though the type and extent of domain wall contributions is still debated. Both Tuttle et al. and Xu et al. proposed that most of the domain wall motion in the thickness range shown in Fig. 11 is due to the motion of domain walls separating 180° domains (ferroelectric domain wall motion, but limited ferroelastic motion).^{77,180} Bastani and Bassiri-Gharb,¹⁸⁵ on the other hand, correlate a critical thickness of 50 nm in the dielectric permittivity with the suppression of ferroelastic/ferroelectric (i.e., non-180°) domain walls, implying that non-180° domain wall motion contributes to the dramatic enhancement in permittivity of films thicker than 50 nm. The origin of the size effect in piezoelectric properties, for example, the d_{33} of thin films shown in Fig. 5(a), is less well understood. A “dynamic poling” model suggests that 180° domains can contribute to this property coefficient, though only indirect measurements of this mechanism have been made.¹⁹⁷

In addition to property reductions due to capacitive mixing rules discussed previously, grain boundaries act as perturbations on the lattice of the ferroelectric and affect the extrinsic response. Grain boundaries change the local electrical and elastic fields in the material and, as a result, will be expected to have a profound local influence on the domain structure,^{113,144,149,158,198} as discussed above for polycrystalline BaTiO₃ ceramics. Advancements in characterization instruments, including PFM, have enabled these grain-boundary domain structure and piezoresponse effects to be carefully studied. Several groups have performed PFM characterization across grain boundaries in epitaxial films on bicrystal substrates. Bicrystal substrates enable properties near grain boundaries with preselected misorientation to be characterized.^{199–203} PFM data recorded across a 24° crystallographic tilt about [001]_{pc} (where *pc* denotes pseudocubic indices) in BiFeO₃ demonstrated that grain boundaries can attract nearby domain walls and restrict the growth of the

