ICAM2009
11th International Conference
on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25

Physical Phenomena in Ferroelectric Solid Solutions

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Abstract – A classical 2-4-6 Landau polynomial is used to describe the generic composition-temperature diagram of ferroelectric solid solutions that display a morphotropic boundary (MB). The theory accounts for disparate physical phenomena observed in morphotropic systems. These phenomena include a sharp reduction in the ferroelectric domain size, the appearance of a dipole glass state, the occurrence of intermediate ferroelectric phases and large extrinsic contributions to the electromechanical properties. The curving of the MB line, the nearly continuous transitions between adjacent ferroelectric phases and the change in the order of the paraelectric to ferroelectric transitions with composition also arise naturally in the theory.

The generic case of a ferroelectric solid solution is considered wherein different symmetry phases located at opposing ends of the diffusionless composition-temperature phase diagram are separated by a morphotropic boundary (MB). It is shown that the classical Landau theory of weak first order phase transformations automatically predicts an extreme reduction in the anisotropy of polarization near the MB. In the lowest-order approximation the isothermal composition change producing the rhombohedral to tetragonal transition along the MB line is dictated by the condition that the polarization anisotropy energy vanishes. Under this condition there is a drastic decrease in domain wall energy that results in the formation of ferroelectric nanodomain states that produce the same diffraction pattern attributed to homogeneous monoclinic phases. The electric field or stress induced reconfiguration of these nanotwins necessarily produces extrinsic contributions to the dielectric and electromechanical properties. The spherical degeneration of the polarization direction also predicts the formation of a polar glass-like state wherein the nanodomains may assume irregular shapes and may exhibit high configurational sensitivity to external forces. A small lifting of the orientational degeneracy of the polarization leads to differing phase diagram topologies wherein an orthorhombic phase may interleave the rhombohedral and tetragonal phase fields. The curving of the MB line, the nearly continuous transitions between adjacent ferroelectric phases and the change in the order of the paraelectric to ferroelectric transitions with composition also arise naturally in the theory. If diffusional processes are operative, all equilibrium boundary lines of the diffusionless phase diagram must be replaced by two-phase fields. Possible topologies of the equilibrium MB phase diagram illustrating these two-phase equilibrium fields are computed. The theory provides insights into the influence of microstructure on the dielectric and piezoelectric properties of morphotropic ferroelectric solid solution systems and the implications for processing-property relations in these materials will be discussed.

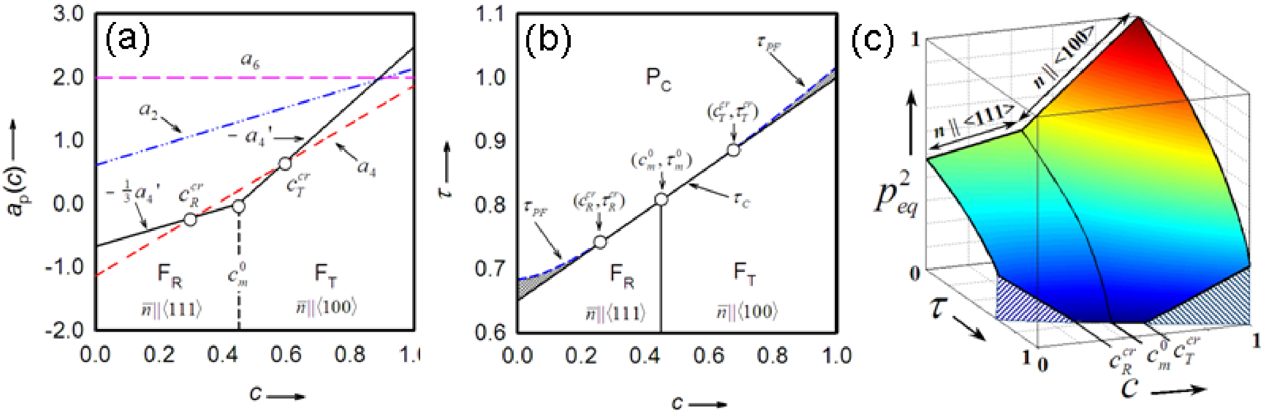

Figure 1: Predictions of the low-order Ginzburg-Landau theory with an isotropic sextic term, **a)** Representative composition variation of the Landau coefficients **b)** Topology of the high temperature portion of the generic diffusionless morphotropic phase diagram and **c)** Variation of the equilibrium saturation polarization in the composition-temperature plane.