

FERROELECTRICITY IN PEROVSKITES BY ATOMIC-LEVEL SIMULATION

SCIENTIFIC ACHIEVEMENT: We have developed and validated an atomic-level approach to the simulation of the phase behavior of perovskite materials including KNbO_3 and BaTiO_3 , both of which manifest three different ferroelectric phases, and KTaO_3 and SrTiO_3 , both high-dielectric-constant paraelectrics. We have used this approach to answer a number of important questions associated with ferroelectric/paraelectric composites (multilayers and solid solutions) and ferroelectric switching.

One key question is the nature of the coupling between the ferroelectric and paraelectric components of nanocomposite materials. We have elucidated one aspect of this issue by determining the ferroelectric and dielectric properties of coherent $\text{KNbO}_3/\text{KTaO}_3$ superlattices. An investigation of the switching behavior shows that for $n > 24$ unit cells, each KNbO_3 layer behaves essentially independently. For $n < 12$, the KNbO_3 layers interact so strongly with each other that the superlattice essentially behaves as a single artificial ferroelectric structure. Consistent with experiments on this system, the Curie temperature for the transition from a polarized to unpolarized state in the modulation direction decreases approximately linearly with modulation length for $n > 12$; for smaller modulation lengths, it is essentially n -independent. We have elucidated a second aspect of the physics of ferroelectric/paraelectric nanocomposites in the context of random solid solutions, showing that the rather diffuse phase transition in $(\text{Ba,Sr})\text{TiO}_3$ can be understood purely in terms of the interaction between paraelectric and ferroelectric components, even in the absence of composition fluctuations over long length scales.

The fundamental property of a ferroelectric is the ability to switch the direction of polarization by the application of an external electric field. We have elucidated the dynamics of the simplest kind of switching behavior, that of a monodomain crystal. We found that under most conditions, switching in KNbO_3 takes place by the rotation of the polarization through a sequence of intermediate structures with symmetries that match those of the perfect crystal at various temperatures.

SIGNIFICANCE: There is a long history of using atomic-level simulation to explore the microstructure-property relationship in metals, semiconductors and ceramics. Our simulations show that the properties of ferroelectric/paraelectric composites are determined by the interplay between the strong electric fields associated with the intrinsic electric dipoles of the ferroelectric with the induced polarization in the paraelectric. The materials specific atomic-level potentials for the $\text{KNbO}_3/\text{KTaO}_3$ system, and our recently developed potentials for the $\text{BaTiO}_3/\text{SrTiO}_3$ system, open up to simulation a large number of problems on the interplay of ferroelectricity and microstructure and on the dynamical behavior of ferroelectric materials.

REFERENCES:

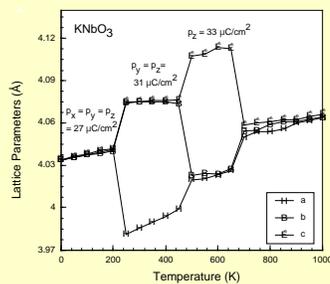
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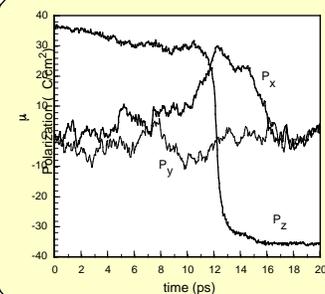
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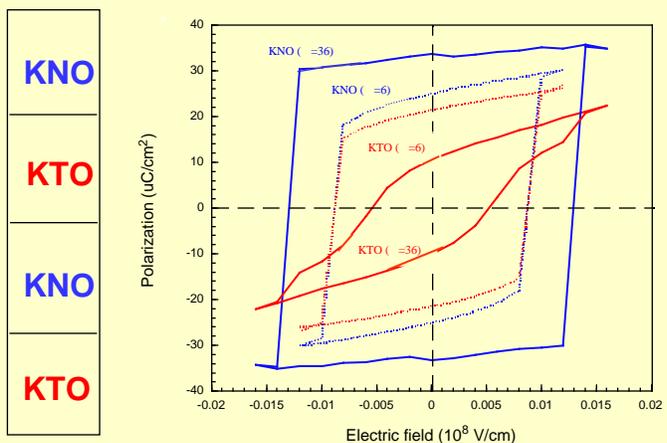
Ferroelectricity in Perovskites by Atomic-Level Simulation



Atomistic simulation reproduces phase diagram and transition temperatures of KNbO₃



Monodomain single crystal switches by polarization rotation



For small modulation lengths, Λ , superlattice behaves as a single artificial ferroelectric structure; for longer modulation lengths, paraelectric and ferroelectric components act almost independently

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