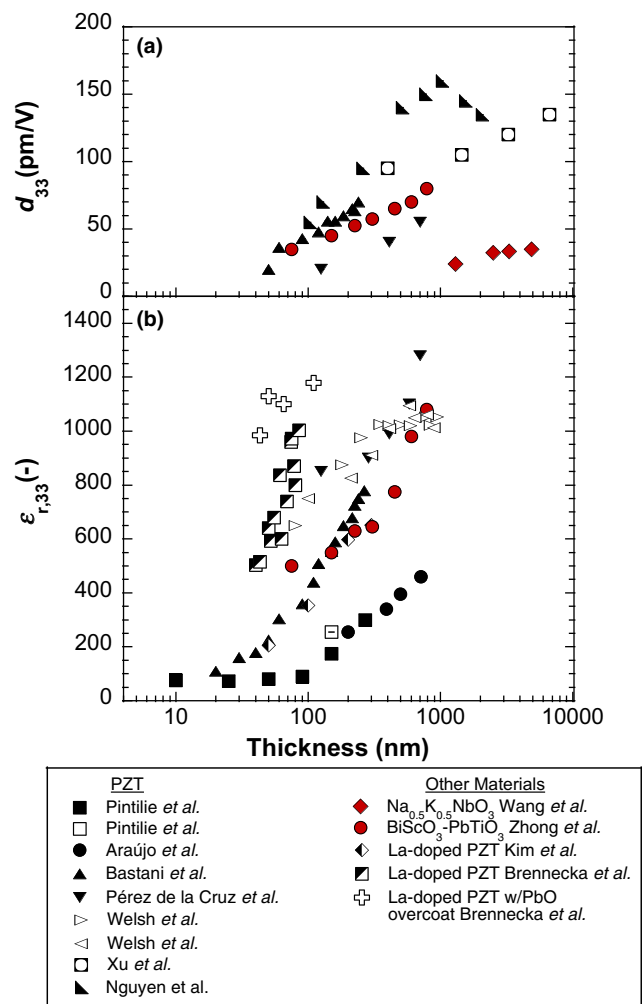


Fig. 11. The thickness dependence of room temperature (a) longitudinal piezoelectric coefficient and (b) relative permittivity in polycrystalline morphotropic-composition PZT,^{180,182,183,185,187–189,191} polycrystalline PLaZT 12/50/50 and PLaZT 12/30/70,¹⁹⁰ polycrystalline PLaZT 5/30/70,¹⁸¹ epitaxial morphotropic phase boundary PZT,¹⁸⁹ and epitaxial PbZr_{0.2}Ti_{0.8}O₃,^{42,182} 0.30BiScO₃–0.70PbTiO₃,¹⁸⁴ and K_{0.5}Na_{0.5}NbO₃¹⁸⁶ thin films extracted from several independent experimental studies. Within each dataset the crystallographic texture and preparation procedures are consistent.

energetically preferred polarization direction.²⁰³ Local electric and strain fields at grain boundaries were also reported to control the local domain structure and domain wall mobility in morphotropic and tetragonal PZT thin films.²⁰² In this case, it was demonstrated that the magnitude of the domain wall contributions to the piezoelectric properties is a function of the tilt and twist angles between the adjacent grains. Small angle grain boundaries (~10° for PbZr_{0.52}Ti_{0.48}O₃) provide local fields, which can be significantly smaller than the drive field. As a result, the domain structure can readily be changed, and local *enhancement* of irreversible motion of domain walls can be observed. In contrast, larger grain-boundary angles act as stronger pinning sites, as reflected in Fig. 12, for example,²⁰² and similar to reports from macroscopic piezoelectric characterization.¹⁵⁰ The spatial influence of a grain boundary on the pinning of domain walls is a complex function of the ferroelectric distortion, domain variants, and the strain energy in a given material. Figure 12 shows a demonstration of how these factors can be strongly dependent on composition. The reduction in piezoelectric activity near a grain boundary occurs over a length scale of ~800 ± 70 nm around the boundary itself in tetragonal PbZr_{0.45}Ti_{0.55}O₃ and only half that distance (450 ± 30 nm) for

a morphotropic phase boundary composition, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$.²⁰¹ This difference is likely to be due to the fact that the more complex domain structure possible at the morphotropic phase boundary means that local stresses and fields can be accommodated in a smaller volume.^{199,200} The large length scale associated with the grain-boundary influence, in-part, explains why scaling effects are frequently observed at length scales that are orders of magnitude larger than those associated with loss of ferroelectricity.

Thickness and grain-size-dependent scaling effects have received significant attention and there is very good agreement in the size scales over which these are observed across multiple ferroelectric material systems. Recently, signatures of ferroelectricity were identified in thin polycrystalline HfO_2 -based films.²⁰⁴ The thicknesses and grain sizes associated with this observation are relatively small compared with other, more conventional, ferroelectrics with polarization switching and piezoelectric response measured in films with thicknesses as low as 5 nm^{205,206} and less,²⁰⁷ and lateral grain sizes between 20 and 30 nm.²⁰⁸ Ferroelectricity in these materials is reported to stem from the stabilization of a noncentrosymmetric orthorhombic phase. Several possible origins for the stability of the phase have been presented, including strain,²⁰⁴ surface energy,²⁰⁹ and oxygen vacancies.²⁰⁸ All these may be expected to have a size scaling dependence and this is supported by the observation that the orthorhombic phase and ferroelectric response is observed in thin layers.

Grain boundaries, thickness, and domain structure affect the scaling of ferroelectric properties in bulk ceramics and thin films. Reductions in size tend to increase the densities of domain walls, which increase extrinsic contributions to permittivity when the domain walls are mobile. However,

regions near grain boundaries have been shown to have minimized piezoelectric response, suggesting that electronic and mechanical boundary conditions at these boundaries limit extrinsic effects. Grain boundaries also impart a biphasic microstructure with low permittivity grain boundaries in series and parallel with high permittivity grain cores. Dielectric mixing of these disparate permittivity phases results in overall decreasing response as the grain size is reduced. Finally, thickness scaling can affect the mobility of domain walls through mechanical clamping.

