Doctoral School on Engineering Sciences
Università Politecnica delle Marche

Extended summary

A Mechanical Model for Ferroelectric Materials: from atomic scale to finite elements

Curriculum: Architettura, Costruzioni e Strutture

Author

Moreno Paciaroni

Tutor

prof. Fabrizio Davì

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Abstract. We deal with the constitutive modeling of the ferroelectric materials, which are used in a lot of applications. We would establish a conceptual link between the atomic scale and the engineering one by a thermodynamic and microstructural model. Some original approaches which we are used lead to interesting results about the phase transitions

Keywords. Constitutive Theory, Ferroelectric Materials, Landau-Devonshire Potentials, Phase Transitions.

1 Problem statement and objectives

Ferroelectric materials are widely used in many applications such as sensors, actuators and non-volatile memories [1]. As piezoelectric devices, they are mainly used in the Structural Control in Civil Engineering. Other interesting and "everyday life" applications concern pressure sensor in the touch pads of mobile phones and pick up devices that converts mechanical vibrations to an electrical signal which can then be amplified, recorded and broadcast.
In recent years, an ever-increasing theoretical investigation generates many analytical and numerical implementations. Single-crystal specimens may be modelled in an easier way than polycrystalline ones, but the technological process is very hard and expensive, so that both are considered. Different approaches are followed depending on what one focuses on, from the atomic level to the macroscopic engineering one. Atomistic models describe the intrinsic behavior and have led to a great improvements in the chemistry of ferroelectric materials; macroscopic phenomenological models capture the empirical static and time-independent behavior.
The present work lies at the interface of two apparently disjointed approaches: it is a thermodynamic and microstructural model that provides a conceptual link between the atomic and the engineering scales.
Lead zirconate titanate ferroelectric ceramic $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and barium titanate $BaTiO_3$ are the archetypal ferroelectric materials which we will refer to throughout the work.

2 Research planning and activities

The research planning had three main sections:
- Background and State of Knowledge: I studied many literature and it was critically evaluated. Moreover I attended some conferences and workshops to reach information about the actual developments on the topics.
- Specific Aims: I clearly declared the proposed researches and how I was going to carry out them.
- Progress Reports: for each topic I made a short report or a paper to attest the developments of the work. Making use of these reports, some works for publications and conferences are emerged.

3 Analysis and discussion of main results

The most important feature of a ferroelectric material is the transition that it undergoes from the paraelectric phase to the ferroelectric one when it is cooled under the Curie temperature: as a result, a spontaneous polarization onsets and it is accompanied by an electric self-field and a spontaneous strain.
Most of the ferroelectric materials exhibits a cubic crystallographic point group in the paraelectric phase and a lower symmetry in the ferroelectric phase: within the Cauchy-Born rule this reflects the distortion of the crystal lattice at the macroscopic scale. The associated

electrostatic and elastic energies are reduced by means of the formation of domains, i.e. uniformly polarized regions in which electric dipoles are aligned in the same direction.
This process does not go on indefinitely, since a certain amount of energy is stored at the so-called domain walls: the latter are thin interfaces (only a few lattice constants) and within them the spontaneous polarization will decrease in magnitude, passing through zero, and increase on the other side with opposite sign. Domain thickness does not approach zero, in fact it has a finite dimension which arises from the competition between the energetic terms. At the equilibrium, ferroelectric materials have a null net polarization.
In order to exhibit piezoelectric properties, the spontaneous polarization must be reoriented in the same direction by applying strong electric fields at high temperature below the Curie point: this process is called domain switching or polarization reversal. The magnitude of the electric fields depends on the size of the grains and of the domains and on the symmetry point group. One of the most widely used ferroelectric material is the lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) which shows a cubic point group in the paraelectric phase above 650K, whereas the symmetry in the ferroelectric phase is defined by the composition of the ceramic: titanium-rich compositions favor cubic-to-tetragonal transition and zirconium-rich compositions which favor cubic-to-rhombohedral transition. Close to the morphotropic phase boundary a stable monoclinic phase was recently discovered [11] and it is at the origin of the exceptional properties of the PZT: indeed such compositions are characterized by a very large piezoelectric coupling between electric and mechanical variables related to the presence of a maximum in the dielectric constant, an ease of poling with a large number of reorientable polarization directions and a maximum mechanical compliance.

