Acta Materialia 112 (2016) 1–10

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

# Instability criterion for ferroelectrics under mechanical/electric multi-fields: Ginzburg-Landau theory based modeling

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ARTICLE INFO

*Article history:*
Received 18 December 2015
Received in revised form
10 March 2016
Accepted 16 March 2016

*Keywords:*
Instability criterion
Ferroelectric material
Ginzburg-Landau theory
Phase-field model

ABSTRACT

Ferroelectric materials interact with not only electric fields, but also with mechanical stress/strain through intriguing cross-coupling between ferroelectric polarization and ferroelastic strain. Such mechanical and/or electric multi-field interactions allow symmetry breaking of the rotationally invariant switching field and cause a variety of complicated instability phenomena in ferroelectric systems, e.g., super switching of in-plane ferroelectric nanodomains in strained thin films, labile and ultrafast switching of ferroelastic nanodomains, and ferroelectric polarization reversal via successive ferroelastic transitions. To systematically understand the nature of instabilities in ferroelectrics, here, we propose an analytical method based on Ginzburg-Landau theory to enable rigorous description of any type of instability in arbitrary morphologies and complex microstructures under a finite electric field and/or mechanical loading. The present theory yields, as an instability criterion, the condition that the minimum eigenvalue of the Hessian matrix of potential energy with respect to displacements, electrical potential, and polarization vectors must be zero. In addition, the corresponding eigenvector represents the polarization behavior at the onset of instability, which is successfully validated by application of the criterion to domain switching and successive ferroelastic transitions in $PbTiO_3$ ferroelectric thin film under electrical and mechanical excitation, respectively. This approach thus provides a novel insight into the cause of instability in ferroelectrics. In addition, the proposed criterion is scale-independent, which enables elucidation of the nature of various types of instability in arbitrary ferroelectric systems so that complicated instability issues in practical situations can be addressed.



## 1. Introduction

Ferroelectric materials are increasingly being considered as critical components in many advanced technologies, such as nonvolatile random access memory (FeRAM) devices [1,2], sensors, actuators, and transducers in micro (nano) electromechanical systems (MEMS/NEMS) [3,4], due to their large ferroelectricity and related electromechanical properties including a large piezoelectric response and high dielectric constant. The utility of ferroelectrics is derived from the ability to reorient or switch the spontaneous polarization between equivalent states under an applied electric field and/or mechanical loading, and by the coupling of such transition to other material properties such as strain [5,6], magnetic order [7], and surface charge [8]. Thus, instability in ferroelectric systems, viz., a rapid or catastrophic change in polarization ordering or reversal of the polarization vector with respect to the multi-fields that shift the system to another configuration with lower energy, essentially characterizes the polarization behavior of materials and leads to diverse functionalities or the critical malfunction of devices. Therefore, loss of stability in the polarization configuration becomes the general mechanism that underlies a wide variety of macroscopic and microscopic features of considerable importance with respect to the behavior of ferroelectric materials under multi-field excitation. However, the instability in ferroelectric materials is generally complicated due to coherent nonlinear interactions between ferroelectricity and ferroelasticity [9–12], which critically prevent further exploitation of the advantageous aspects of these materials and the avoidance of problems associated with instability. Therefore, understanding the nature of

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[1] Equal Contribution.

http://dx.doi.org/10.1016/j.actamat.2016.03.081
1359-6454/

the instability is both scientifically interesting and technologically important for ferroelectric materials.

The Ginzburg-Landau theory was proposed on the basis of the fundamental principles of thermodynamics and kinetics to describe the dynamic behavior of ferroelectrics using a polarization vector as an order parameter [13–16]. Phase field modeling based on the Ginzburg-Landau theory has been commonly used to study domain structures in ferroelectric materials, and polarization switching under static electric field and/or mechanical loading [17–21]. In recent years, phase field modeling has been extended for simulations in real-space [22–27], which has enabled any ferroelectric structures with arbitrary geometries and boundary conditions to be addressed [28,29]. Although the phase field model provides an unprecedented look at the temporal and spatial evolution of polarization, the absence of theory to describe instability in ferroelectric systems makes it difficult to capture the onset of instability events that occur not only globally but also more often locally. Therefore, an analytical criterion for instability in ferroelectrics is essential to detect their onset, from local to global events.

Various different criteria, such as the Maxwell stability criterion, lattice stability criteria, and phonon soft modes, have been proposed to separately describe each type of mechanical instability, including kink banding, buckling, dislocation, cleavage fracture, delamination of thin film from a substrate, and highly disordered amorphous metals [30–36]. We have previously proposed a criterion to rigorously describe the onset of mechanical instability and the deformation mode at the instability in arbitrary structures by explicitly taking into account the total energy of the system including the potential energy and work done by an external load and/or constraint with respect to all the degrees of freedom (DOFs) of the system [37–41]. The advantage of the proposed theory is the capability to elucidate the nature of various mechanical instabilities in arbitrary structures without limitations or assumptions and its flexibility for other systems with different DOFs [42–45]. Thus, it should also be possible to develop a criterion for instability in ferroelectric systems by extending this theory through the incorporation of the displacement, electrical potential, and polarization DOFs into the formulation.

