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# An effective constitutive model for polycrystalline ferroelectric ceramics: Theoretical framework and numerical examples

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ABSTRACT

We present an efficient, physics-based constitutive model for bulk polycrystalline ferroelectric ceramics, which links domain switching mechanisms and phase transitions at the microscale to the observed electro-thermo-mechanically coupled material response at the macroscale. In particular, a convexified energy density is formulated based on domain volume fractions and extended to polycrystals via the common Taylor assumption of uniform strains (alternative descriptions are discussed as well). The chosen kinetic relations admit to account for differences in 90°- and 180°-domain wall motion and rate effects. The model is applied to tetragonal barium titanate ($BaTiO_3$) and we present results for both material point calculations and finite element simulations, which demonstrate good qualitative agreement with experiments. We deliberately target bulk polycrystalline ferroelectrics in contrast to thin films that have been studied extensively.



## 1. Introduction

Ferroelectric ceramics form the basis of sensors and actuators, energy harvesters, and vibration dampers, among others. Their electro-mechanical coupling stems from an atomic-level dipole crystal structure that facilitates the conversion of mechanical strains into an electrical charge separation and thus into a voltage, and vice versa. The piezoelectric effect of ferroelectrics is a key mechanism that makes active materials responsive to applied electric fields [1,2]. Piezoelectric materials are ferroelectrics which, in case of ceramics, possess a tetragonal, rhombohedral or orthorhombic lattice structure [3–5] which results in a spontaneous polarization below their Curie temperature [6]. Technologically relevant piezo-ceramics are, among others, the synthetic perovskites lead titanate ($PbTiO_3$), lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$, or PZT), further barium titanate ($BaTiO_3$) as well as synthetic ceramics such as bismuth ferrite ($BiFe_3$) or sodium niobate ($NaNbO_3$). More recently, electroactive polymers such as polyvinylidene difluoride (PVDF) and its copolymers have become attractive for their low weight.

Large electric fields can permanently switch the polarization in ferroelectrics, which is commonly used to pole piezo-devices but was also shown to produce large mechanical damping [7–12], significant electrostrictive strains [13], and pronounced changes of the elastic moduli [14]. The switching of ferroelectric domains occurs under large electric fields that drive the material beyond the linear piezoelectric regime. The associated change of the spontaneous polarization is accommodated by the nucleation of domains and, most importantly, the motion of domain walls. Domain wall motion [15,16] and the interaction of domain walls with lattice defects [17,18] dissipate energy, which is rate-dependent and thus leads to dielectric losses [19] and hysteresis during electric cycling [20–23]. The dissipative nature of domain wall motion manifests itself, e.g., through pronounced damping in ferromagnetics [24] or in ferroelastic and ferroelectric solids [6,25]. Pronounced damping was also shown in $BaTiO_3$ and PZT under large stresses (1–100 MPa) which align domains [26] and thus yield significant damping [27,14] by promoting non-180° domain wall motion. The combined effects of constant electric bias and constant or cyclic compression were investigated, e.g., in Chaplya and Carman [9] and Zhou et al. [28].

The energetics and thus the equilibrium response of ferroelectrics are understood fairly well and have been modeled extensively, beginning with the seminal works of Landau [29] and Devonshire [30,31]. On the single-crystal level, microscopically-motivated phase field models [32–37] as well as atomistic [38,39] or relaxation-based approaches [40,41] have given insight into the electro-mechanical coupling and the

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(quasistatic) electrical hysteresis [42–46,32–34,47]. The macroscopic behavior of polycrystalline ferroelectrics has been investigated by both phenomenological [48–52] and thermodynamics-based approaches [53–59], see also Kamlah [60], Landis [61] for reviews. Models and experiments have also highlighted the dependence of the electrical hysteresis on the material's microstructure, see, e.g. [62–66]. In contrast to the quasistatic performance, the temperature-, electric field-, and stress-dependent kinetics of the rate-dependent domain switching process have left many open questions. A major focus has been on *thin films* whose behavior was studied computationally [32,67–69] and experimentally [70,67,68] and is affected by the free surfaces. By contrast, for the macroscopic scale of polycrystalline-polydomain *bulk* ferroelectric ceramics, only a few models exist that efficiently and accurately describe the nonlinear electrical hysteresis and the associated physics of domain switching [71].

Here, we present a variational constitutive model for polycrystalline ferroelectric ceramics which describes the electro-mechanically-coupled performance under externally applied bias electric fields and stresses under isothermal conditions; the model can further be extended to capture structural transitions such as the martensitic transformation at the Curie temperature of perovskites (although this is not the focus here). Our goal is to retain as much microstructural information as possible (e.g., resolving the individual domain volume fractions in each grain of the polycrystal) but to formulate a model that is sufficiently efficient to be used in macroscopic simulations at the structural and device level, as demonstrated by finite element calculations. While the general model outlined here is versatile and sufficiently general to be applied to various materials systems, it is specialized for the description of tetragonal perovskites and applied to simulate the response of $BaTiO_3$. In Section 2 we summarize the constitutive model (starting on the single-domain level and advancing to a polycrystal-polydomain model). Section 3 describes the specific assumptions and material parameters for $BaTiO_3$. Section 4 gives an overview of simulation results, and Section 5 concludes this contribution.