V. Processing-Related Scaling Effects

The processing of a ferroelectric material can have a profound effect on its resulting properties. While many of the causes of scaling lend themselves to modeling to aid in understanding of their influence (e.g., depolarization fields, mechanical constraints, dielectric mixing rules, etc.), it can be more difficult to fundamentally qualify and quantify the effects that processing-related imperfections have on resulting properties. In this section scaling effects associated with the methods by which materials are prepared are discussed.

(1) Density, Thermal Treatment, and Crystalline Quality Effects

The influence of processing has been a noted contributor to scaling effects in BaTiO_3 ceramics.^{100,152} BaTiO_3 is a refractory material, with high temperatures needed for crystallization and carbon and hydroxyl removal. In scaling effects studies, however, temperature restriction is the most commonly used method for controlling grain sizes both for bulk

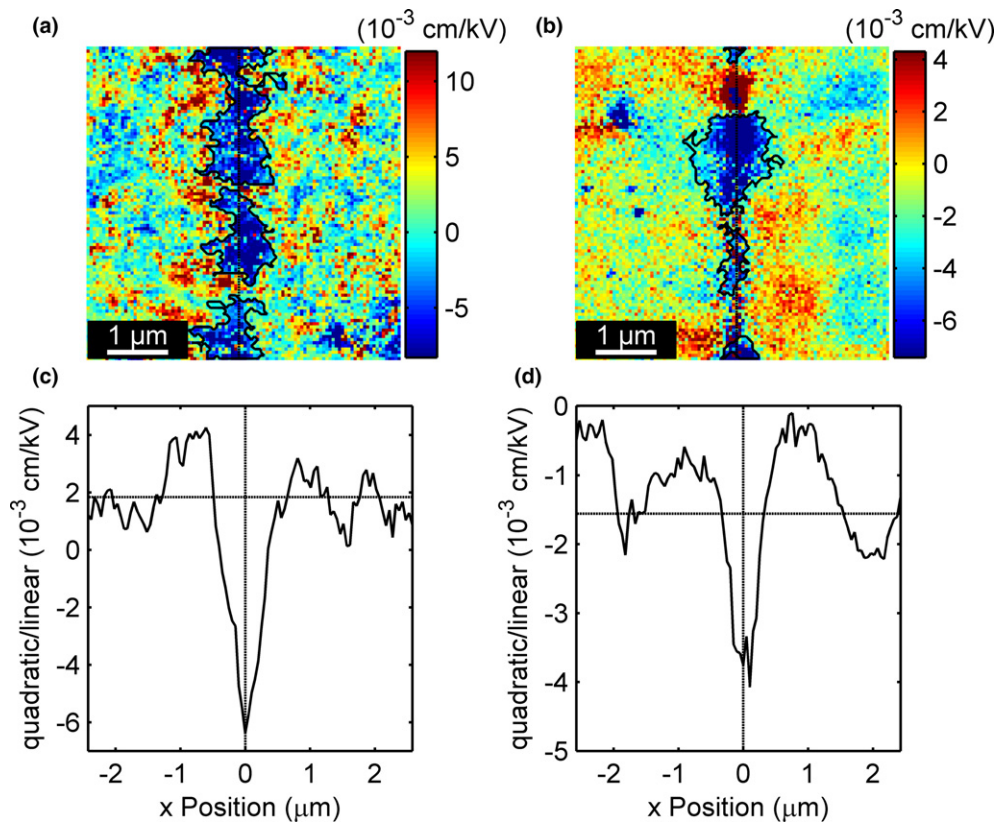


Fig. 12. Nonlinear response (quadratic divided by linear response for $d_{33,l}$) maps measured across the 24° grain boundary for (a) PZT 45/55, and (b) PZT 52/48. Dotted lines denote the location of the grain boundary and solid lines border the regions of low response across the boundary. Plots (c–d) show the nonlinear response quadratic and linear for maps averaged across y positions where (c) corresponds to map (a), and (d) corresponds to map (b). The vertical line denotes the grain boundary and the horizontal line is the off-boundary average nonlinear response. Reprinted with permission from D.M. Marincel, H. Zhang, A. Kumar, S. Jesse, S. V. Kalinin, W.M. Rainforth, I.M. Reaney, C.A. Randall, and S. Trolier-McKinstry, *Adv. Funct. Mater.*, 24, [10], 1409–1417, 2014, Copyright 2014 by John Wiley and Sons, and D.M. Marincel, H.R. Zhang, J. Britson, A. Belianinov, S. Jesse, S. V. Kalinin, L.Q. Chen, W.M. Rainforth, I.M. Reaney, C.A. Randall, and S. Trolier-McKinstry, *Phys. Rev. B*, 91, 134113, 2015, Copyright 2015, by the American Physical Society.

