

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.