Computational Materials Science 96 (2015) 327–335

Contents lists available at ScienceDirect

Computational Materials Science

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

Analytical intrinsic electromechanical properties of ferroelectric ceramics under the saturated and unsaturated poling states

Jiankun Hou, Yugong Wu *, Zhiyuan Wang

Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 10 May 2014
Received in revised form 25 August 2014
Accepted 30 August 2014

Keywords:
Analytical modeling
Domain switching
Ferroelectricity
Dielectricity
Piezoelectricity

ABSTRACT

Probability density functions of orientation (PDFOs) of ferroelectric domains and electromechanical properties of the saturated and unsaturated poled ceramics for three phases (tetragonal (4mm), rhombohedral (3m) and orthorhombic (mm2)) are explicitly derived in this paper. With the domain switching criterion, the three-dimensional orientation space is divided into subfields for different switching types. The PDFOs before poling are then transformed into PDFOs after poling through standard probability theoretical calculation. The PDFO method enables the treatment of saturated and unsaturated poling in one work frame. Possible extension of this generic method is also proposed.

1. Introduction

Ferroelectric oxides are widely utilized since the phenomenon of ferroelectricity was found in the 1940s [1]. Their most intensive application is perhaps as piezoelectric ceramics: ferroelectric materials can switch their spontaneous polarization direction under an applied electromechanical field [2,3]. The most widely used ferroelectrics are perovskite-type crystals such as barium titanate, lead zirconate titanate (PZT) [2,3].

Ferroelectric perovskite-type crystal is in cubic (m3m) paraelectric phase above the Curie temperatures T_C, while below T_C it exhibits tetragonal (4mm), rhombohedral (3m) or orthorhombic (mm2) ferroelectric phases, depending on whether the spontaneous polarization is along the pseudocubic [001], [111] or [101] directions of the parent cubic perovskite lattice [1–3]. Under high electromechanical loading, ferroelectric domains may switch their directions to minimize the electrical field energy involved and the poled ferroelectric ceramic becomes non-centric symmetric and piezoelectric. Note that poling of ferroelectric ceramic is a dynamic process which is rarely complete; it is unsaturated poling, rather than saturated poling, that occurs in the preparation of piezoelectric ceramics.

Physical properties of ferroelectric ceramics thus have two kinds of origin. Intrinsic effects depend on lattice dynamics and are equivalent to that of single-domain single crystal. Extrinsic effects are non-lattice and manifest on various scales, such as domain wall and grain boundary. Separation of the two contributions is of theoretical interest and may benefit the design of piezoelectric ceramics with tailored properties [4–6].

Intrinsic electromechanical properties of ferroelectric ceramics in saturated poling state had been addressed numerically and analytically by several authors via pole figures, inverse pole figure and/or orientation distribution function (ODF) method [7–9]. Li and Rajapakse [7] made the first try to acquire analytical solutions of intrinsic electromechanical properties of ferroelectric ceramics of all three perovskite phases: 4mm, 3m and mm2. While their method is quite successful in dealing with first order tensor (the maximum remnant spontaneous polarization), since inverse pole figure is a useful way to describe the distribution of specific crystallographic direction, its applications on second order tensor (dielectric constant) and third order tensor (piezoelectric coefficient), however, are dubious. More importantly, this method cannot be extended to the unsaturated poling state [7]. To the best of our knowledge, a unified work frame to estimate intrinsic electromechanical properties of ferroelectric ceramics both in the saturated and unsaturated poling state is still absent. While model for ideal saturated poling may provide an upper limit to the properties of the ferroelectric materials [7], one for unsaturated poling state is much more realistic and relevant to the research and development of piezoelectric ceramics.

* Corresponding author. Tel.: +86 13752034044.
E-mail address: wuyugong@tju.edu.cn (Y. Wu).

http://dx.doi.org/10.1016/j.commatsci.2014.08.046
0927-0256/

This paper therefore mainly focuses on the present of a feasible and flexible method to estimate intrinsic contribution of ferroelectric and piezoelectric properties in both saturated and unsaturated poling state with the Reuss approximation. We show that the degree of reorientation can be easily treated by the introduction of mathematically valid probability density functions. In Section 2, we present a model to treat the domain orientation distributions in piezoelectric ceramic via a probability density function of orientation (PDFO). In Section 3, we define the PDFO expressions of saturated poling, and give the analytical results for the marginal distributions of PDFO and macroscopic properties of the ceramics. These results are compared with the misleading ones shown in [7]. In Section 4, the unsaturated poling states are discussed, which is made possible for the first time by the introduction of PDFOs. In Section 5, we draw a conclusion for this paper and raise expectations for future works.