ceramics^{100,140,152,156,164} and films.^{113,114,167,169,172,210} Reductions in thermal budget necessarily changes the time and amount of diffusion and could lead to property depression from poorly crystallized material, impurities that were not properly removed, or high defect concentrations. Processing that results in poor density, crystallinity, or purity can lead to depressed properties and play an important role in poor properties seen in many thin film perovskite ferroelectrics.

In bulk ceramic BaTiO₃ improvements in the ability to prepare dense fine-grained material has resulted in a continual increase in measured permittivity over time. This is summarized in Fig. 13 showing the evolution of 70°C permittivity of sub-100 nm grained BaTiO₃.^{100,143,155,156,211} On this figure, the densities of the materials are provided. It is clear from this data that the consolidation and sintering process used greatly affects the density and measured permittivity and that achieving high density is critical for measuring high permittivities. Focusing on the ceramics with grain sizes between 60 and 100 nm, for example, shows a progression of increasing permittivity concomitant with increasing density as a 60 nm grain size 95% dense sample has a permittivity that is approximately 5× lower than an 80 nm grain size 98.6% dense sample. One source of difference in permittivity is the differing volumetric concentrations of grain boundaries, which would reduce permittivity due to dielectric mixing rules as discussed in Section IV, but this cannot account for such a large difference—especially considering that these two samples were prepared from the same chemical precursors and have the same nominal dopant concentrations.¹⁴³ The processing method and density of the sintered body is clearly a critical factor in determining the dielectric properties of fine-grained ferroelectrics.

Prior to ~2002, the measurement of a permittivity greater than 1000 on a BaTiO₃-based thin film was rare and was only observed on refractory single crystal or noble metal substrates.^{212–214} Indeed, some of the earliest research on BaTiO₃ films on platinized silicon substrates indicated a total lack of ferroelectricity owing to grain sizes less than 25 nm in diameter.²¹⁵ While ferroelectric BaTiO₃ thin films prepared on platinized silicon substrates were demonstrated soon thereafter, the properties of these films were dramatically reduced in comparison to their bulk counterparts.