In this paper, we propose a criterion for instability in a continuum ferroelectric system by explicitly taking into account the total energy of the system including the potential energy and work done by an external field with respect to the displacement, electrical potential, and polarization DOFs on the basis of the Ginzburg-Landau theory. Our theory gives an instability criterion where the minimum eigenvalue of the Hessian matrix of potential energy is zero. The proposed criterion is validated by application of the criterion to several situations of interest, such as domain switching in ferroelectric $PbTiO_3$ thin film under an electric field and successive ferroelastic transitions under mechanical excitation. We further demonstrate that the eigenvector according to the lowest eigenvalue directly yields the direction of polarization change associated with the instability mode, which readily allows identification of the type of instability.

## 2. Proposal of instability criterion for ferroelectrics

### 2.1. Theory of instability in ferroelectrics

Consider a finite element of a continuum ferroelectric system consisting of $N$ nodes under an external electric field and/or mechanical load. The potential energy of the system $U$, can be described by the continuous displacements $\boldsymbol{d}$, electrical potential $\boldsymbol{\phi}$, and polarization vectors $\boldsymbol{P}$,

$$U = U(\boldsymbol{d}, \boldsymbol{\phi}, \boldsymbol{P}), \tag{1}$$

where

$$\boldsymbol{d} = \left(d_x^1, d_y^1, d_z^1, d_x^2, d_y^2, d_z^2, \ldots, d_x^N, d_y^N, d_z^N\right)^T, \tag{2}$$

$$\boldsymbol{\phi} = \left(\phi^1, \phi^1, \ldots, \phi^N\right)^T, \text{ and} \tag{3}$$

$$\boldsymbol{P} = \left(p_x^1, p_y^1, p_z^1, p_x^2, p_y^2, p_z^2, \ldots, p_x^N, p_y^N, p_z^N\right)^T. \tag{4}$$

In the above, $d_i^\alpha$, $\phi^\alpha$, and $p_i^\alpha$ denote the displacement, electrical potential, and the polarization vector at the node $\alpha$ (=1, 2, …, N) in the $i$ (=$x$, $y$, $z$) direction. The irreducible number of displacement DOFs in the system is $I_R = 3N - 6$ because the DOFs for the rigid body translation (3) and rotation (3) are subtracted from the total DOFs of the node displacements (3N). The irreducible number of electrical potential DOFs is $I_\phi = N - 1$, since one nodal DOF for the potential should be fixed to represent connection to ground, i.e. zero voltage. On the other hand, the number of polarization DOFs is $I_P = 3N$. Therefore, the total irreducible DOFs in the system is $I = I_R + I_P + I_\phi = 7N–7$. Here, an arbitrary deformation and/or perturbation of the polarization vector for the system can be represented by a change in the following $m$-dimensional vector $\boldsymbol{X}$, which consists of all DOFs:

$$\begin{aligned}\mathrm{X} &= \left(d_z^2, d_x^3, d_y^3, d_x^4, d_y^4, d_z^4, \ldots, d_x^N, d_y^N, d_z^N, \phi^1, \phi^2, \ldots, \phi^N, p_x^1, p_y^1, p_z^1, p_x^2, p_y^2, p_z^2, \ldots, p_x^N, p_y^N, p_z^N\right)^T \\ &= (X_1, \ldots, X_i, \ldots, X_m)^T.\end{aligned} \tag{5}$$

When the system is at equilibrium ($\boldsymbol{X} = \boldsymbol{X}_0$) under a static external electric field and/or mechanical load, the total energy of the system $\Pi$, consists of the potential energy $U$, the work done by an external mechanical load $W$, and the work done by an external electric field $\Phi$, and is given by:

$$\Pi = U + W + \Phi \tag{6}$$

The total energy of the system in terms of an infinitesimal deformation and/or perturbation of the polarization vector, $\Pi(\boldsymbol{X}_0 + \Delta\boldsymbol{X})$, can be described by the Taylor series expansion of the total energy, $\Pi(\boldsymbol{X}_0)$, by $\Delta\boldsymbol{X}$, and is given by:

$$\Pi(\mathrm{X}_0 + \Delta\mathrm{X}) = \Pi(\mathrm{X}_0) + \sum_{k=1}^{m} \left.\frac{\partial \Pi}{\partial X_k}\right|_{\mathrm{X}=\mathrm{X}_0} \Delta X_k + \frac{1}{2}\sum_{k=1}^{m}\sum_{l=1}^{m} \left.\frac{\partial^2 \Pi}{\partial X_k \partial X_l}\right|_{\mathrm{X}=\mathrm{X}_0} \Delta X_k \Delta X_l + \ldots \tag{7}$$