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Ferroelectric domain continuity over grain boundaries

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ABSTRACT

Formation and mobility of domain walls in ferroelectric materials is responsible for many of their electrical and mechanical properties. Domain wall continuity across grain boundaries has been observed since the 1950's and is speculated to affect the grain boundary-domain interactions, thereby impacting macroscopic ferroelectric properties in polycrystalline systems. However detailed studies of such correlated domain structures across grain boundaries are limited. In this work, we have developed the mathematical requirements for domain wall plane matching at grain boundaries of any given orientation. We have also incorporated the effect of grain boundary ferroelectric polarization charge created when any two domains meet at the grain boundary plane. The probability of domain wall continuity for three specific grain misorientations is studied. Use of this knowledge to optimize processing techniques in manipulating the micro-structure and domain structure to result in desired interactions between neighbouring grains could prove to be beneficial for future polycrystalline ferroelectric materials.

1. Introduction

Ferroelectric materials are utilized in a range of technologically important devices where the coupling of the electrical polarization with an external field is exploited. This electrical polarization arises when the crystallographic structure is non-centro-symmetric and contains a distribution of charged atoms within the unit cell. Generally, at high temperatures during processing, these materials are paraelectric with no electrical polarization. However, on cooling through the transition temperature, T_C, these materials undergo a paraelectric to ferroelectric phase transition. In order to decrease depolarization fields and release stresses arising from lattice deformation below T_C, the material spontaneously forms regions of uniform polarization within single crystallites called domains [1,2]. The crystallographic planes, which separate these domains, are the ferroelectric domain walls. The domain walls are required to have continuity of lattice spacing as well as continuity of the normal component of the polarization vectors at the domain boundary in order to minimize strain and electrical energies, respectively [3]. Thus, domain walls occur on fixed planes based on the crystallographic symmetry, ferroelectric polarization direction and elastic strain tensor. For tetragonal ferroelectrics with [001] polar directions, like the prototypical perovskite ferroelectric barium titanate at room temperature, the domain walls occur on the {110} planes for 90° domain walls and mostly, but not exclusively, {100} planes for 180° domain walls. They are named 90° or 180° domain walls on account of the angle between the polarizations in the two neighbouring domains.

The polycrystalline state of ferroelectrics adds an additional parameter that influences the domain structure within the single crystal grains. It has long been known that the grain size in a polycrystalline ferroelectric influences the resulting domain structures [4,5]. Grain boundaries connect crystallites of different orientations, thus, if the misorientations between grains are random, it might be expected that the requirement for lattice spacing and polarization continuity of the ferroelectric domains at the grain boundaries is rarely fulfilled. However, observations of domain structures in polycrystalline ferroelectrics show that domain walls regularly traverse across grain boundaries. Published in 1956, De Vries et al. [6] reported continuous 90° ferroelectric domains across grain boundaries in polycrystalline barium titanate. Such continuous domain walls across grain boundaries have been reported in many studies on barium titanate [5,7] and lead zirconate-lead titanate solid solution [8].

The nucleation and growth of domains and their subsequent mobility greatly impacts macroscopic ferroelectric properties

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[9–12]. When considering grain boundary types that do not allow for domain wall continuity, these grain boundaries are speculated to act as pinning centres for the ferroelectric domains, thereby generally restricting the domain wall motion, which in turn reduces the magnitude of bulk polarization change during external stimulus [13–15]. Alternatively, if the conditions are such that domain wall planes can meet at the grain boundary, and this coincides with a polarization geometry that gives minimized strain and electrical energy, this will likely allow for domain wall continuity over the grain boundary as has been observed. However, the impact of continuous domains over grain boundaries on bulk ferroelectric properties is not clear. Some previous works have considered this continuity to inhibit the domain wall motion in the grain [4,15] while others implied that these correlated structures might enhance the bulk ferroelectric properties [7,16]. An interesting result of this longer length-scale domain continuity is the possibility of a collective response of neighbouring grains. This collective response might lead to a change in ferroelectric domain structure of one grain due to the excitation of neighbouring grain [17,18].

Few works discuss the geometrical requirements for the formation of such microstructures. In the case of a tetragonal ferroelectric with [001] polar direction, {110} 90° domain walls are observed to be continuous over grain boundaries [6–8]. In order to allow this, the grain boundaries must be plane matching boundaries for the {110} planes in each grain. Tsurekawa et al. [8] attempted to explain domain wall continuity at grain boundaries using such a plane matching grain boundary model. However, in order to completely understand this property, a full account of the behaviour over 5-dimensional grain boundary space must be considered. Development of 3D microstructural modelling methods [19–22] opens opportunities to experimentally observe these grain boundary distributions and correlate processing parameters to final material properties.