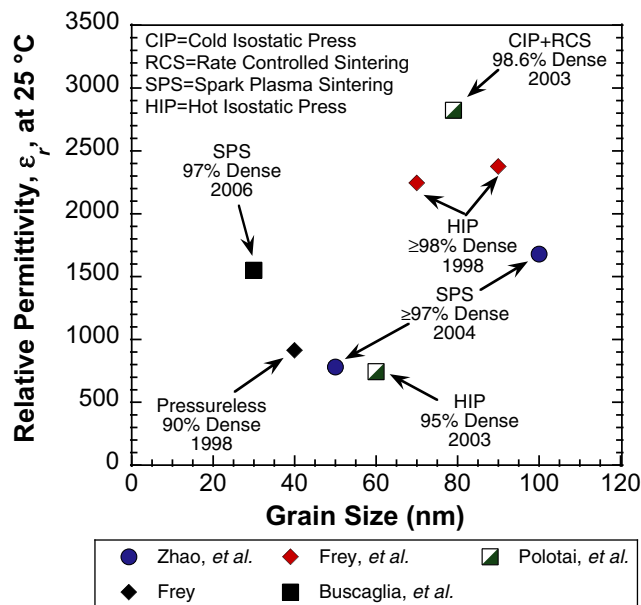


Fig. 13. Grain size dependence of 70°C permittivity for sub-100 nm grain size BaTiO₃ ceramics showing the effect of processing method and density on dielectric properties.^{100,143,155,156,211} Processes that result in lower levels of porosity result in greatly increased permittivity.

A processing advancement was made by utilizing controlled atmosphere crystallization anneals to directly integrate these films with base metal tape and foil substrates, which enabled higher processing temperatures.^{111,112,117,216} With processing temperatures up to 900°C, room-temperature permittivities in excess of 1500 were measured.^{111,112,117} To isolate the effect of processing temperature on the resulting permittivity and the microstructure a study was conducted where the measured physical grain size was compared with the crystal coherence length calculated from X-ray scattering measurements.¹¹³ It was found that the measured coherence length and grain size converged as the processing temperature increased; this increased crystallite size was correlated with increased permittivity as shown in Fig. 14. The implication of this observation was that lower temperature processes not only resulted in finer grain sizes, but that these fine grains were also more defective and these defects inhibit the response that lead to high permittivities. A graphical representation of this subgrain structure is shown in Fig. 9(b) where these defects result in crystalline regions smaller than the physical grain size. While these high permittivity results were demonstrated on foil substrates where the amount of residual strain may be minimal, recently polycrystalline BaTiO₃ and Ba_{1-x}Sr_xTiO₃ films have been demonstrated on rigid silicon and MgO substrates with permittivities ranging from 1300^{101,217} to above 2000²¹⁸ when a processing temperature of 900°C was used, demonstrating the strong effect that increased process temperatures and improved crystallinity may have on resulting properties. These process temperature-property trends are summarized in Fig. 15, where a variety of literature reports were surveyed and it was found that processing temperature was the major determinant of the final dielectric properties, regardless of measured grain size.^{114,115} For films processed at 900°C and above, bulk-like permittivities and temperature response can be achieved,^{101,108,111,113,114,219,220} however, films restricted to process temperatures below 700°C result in dielectric constants well below 1000 despite similar grain sizes and thicknesses.^{168–170,172,175,193,221–225} The effect was substrate independent, suggesting that mechanical boundary conditions cannot account for the differences. The same general trends observed in bulk ceramics (and the brick-wall capacitance model for permittivity dilution) fits data for grain size in polycrystalline films, with a predicted permittivity of 65 for 0.8 nm grain boundaries for films processed above 900°C.¹¹⁵ This grain-boundary permittivity is lower than that found for bulk ceramics,¹⁰⁰ which may indicate the additional difficulty of processing thin films (such as limited thermal budget), that electrode effects in the thin film system have been neglected, or that the grain boundaries may be effectively broader.

(2) Chemical Purity, Point Defects, and Composition Heterogeneities

Depending on the processing approach, there can be residual chemical species that result in performance reductions. For example, chemical solution preparation of ferroelectrics is attractive for its scalability and use in producing nm-scale powders, but requires care in processing to remove precursors and organics. Decreases to the ramp rate during annealing can increase the amount of crystallization relative to densification, leading to porosity.²²⁶ Furthermore, it is known that intermediate carbonate and oxycarbonate phases can form during the crystallization process, as has been observed in BaTiO₃-based powders and films.^{179,227–230} Decomposition of these carbonaceous phases can result in porosity and subsequently degraded properties. As such, many groups have explored routes to minimize the formation of these phases. For example, it has been shown that selection of the appropriate chemical precursors can avoid carbon-containing phases or decrease the temperatures at which