3.1 From Atomistic Models to Continuum Mechanics

In this Chapter we give an overview about the polarization [4] and we show why the classical theory is enough for us in place of the modern one [5]. Then we propose an original approach to establish a conceptual link between the atomistic and the macroscopic continuum models: to this effect, we begin from the Density Functional Theory which is used in the solid state physics to describe the structure of complex atoms, molecules and crystals and their interactions. The result is the following Ferroelectric Functional:

$$F_{FE}(p,\mathrm{F}) = F_d(p) + F_\sigma(\mathrm{F}) + F_p(p,\nabla p) \qquad (1)$$

where p is the polarization vector field and F is the deformation gradient. The three terms on the right hand side represent in order the depolarization energy, the elastic energy and the exchange-correlation energy related to the long-range interactions between electric dipoles.
The solution, i.e. the equilibrium state of the ferroelectric material, is reached by the minimization problem in the Sobolev Space $W^{1,2}$.

3.2 Landau-Devonshire Potentials

In this Chapter we introduce the Landau Theory for phase transitions within the context of ferroelectric materials [7,8]. We consider both the one dimensional model and the three dimensional one with a cubic reference configuration. Then we propose an original approach in which below the transition temperature (and accordingly in a ferroelectric

phase) the parameters of the crystallographic potential depend on the composition of the ceramic: starting from a monoclinic reference configuration we attempt to describe all the possible symmetries with a fourth-order expansion of the spontaneous polarization:

$$W(p_i, p_j, p_k) = W_0 - \frac{1}{2}\left[\alpha_1\left(p_i^2 + p_j^2\right) + \alpha_2 p_k^2\right] + \\ + \frac{1}{4}\left[\beta_1\left(p_i^2 + p_j^2\right) + \beta_2 p_k^2\right] + \frac{1}{2}\left[\beta_3 p_i^2 p_j^2 + \beta_4\left(p_i^2 + p_j^2\right)p_k^2\right] \tag{2}$$

By the minimization problem we obtain the magnitude of the spontaneous polarization and the preferred crystallographic directions: using this results we plot a set of phase diagrams which are able to describe all the symmetries of the most of ferroelectric materials included PZT ceramic.

3.3 Twins and Domain Walls

Because of the formation of domains, different deformations associated with different polarizations may occur within the same grain: for this reason we study the compatibility at the interface between ferroelectric variants through the well-known Hadamard's conditions [9] or the Ericksen-Silhavy condition [10].
Extending the results contained in [2,3], we give a complete description of twins arising in PZT and in $BaTiO_3$ and some other non generic non conventional twins which are predicted by our developments from the Landau theory:
- tetragonal-monoclinic twins;
- rhombohedral-monoclinic twins;
- tetragonal-orthorhombic twins;
- orthorhombic-monoclinic twins.

Some authors studied twins between rhombohedral and finely twinned laminate tetragonal variants [12]: in the present work we show some further results about the symmetry whose solutions exhibit. In particular:
- two concentration σ and $(1-\sigma)$ are possible;
- a solution for a concentration is related to the solution of the other concentration by a rotation or a reflection.

Moreover we obtain the domain wall angle by applying the weak condition on the solenoidal electric displacement field.

3.4 Minimization

In this Chapter we deal with the minimization of the ferroelectric functional and we obtain the Euler-Lagrange equations, which are integro-differential ones. We propose a one-dimensional model on which both the stability and the finite element analyses are performed. From the first one we reach the Duffing nonlinear equation, whereas from the second one we obtain solutions close to the square wave.

4 Conclusions

The approach used to model the electromechanical behavior of ferroelectric materials allows for any further development in a natural way: a better representation of the exchange-correlation energy which will be take into account some secondary effects that have been neglected so far.
The Landau-Devonshire potential compatible with the monoclinic phase does not predict the triclinic phase: in fact, the triclinic polarization has not been observed so far. However, if the exceptional properties of the PZT near the morphotropic phase boundary are related to the existence of a monoclinic phase, a triclinic ferroelectric material will be even better. A further development of our approach allows to describe all the possible phase transitions starting from the triclinic configuration.
The exceptional properties of PZT in composition close to the morphotropic phase boundary are related to the existence of the monoclinic symmetry: the crystallographic potential is minimized along 24 different directions, so that a monoclinic ceramic is easy to pole and the resulting piezoelectric material is highly performing. Actually it is well-known that an appropriate amount of zirconate makes the monoclinic symmetry appear in lead titanate; on the other hand we think that some other ferroelectric material could show the monoclinic symmetry (or even the triclinic one which exhibits 48 polarization directions) when it is doped with a suitable element. The Landau theory which we are developed would be able to predict the ferroelectric symmetry whenever the effect of a doping element on the expansion coefficients is known. In such a desirable situation, it could be driven the industrial process of high performing ferroelectric ceramics.

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