2. Model

2.1. Euler angles and transition matrix R

As shown in Fig. 1, when treating piezoelectric ceramics from the view point of crystallographic physics, at least two kinds of coordinate systems are encountered: a macroscopic (global) one $\{X_1, X_2, X_3\}$ on the sample and a microscopic (local) one $\{x_1, x_2, x_3\}$ on each ferroelectric domain [10].

The orientation relation between the global coordinate system and a local one is defined by the transition matrix from $\{X_1, X_2, X_3\}$ to $\{x_1, x_2, x_3\}$

$$[R] = \begin{bmatrix} \cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi & \cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi & -\sin\theta\cos\psi \\ -\cos\theta\cos\phi\sin\psi - \sin\phi\cos\psi & -\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi & \sin\theta\sin\psi \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \tag{2.1}$$

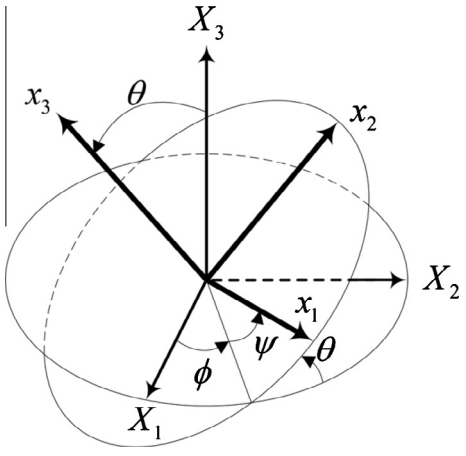

Fig. 1. Two coordinate systems and the *y-convention* Euler angles characterizing their orientation relation. The reorientation from $\{X_1, X_2, X_3\}$ to $\{x_1, x_2, x_3\}$ is a combination of three rotations in sequence that defined by three Euler angles (θ, ϕ, ψ): (1) a rotation ϕ around X_3 axis; (2) a rotation θ around the new X_1 axis; (3) a rotation ψ around the new X_3 axis. (All figures in this manuscript are single-column fitting images.)

and the Euler angles (θ, ϕ, ψ) are uniquely defined in the space Ω_0:

$$\Omega_0 = \{(\theta, \phi, \psi) | 0 \leqslant \theta \leqslant \pi, 0 \leqslant \phi, \psi \leqslant 2\pi\} \tag{2.2}$$

The infinitesimal volume element in Ω_0 is $\sin\theta d\theta d\phi d\psi$ [11]. If we define

$$x_\theta = -\cos\theta \in [-1, 1] \tag{2.3}$$

the space Ω_0 is transformed to a new space

$$\Omega = \{(x_\theta, \phi, \psi) | -1 \leqslant x_\theta \leqslant 1, 0 \leqslant \phi, \psi \leqslant 2\pi\} \tag{2.4}$$

with an infinitesimal volume element of $dx_\theta d\phi d\psi$. These two representations of orientation space as Ω_0 or Ω are completely equivalent and the choice we made in this paper depends on the circumstances encountered.

2.2. Three ferroelectric phases

When it is below the Curie temperature T_C, ferroelectric perovskite ceramics may exhibit tetragonal (4mm), rhombohedral (3m) or orthorhombic (mm2) ferroelectric phases, depending on which direction of the parent pseudocubic lattice ([001], [111] or [101]) is adopted as the direction of the spontaneous polarization. So in this paper we mainly study on these three phases: a capital letter X (=T, R or O) stands for the ferroelectric 4mm, 3m or mm2 phase.

As well known, the spontaneous polarization of X (=T, R or O) phase can switch among N (=6, 8 or 12, respectively) directions, when the ceramics are subjected to electrical loading. Take 'X = T' phase as an example. According to the convention of crystallography, each domain has its spontaneous polarization directions in [001] under its crystallographic coordinate system [12]. Under electric field, the spontaneous polarization may remain still or switch to one of the other five directions. We can thus define six types of domain switching as TS: T1, T2,...,T6. Viewed in the initial local coordinate system, six types of domain switching will redirect the spontaneous polarization to the six directions: [001], [00$\bar{1}$], [010], [0$\bar{1}$0], [100], [$\bar{1}$00], respectively and T1 switching is just non-switching.

Similarly we can define R1, R2,...,R8 and O1, O2,...,O12 of domain switchings for 3m and mm2 phases respectively. The information for all switching types is shown in Table 1.

2.3. Probability density function of orientation (PDFO)

Orientation of grains and ferroelectric domains in as-sintered ceramics is stochastic in nature. Therefore it is natural to treat the set of three Euler angles (θ, ϕ, ψ) (or (x_θ, ϕ, ψ) equivalently), which defines the domain orientation, as a multivariate random variable. So in this paper, we introduce the PDFOs below to depict the domain orientation distribution patterns in a ferroelectric ceramic. Our PDFOs observe formalism of probability theory.