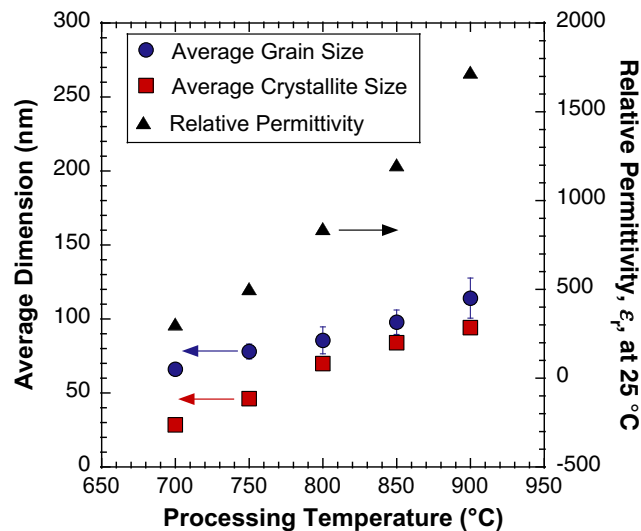


Fig. 14. Processing temperature dependence of grain size, crystal coherence length, and room-temperature relative permittivity for BaTiO₃ films prepared on copper foil substrates.¹¹³ Adapted with permission from Ihlefeld et al., *J. Appl. Phys.* 103, 074112 (2008). Copyright 2008, AIP Publishing, LLC.

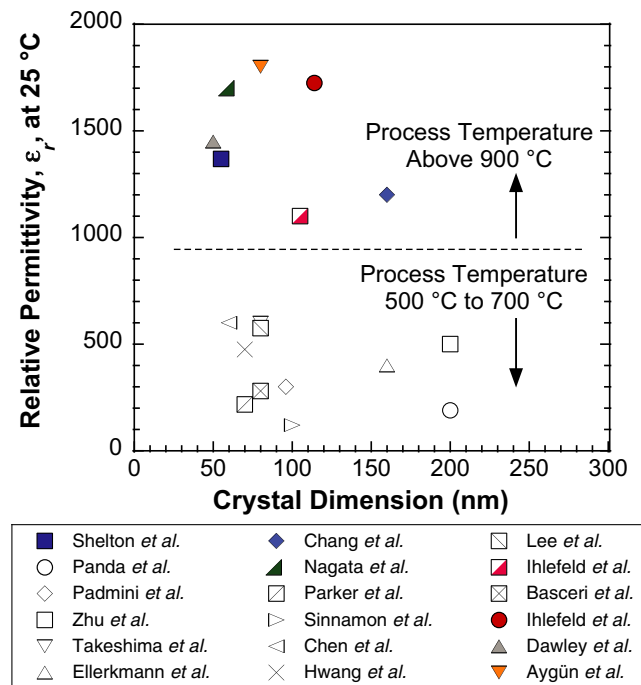


Fig. 15. Room-temperature relative permittivity for polycrystalline BaTiO₃ and (Ba,Sr)TiO₃ thin films as a function of crystal dimension extracted from several experimental studies. Films processed at 700 °C and lower^{168–170,172,175,193,221–225} possess lower relative permittivities and those processed at 900 °C and higher^{101,108,111,113,114,219,220} possess much higher relative permittivities. Adapted with permission from Aygün, et al., *J. Appl. Phys.* 103, 084123 (2008). Copyright 2008, AIP Publishing, LLC.