## 2. Constitutive model

In the following, we discuss the basic concepts of the constitutive model with increasing complexity, starting with a single ferroelectric domain, extending the former to single-crystals containing multiple domains, and finally relaxing the single-crystal model into an effective polycrystal description; see the schematic in Fig. 1. Throughout, we focus on ferroelectric ceramics whose typically small strains allow for the use of linearized kinematics. In addition, we start by assuming isothermal conditions as well as loading scenarios sufficiently slow for assuming quasistatic governing equations (i.e., we capture rate effects but neglect the influence of inertia and resonance phenomena; the extension to dynamics is straight-forward because it does not affect the constitutive model but is handled at the finite element level). We note that for the electro-mechanical field variables we choose common continuum-mechanics notation (other communities may prefer another set of symbols).

### 2.1. Single-crystal single-domain description of ferroelectrics

Consider a single-crystal consisting of only a single ferroelectric domain described by the polarization vector $\boldsymbol{p}$, electric field vector $\boldsymbol{e} = -\mathrm{grad}\,\varphi$ (where $\varphi$ denotes the electric potential), and a uniform infinitesimal strain tensor $\boldsymbol{\varepsilon}$. The stored energy density of the crystal (usually referred to as the *electric enthalpy*) is assumed to additively decompose into mechanical and electrical energy density [32,34], i.e.,

$$W(\boldsymbol{\varepsilon}^e, \boldsymbol{e}, \boldsymbol{p}) = \frac{1}{2}\boldsymbol{\varepsilon}^e \cdot \mathbb{C}(\boldsymbol{e}, \boldsymbol{p})\,\boldsymbol{\varepsilon}^e - \frac{\epsilon}{2}\boldsymbol{e}\cdot\boldsymbol{e} - \boldsymbol{e}\cdot\boldsymbol{p}, \tag{1}$$

where

$$\boldsymbol{\varepsilon}^e = \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^r \tag{2}$$

is the elastic contribution to the total strain tensor $\boldsymbol{\varepsilon}$, and $\boldsymbol{\varepsilon}^r = \boldsymbol{\varepsilon}^r(\boldsymbol{e}, \boldsymbol{p})$ is the remanent strain tensor. In general, the elastic modulus tensor $\mathbb{C}$ is anisotropic and depends on both the applied electric field $\boldsymbol{e}$ and the polarization $\boldsymbol{p}$, see Liu and Huber [72], so that the two energetic contributions are strongly coupled. For simplicity (and because this is approximately the case in the studied materials systems), we assume an orientation-independent electric permittivity $\epsilon$.

The infinitesimal stress tensor $\boldsymbol{\sigma}$ follows from the electric enthalpy density by differentiation, viz.

$$\boldsymbol{\sigma} = \frac{\partial W}{\partial \boldsymbol{\varepsilon}} = \mathbb{C}(\boldsymbol{e}, \boldsymbol{p})\,(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^r), \tag{3}$$

Note that Maxwell stresses are negligible in ferroelectric ceramics at small strains, which is why they are neglected here. Linear momentum balance in the absence of body forces or inertial effects requires

$$\mathrm{div}\boldsymbol{\sigma} = \boldsymbol{0}. \tag{4}$$

Similarly, the electric displacement vector $\boldsymbol{d}$ and the thermodynamic driving force $\boldsymbol{y}$ conjugate to the polarization are, respectively,

$$\boldsymbol{d} = -\frac{\partial W}{\partial \boldsymbol{e}} = \epsilon\boldsymbol{e} + \boldsymbol{p}, \qquad \boldsymbol{y} = -\frac{\partial W}{\partial \boldsymbol{p}}, \tag{5}$$

and Gauss' law for quasistatics (assuming no free charges are present) implies that

$$\mathrm{div}\,\boldsymbol{d} = \boldsymbol{0}. \tag{6}$$

The above constitutive framework must be completed by a kinetic relation for the evolution of the polarization $\boldsymbol{p}$, which is generally a dissipative process. Examples of phenomenological kinetic laws can be found in Miehe and Rosato [59] or Idiart [73].

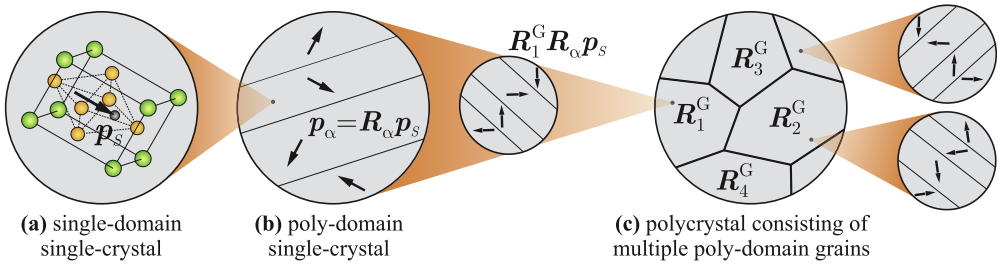


**Fig. 1.** Constitutive model construction from single-domain single-crystals to multi-domain polycrystals of tetragonal perovskites.