Mapping 180° Polar Domains Using Electron Backscatter Diffraction and Dynamical Scattering Simulations

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Keywords: EBSD; Ferroelectric; Ferroelectric Domain; Electron Backscatter Diffraction;

Abstract

A novel technique, which directly and nondestructively maps polar domains using electron backscatter diffraction (EBSD) is described and demonstrated. Through dynamical diffraction simulations and quantitative comparison to experimental EBSD patterns, the absolute orientation of a non-centrosymmetric crystal can be determined. With this information, the polar domains of a material can be mapped. The technique is demonstrated by mapping the non-ferroelastic, or 180°, ferroelectric domains in periodically poled LiNbO₃ single crystals. Further, the authors demonstrate the possibility of mapping polarity using this technique in other polar materials system.

Introduction

The extrinsic contribution from ferroelectric domain wall motion is important to the large permittivity and piezoelectricity in many ferroelectric ceramic oxides [1]–[5]. Due to the importance of domain structures in ferroelectric materials, significant work has been devoted to understanding domain configurations and behavior since the discovery of barium titanate, the first perovskite ferroelectric [4]–[7]. Through these various studies, 90° domains within tetragonal ferroelectrics have been identified and well characterized, with one of the most common techniques based on diffraction-contrast transmission electron microscopy (TEM) imaging [6], [7].

While 90° domains have been thoroughly investigated in bulk ferroelectrics, the characterization of 180° domain structures remains challenging because, according to Friedel's law, purely kinematic elastic scattering is not sensitive to the unit cell inversion associated with 180° domains. Friedel's law is violated, however, for anomalous or dynamical diffraction from non-centrosymmetric crystal structures [8], [9]. Recently, anomalous x-ray scattering has been used to quantify polarity phase fractions in crystals and thin-films, but this technique has limited spatial resolution and is applicable only to material compositions that have a strong absorption edge that falls within the spectrum of the x-ray source [10]. More recently, anomalous x-ray scattering has also been used to simultaneously quantify the 90° domains and identify 180° polar domains in bulk ferroelectrics using a high energy x-ray source [11]. Diffraction-based techniques that are not heavily influenced by anomalous absorption or dynamical scattering will not be sensitive to 180° domain structures [6], [8], [9], [12].

Other non-diffraction-based techniques have been developed to image 180° domains. The most common technique is piezoresponse force (PFM) microscopy. In

PFM, a scanning probe is used in conjunction with a tip bias to observe local changes in surface polarization. The sample is generally mounted with a bottom ground electrode and a probe tip, with a small applied A/C voltage, is rastered across the surface of the sample. As the tip interacts with the surface polarization, it will lead to changes in the measured field, and a map of the polarization direction can be generated from point-by-point measurements [13]–[17]. A drawback of PFM is that this imaging technique is susceptible to artificial contrast, which can be interpreted as polarization contrast, due to poor probe tip shape, charge injection, and sample preparation, and cannot be applied to highly conductive samples [18], [19].

Another common technique to image 180° domains is to chemically etch the surface of a material and then image the surface topography with surface-sensitive techniques such as scanning electron microscopy (SEM) or atomic force microscopy. Etching the surface will bring contrast to the domain structure because each domain orientation will etch with different rates, and the topography can be used to characterize both 90° and 180° domain structures [6].

Optical birefringence in ferroelectrics can also be used to image directly 180° domain *walls* through polarized light microscopy [20]. However, not all 180° domain walls exhibit strong birefringence, such as barium titanate where the 180° domain walls are only visible with an applied electric field; once the field is removed the contrast disappears [20]–[22]. Furthermore, birefringence cannot be used to determine the polarization direction on either side of a domain wall.

Dynamical diffraction theory is well known to predict subtle changes within experimental diffraction patterns that can occur as a result of changes within the structure

of the unit cell that cannot be determined using kinematical diffraction theory [23], [24]. Because electron scattering in solids is highly dynamical, convergent beam electron diffraction has been used extensively to identify polar orientations in ferroelectrics and other polar materials, but this requires the preparation of electron-transparent films and is typically limited to square micrometer fields of view. Winkelmann et al. previously demonstrated that dynamical diffraction can be leveraged in electron backscatter diffraction (EBSD) for the determination of chirality in quartz crystals via cross-correlation of experimental and dynamically simulated EBSD patterns [24]. In the present work, we extend this approach and present a method to directly image 180° domain structures in ferroelectric oxides through EBSD mapping and EBSD dynamical diffraction simulations [25]. The spatial resolution of the technique is only limited by the interaction volume of the electron probe within the sample, and thus can be on the order of 100 nm or smaller.