they decompose and result in improved density and increased permittivities.^{231–233} Most of these studies relied on *ex-situ* X-ray diffraction or infrared spectroscopic analysis to identify these phases. Aygün et al. used *in situ* gas analysis during annealing of chemical solution deposited film on copper foils to analyze decomposition of carbonates and crystallization of BaTiO₃.²³⁴ Slow ramp rates resulted in crystallization at lower temperatures, cracking, and lower device yields. Importantly, it was found that in the reducing atmospheres

necessary for integration with inexpensive base metal electrodes, complete carbon removal occurred at temperatures above where many thin film systems are processed. In addition, lower oxygen partial pressures increase the decomposition temperature of the intermediate carbonate phases.^{234,235} Residual carbon can change the local oxygen partial pressure, result in the potential for increased concentrations of oxygen vacancies, and may reduce reliability.^{8,9,236} The choice of chemical precursors and solvent can also lead to systems with better densification or carbon removal pathways.²³⁶ Utilizing a high-temperature crystallization step after each coating step enables significant improvements to film density^{111,179} and by utilizing high temperatures that enable improved carbon-species removal and increases in crystalline quality, BaTiO₃ films with room-temperature permittivities of 3000 may be realized.¹¹⁵ When controlling for the total thermal budget, the grain size increases only moderately, but the properties undergo large improvements. This suggests that residual carbon contaminants can lead to decreases in measured properties. Optimization of growth and processing can also make large differences in physical vapor deposited films, where deposition of Ba_{1–x}Sr_xTiO₃ films on flexible nickel foils showed large improvements in permittivity with increased deposition temperature without varying the subsequent high-temperature anneal.¹¹⁴

Local stoichiometry and chemical gradients are also known to affect the measured dielectric and piezoelectric properties of thin films and bulk ceramics. In thin films, the presence of chemical gradients in morphotropic-composition PZT typically results in depressed properties as has been shown in piezoelectric,²³⁷ dielectric,^{101,238} and ferroelectric response.¹⁰¹ One source of chemical gradients and degraded response in films is diffusion of species, such as titanium, from the electrode stacks^{239–242} that have resulted in decreased performance in not only PZT,^{101,238,243} but also BaTiO₃,¹⁰¹ BST,²⁴⁴ and SrBi₂Ta₂O₉ (SBT) films.²⁴⁵ Elimination of the chemical gradient or foreign species in the films has been shown to result in more bulk-like responses, including high piezoelectric coefficients in morphotropic PZT,²³⁷ high remanent polarizations in SBT,²⁴⁵ and bulk-like permittivity in BaTiO₃.¹⁰¹ An additional source of gradients in PZT has been postulated to arise from preferential nucleation of PbTiO₃ over PbZrO₃²⁴⁶ and is used to explain so-called sawtooth composition profiles through the thickness of films prepared via multiple deposition and crystallization annealing steps.^{237,247,248} Recent work has shown that these gradients may be influenced by the heating method used to crystallize films. In particular, while conventional furnace heating did not result in gradient formation, use of a rapid thermal annealer did result in chemical gradients.²⁴² Finally, it should be noted that in special cases chemical gradients have been reported to enhance response, such as formation of superlattice-like structures with increased polarization response²⁴⁸ and epitaxial chemically graded films with reduced permittivity but stable polarization²⁴⁹ and enhanced local piezoresponse.²⁵⁰

Processing-related point defects must also be considered as potential sources of scaling effects in ferroelectrics. Point defects are potential domain wall pinning centers, which would reduce extrinsic contributions to the dielectric and piezoelectric response.¹⁸ By altering the lead stoichiometry of polycrystalline PZT films of morphotropic and tetragonal compositions after they had crystallized into the perovskite phase, the dielectric and piezoelectric properties were shown to be weakly dependent on lead content in PZT thin films. It was found that lead vacancies reduced domain wall motion at modest electric fields, but that the effects were minor.²⁵¹ Lead nonstoichiometry was qualitatively shown by Brennecke and Tuttle to result in decreased dielectric response in lanthanum-doped PZT films.¹⁹⁰ By incorporating a thin PbO overcoat on their films during the crystallization anneal, the room-temperature permittivity of films of several different