In the following paper, we formulate the geometrical requirements for the grain boundaries that allow domain wall continuity to occur. Additionally, we consider the grain boundary polarization charge that may exist when the domains of the neighbouring grains meet at the grain boundary. The propensity for domain continuity for three specified neighbouring grain misorientations are presented for a tetragonal ferroelectric with [001] polar vector; however, the method can be applied to any misorientation and crystallographic symmetry.

2. Methods

2.1. 5-Dimensional visualization of the grain boundary

A grain boundary requires five parameters to unambiguously define (Fig. 1). The misorientation between neighbouring grains is represented by either three Euler angles (φ_1, ϕ, φ_2) or, in alternate notation, an axis of rotation (two angles) and an angle of rotation pair ($\hat{u}$, ω). The grain boundary plane separating the two grains is then represented by two spherical angles for the plane normal vector relative to crystallographic coordinate axes in one of the grains. The Euler angles used here follow the Bunge convention [23].

According to coincidence site lattice theory [24,25], special grain boundaries are represented using their $\sum$ value. The $\sum$ value represents the misorientation between two grains i.e., the three Euler angles. However, the $\sum$ value does not completely describe a point in 5-dimensional grain boundary space, as it does not specify a grain boundary normal. In order to understand the propensity for ferroelectric domain wall continuity over grain boundaries, it is required to know their full 5-dimensional nature.

2.2. Mathematical condition for domain wall continuity

The continuity of ferroic domain walls across a grain boundary can be visualized as the continuity of two planes, Plane A and Plane B respectively, in the two neighbouring grains through the grain boundary. Fig. 2 demonstrates the necessary condition for the domain walls to be continuous across a given grain boundary, namely that the line of intersection between the two planes lies in the grain boundary plane. Thus, the grain boundary plane normal should be perpendicular to this intersection line vector. This is schematically shown in Fig. 2(a). Here, two misoriented grains have their domain planes sharing a line of intersection with the grain boundary plane. To demonstrate that this line of intersection is dependent on both the grain misorientation and the grain boundary plane orientation, Fig. 2(b) and (c) show these cases.

This requirement for ferroelectric domain wall continuity is mathematically represented by Equation (1).

$$\hat{n}_{GBPlane} \cdot \left(\hat{n}_{Plane\ A} \times \hat{n}_{Plane\ B} \right) = 0 \quad (1)$$

Where $\hat{n}_{GBPlane}$ represents the grain boundary plane normal, $\hat{n}_{Plane\ A}$ and $\hat{n}_{Plane\ B}$ represent the normal vector of domain wall plane A and B, respectively.

Two neighbouring grains can have any misorientation and the grain boundary normal that separates them can likewise have a range of orientations. Here, the misorientation between a pair of neighbouring grains is used to calculate the sets of planes corresponding to the domain walls in both grains. From these, the probability of domain wall continuity for any grain boundary plane normal over the full orientation space can be derived. Considering the tetragonal ferroelectric material case, all six crystallographic equivalent {110} domain walls are possible in both grains. Every domain wall plane in Grain A can be continuous with any of the six

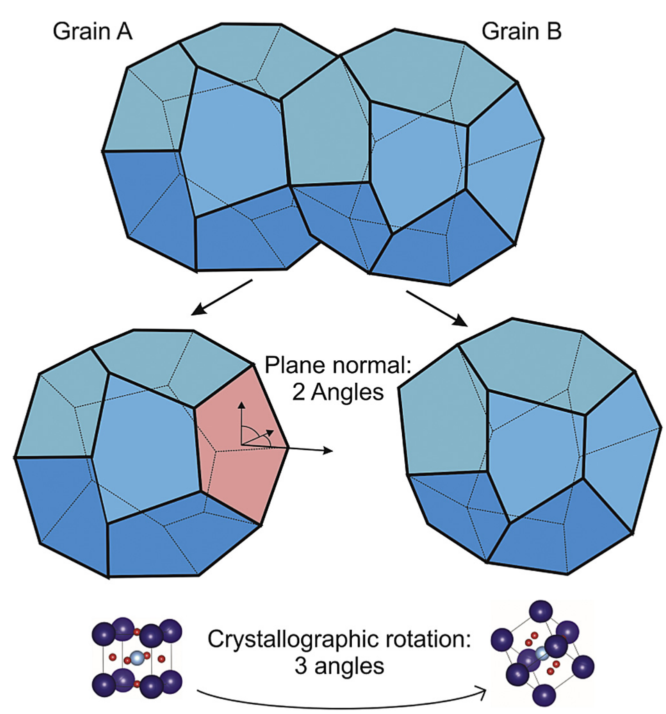

Fig. 1. 5-dimensionality of a grain boundary. The misorientation between the two grains is shown by the rotated crystal structure and can be defined using three angular parameters. The grain boundary plane normal as shown can be defined by two angles with respect to the crystallographic orientation of Grain A.