Materials and Methods

To develop the experimental approach, we studied periodically poled LiNbO_3 single crystals (R3C space group) that contain well-defined 180° domains. Single crystals were purchased from Deltronic Crystal Industries, Inc. in Dover, NJ USA and were polished at the manufacturer with a roughness below 40-80 nm. The grating period was 11.2-12.0 μm and the crystals were left un-polished upon reception but were coated with a thin coating of amorphous carbon to prevent charging under the electron-beam irradiation.

EBSD experiments were performed in a field-emission FEI Quanta Dual-Beam SEM/FIB operated at 20 kV with electron probe current of 3-9 nA. The sample was

mounted and tilted to 75° towards the EBSD detector. Under these experimental conditions the interaction volume of the electron beam within the sample is expected to be 30-40 nm laterally and 50-100 nm longitudinally, according to Monte Carlo simulations [26]. The sample working distance was 11.2 mm and the sample-to-detector distance was 18.4 mm. An Oxford NordlysNano EBSD detector was used to collect EBSD patterns with a full resolution of 1344x1024 pixels. A static background image was subtracted from each pattern to remove any non-linearities inherent to the detector.

The EMsoft software was utilized to simulate dynamical EBSD patterns [25]. The EBSD pattern center was iteratively optimized by cross correlating distinct regions of interest to minimize the difference between experimental and simulated EBSD patterns. Both the positive and negative polarization directions were then simulated for each crystal orientation by inverting the Euler angles using the simple inversion formula: $\varphi'_1 = \varphi_1 - 180$, $\Phi' = 180 - \Phi$, $\varphi'_2 = 180 - \varphi_2$. For each normalized experimental EBSD pattern, a direct mean intensity variation (MIV) between the experimental pattern and each of the two simulated patterns was calculated. The MIV reflects the average absolute difference in intensity between two patterns, the equation is shown below:

$$MIV = \frac{\sum_i^N (abs|\hat{I}_i^R - \hat{I}_i^E|)}{N}$$

where $\hat{I}^{E,R}$ represent the normalized intensity of an experimental (E) and reference or simulated (R) diffraction pattern, respectively, and N is the total number of pixels in the diffraction pattern. This procedure was performed for each pattern within an EBSD map and the resultant values were plotted with respect to both polar variants. Lower MIV values indicate a better correlation between the experimental and simulated pattern, and

in principal, the MIV maps of both polar variants should be complementary for patterns that are free of extraneous artifacts (e.g., lattice strain or pattern overlap at domain and grain boundaries).

Alternatively, a dot product between an experimental and reference pattern can be used to calculate the phase angle between the two patterns, a measure of pattern similarity [27]:

$$\theta = \arccos\left(\sum_i^N (\hat{I}_i^E \cdot \hat{I}_i^R)\right)$$

Diffraction patterns are normalized using the following expression:

$$\hat{I} = \frac{I}{\sqrt{I \cdot I}}$$

Results and Discussion

Figure 1 shows representative experimental EBSD patterns for the two antiparallel domain orientations in the LiNbO₃ sample (polar pairs). The differences in the patterns are observable to the naked eye, particularly at the middle of the zone axis in the center of the EBSD pattern where intensities are inverted with respect to the opposite orientation (this is shown clearer in Figure 3). It should be emphasized that there is no change in the band location or angles; rather, the only differences between the patterns arise from inversions in the intensities of (hkil) (l≠0) Kikuchi bands.

Figure 1: Experimental EBSD patterns from LiNbO_3 with (a) being the positive polarization direction (0001) and (b) being the inverse polarization direction ($000\bar{1}$).

Figure 2 presents the simulated LiNbO_3 with the same orientations shown in figure 1a. Figure 2a corresponds to the (0001) sample normal or positive polarization direction, while the negative polarization direction is shown in figure 2b.

Figure 2: Simulated EBSD patterns with the same orientations as Figure 1: (a) corresponds to a (0001) sample normal and (b) to a ($000\bar{1}$) normal

To emphasize the differences between the (0001) and (000 $\bar{1}$) orientations of LiNbO₃ EBSD patterns, magnified views of the central zone axis for both antiparallel orientations are shown in figure 3 for both simulated and experimental patterns. It should be emphasized that high quality patterns with a large pixel density are needed to resolve the fine structure within the Kikuchi bands and zone axes to clearly distinguish one orientation from its inverse. In this work, experimental patterns were measured using the full detector resolution (1344x1024 pixels); resolutions below this threshold did not produce experimental patterns with sufficient quality to determine the polarization direction reliably.

Figure 3: A comparison of the fine-structure in the zone axis from the diffraction patterns shown previously for the two different orientations for a) experimental and b) simulated diffraction patterns.

Figure 4a shows an SEM micrograph of the LiNbO₃ single crystal, where the 180° domains are evident because there is a slight height difference between the domains in the as-received sample. To emphasize that traditional EBSD indexing is insensitive to

the 180° domain structure, the inverse pole figure (IPF) map, calculated using the Tango software by Oxford, is shown in figure 4b, where the uniform color corresponds to the c-axis orientation.