compositions was found to increase (it is important to note that fluorite or pyrochlore phases were not observed, which would result in a decreased measured capacitance) [G. Brennecke, "Personal Communication" (2015)]. This increase is reflected in Fig. 5(b) where the PbO overcoat samples exhibit less thickness scaling than those prepared without an overcoat. In the absence of grain boundaries, Paruch et al. found that oxygen vacancies in epitaxial PZT 20/80 films play an important role in domain wall pinning, even enabling stabilization of very fine domains in films with high oxygen vacancy concentrations.²⁵² Oxygen nonstoichiometry in BaTiO₃ based films also can manifest in reduced dielectric response. Films prepared in reducing conditions without further annealing in higher oxygen partial pressures display permittivities that are 75% that of the same film after a reoxidation anneal.²⁵³ The oxygen vacancies in these films likely also pin domain wall motion, resulting in reduced extrinsic contributions to permittivity. Combined, these studies show that control of stoichiometry—even for nominally phase-pure thin films—is critical to minimizing property degradations that are commonly attributed to scaling effects.

Processing-related point defects and chemical gradients are not isolated to thin film ferroelectrics. For example, chemical inhomogeneity has been observed in PZT ceramics^{254–256} and can substantially affect piezoelectric coupling factors and phase transition behavior.^{254,255} Recently, significant strain gradients attributed to microscale chemical inhomogeneity have been identified in BST ceramics.²⁵⁷ While this inhomogeneity was shown to affect apparent flexoelectric response, its implications on dielectric and piezoelectric response should not be ignored on the basis of strong effects observed in films. Oxygen point defects in BaTiO₃ compositions can have deleterious effects on permittivity and leakage current, an effect that has been widely studied in the development of both positive temperature coefficient of resistance materials and capacitors.^{8, 125,258–265} Finally, as the concentration of oxygen vacancies is a function of distance from grain boundaries owing to grain-boundary Schottky barriers,²⁶⁶ the effects of point defects can be anticipated to become increasingly complex as the grain size is reduced.

Scaling effects are commonly studied in polycrystalline systems by decreasing the processing temperature used to minimize grain growth. Doing so may result in increased porosity and lesser crystalline perfection. In both bulk and thin film systems, porosity and poor crystalline quality can result in decreased responses commonly attributed to scaling. Chemical impurities and composition heterogeneities can also exist in bulk and film systems. The origin of these chemical and structural imperfections can stem from the originating chemical precursors, substrate metallization stacks, and processing atmospheres. These impurities may ultimately result in degraded responses and care must be taken to decouple these from observed property changes as dimensions scale.

VI. Conclusions

In this review article, we have provided the current state of understanding of scaling effects in perovskite ferroelectric materials. While intrinsic size effects establish the absolute limit to the number of unit cells necessary to have a stable ferroelectric phase, many extrinsic scaling effects can contribute to property reductions being observed at much larger sizes. These extrinsic scaling effects include: (1) electrode charge screening and depolarization fields, (2) mechanical clamping affecting phase transition temperatures and domain wall motion, (3) grain boundaries diluting the dielectric response, (4) grain boundaries inhibiting domain boundary motion, (5) processing temperature reductions resulting in crystal imperfections, and (6) point defects and chemical inhomogeneity. There are several means by which these scaling effects can be minimized to realize higher performance properties. These include: (1) selection of material-system-

specific electrodes that minimize depolarization effects, (2) minimizing mechanical strain via substrate selection and mechanical clamping via microfabrication in thin films, (3) increasing grain size to increase both domain wall populations and mobility and reduce domain boundary dilution effects, and (4) realizing high crystalline quality, low defect density materials through careful processing control. The state of understanding of scaling effects has increased substantially over the last two decades and it can be anticipated that as increasingly sophisticated processing methods for nanoscale materials and tools for their analysis are developed, our degree of understanding the complex interplay of intrinsic size effects and extrinsic scaling effects will be further improved.

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