Using the mean intensity variation method described in the Experimental Methods section, a map of the mean intensity variation for LiNbO_3 with respect to the (0001) orientation is shown in figure 4c, where the dark regions correspond to the regions of the sample with that polar orientation. Figure 4d presents the mean intensity variation with respect to the $(000\bar{1})$ direction. The fact that the maps are complementary provides confidence in the correct domain identification in LiNbO_3 . The transition between two domains occurs within 1 pixels, or $1\ \mu\text{m}$.

Figure 4:(a) An SEM micrograph of periodically poled LiNbO₃ showing the 180° domains. (b) A Euler angles map determined from indexing of the EBSD patterns of LiNbO₃ (Legend is shown below). The mean intensity variation map between the experimental EBSD patterns and the dynamical simulated patterns corresponding to (c) (0001) and (d) (000 $\bar{1}$). Dark areas in c and d correspond to domains with a (0001) and (000 $\bar{1}$) polarization direction, respectively, while the lighter regions correspond to the inverse orientation (the scale is normalized to the maximum mean intensity variation value).

To illustrate the general applicability of this technique, we simulated polar pairs of EBSD patterns for other important materials, namely BaTiO₃ and AlN. Simulated polar pairs are shown along with a corresponding normalized intensity variation map presented in figure 5. The intensity inversion across the Kikuchi bands is evident in the difference map. The MIV between the two orientations was calculated for each Friedel pair of patterns, and is presented in Table I. For comparison, the analysis via the dot-product method is also included in Table I, and shows similar results to the MIV method. The largest intensity variation between polar pairs is found for LiNbO₃, while BaTiO₃ exhibits the smallest differences of the three materials investigated. The magnitude of the MIV between polar pairs arises from differences in the non-polar structures and atomic scattering factors for each material [23], [28]. However, even in the case of BaTiO₃, which is only slightly distorted from the centrosymmetric cubic $Pm-3m$ space group, the intensity differences (locally up to 30%) should be sufficient to distinguish between each polar pair with high quality patterns.

Figure 5: Simulated diffraction pattern of material systems with the polarization direction positive and negative, with their corresponding Friedel intensity difference maps on an absolute percentage scale.

Table I: Summary of the calculated Friedel mean intensity variation (MIV) and phase angle difference between simulated polar pairs of EBSD patterns.

Material (Space Group)	MIV (average per pixel intensity variation)	Dot-Product method (degrees)
BaTiO ₃ (P4mm)	4.42	3.21
AlN (P6 ₃ mc)	8.72	8.96

LiNbO ₃ (R3c)	10.25	10.57
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The simulated patterns shown in figure 5 demonstrate the differentiation and identification of the absolute polarization direction in a variety of materials. The presented technique opens the possibility to map 180° domains over many 100's x 100's of μm . This provides a method to quantify relative populations and spatial distributions of 180° non-ferroelastic domains in addition to 90° ferroelastic domains in ferroelectric materials, which has been an area of interest and debate for decades [1], [27],[28]. This technique could be extended to *in-situ* studies to observe how the population, and structure of ferroelectric domains evolve as a function of temperature and/or applied field. While demonstrated for ferroelectric oxides, the method is broadly applicable and, in principle, can be utilized for studying any non-centrosymmetric structure. For example, the nitrides community grows GaN thin films with either Ga-polarity or N-polarity, with two of the most common techniques utilized to determine the polar direction being chemical etching or convergent beam electron diffraction, both of which are destructive techniques [31], [32]. The use of EBSD and dynamical scattering simulations will lead to a simple and non-destructive way to map polar orientations. Further, the methodology could be extended to transmission Kikuchi diffraction [33]–[35], which is a technique similar to EBSD, but is able to achieve much higher spatial resolutions.

Conclusions

We demonstrate that the intrinsic intensity variations in experimental EBSD patterns that arise from dynamical scattering can be used to distinguish between polar pairs, and map 180° ferroelectric domains. A simple and computationally inexpensive mean intensity variation between the experimental and dynamically simulated EBSD patterns is calculated for both polar variants. Using periodically poled LiNbO₃ as an example, we map the absolute polar orientations over a large (100 um x 10 um) area. The technique opens the possibility for mapping polar domain structures, and absolute domain orientations in a variety of technologically important materials in a non-destructive manner.

Acknowledgments

This material is based upon work supported by the National Science Foundation, as part of the Center for Dielectrics and Piezoelectrics under Grant Nos. IIP-1361571 and IIP-1361503 and the National Science Foundation Graduate Research Fellowship for M.J. Burch under Grant No. DGE-0946818. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation. This work was performed in part at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI). MDG would like to acknowledge

an Air Force Office of Scientific Research (AFOSR) MURI program (contract \# FA9550-12-1-0458) for support in the development of the EMsoft package.

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