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A three-dimensional polarization domain retrieval method from electron diffraction data

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ABSTRACT

We present an algorithm for retrieving three-dimensional domains of picometer-scale shifts in atomic positions from electron diffraction data, and apply it to simulations of ferroelectric polarization in $BaTiO_3$. Our algorithm successfully and correctly retrieves polarization domains in which the Ti atom positions differ by less than 3 pm (0.4% of the unit cell diagonal distance) with 5 and 10 nm depth resolution along the beam direction, and we also retrieve unit cell strain, corresponding to tetragonal-to-cubic unit cell distortions, for 10 nm domains. Experimental applicability is also discussed.

1. Introduction

Characterization of ferroelectric materials' polarization and strain states using nanometer-scale spatial selectivity has been of great interest in recent years [1–6]. The polarization state of ferroelectric materials is related to picometer-scale atomic position shifts within the unit cell and strained distortions of the unit cell, observable using the transmission electron microscope (TEM) [1,5,7–10]. Previously, nanometer-scale local polarization domains inside large grains have been mapped in two dimensions using the TEM [5,10], but a two-dimensional map neglects the third dimension. X-rays with nanometer-scale selectivity and electrons with Angstrom-scale selectivity have both been used to examine thin specimens, but very thin specimens may not be representative of the polarization state in a thicker, more realistic specimen [11,1,8,3,9,12]. Thus, an algorithm to three-dimensionally map these nanoscale domains for specimens thick enough to avoid surface effects would provide a useful general tool for atomic-scale materials physics [11,12], but this algorithm would require full three-dimensional characterization with nanometer-scale spatial selectivity of picometer-scale atomic displacements for thick specimens. The TEM easily provides sufficient spatial selectivity in two dimensions, but mapping these domains along the beam direction is difficult due to multiple scattering of the electrons, which can be simulated from a known specimen using various algorithms, but which cannot be analytically inverted to determine an unknown specimen [13–18]. Recently, we have developed an algorithm that efficiently uses diffraction data to retrieve TEM specimens with variations along the beam direction using artificial neural network tools and the stacked-Bloch-wave forward-simulation method [19,20]. This algorithm was previously applied to only rigid-body unit-cell properties including unit-cell rotation; neither individual atom positions inside the unit cell nor non-rotational unit cell distortions were examined [19,20]. In this work, we apply this algorithm to the different problem of solving polarization and non-rotational strain state, and retrieve beam-direction variations in picometer-scale atomic displacements and lattice distortions from noisy simulated data. Only simulated data is used in this work because we require a completely known specimen to demonstrate our algorithm's theoretical accuracy, but we also discuss guidelines for experimental realization.

Polarization and strain in $BaTiO_3$ have been characterized using the TEM and are an ideal test case for our algorithm. The polarized $BaTiO_3$ crystal can have large grains where the average polarization is both in one direction and formed by Ti atom displacements of approximately 13 pm (or 2% of the unit cell diagonal distance) along the ⟨111⟩ directions [21]; this shift has been shown to have a significant influence on TEM convergent-beam electron diffraction (CBED) patterns [5]. The Ti displacements also depend on the unit cell distortion, which corresponds to a strain tensor [21,5,10]. Inside these large grains, the polarization is non-uniform, with

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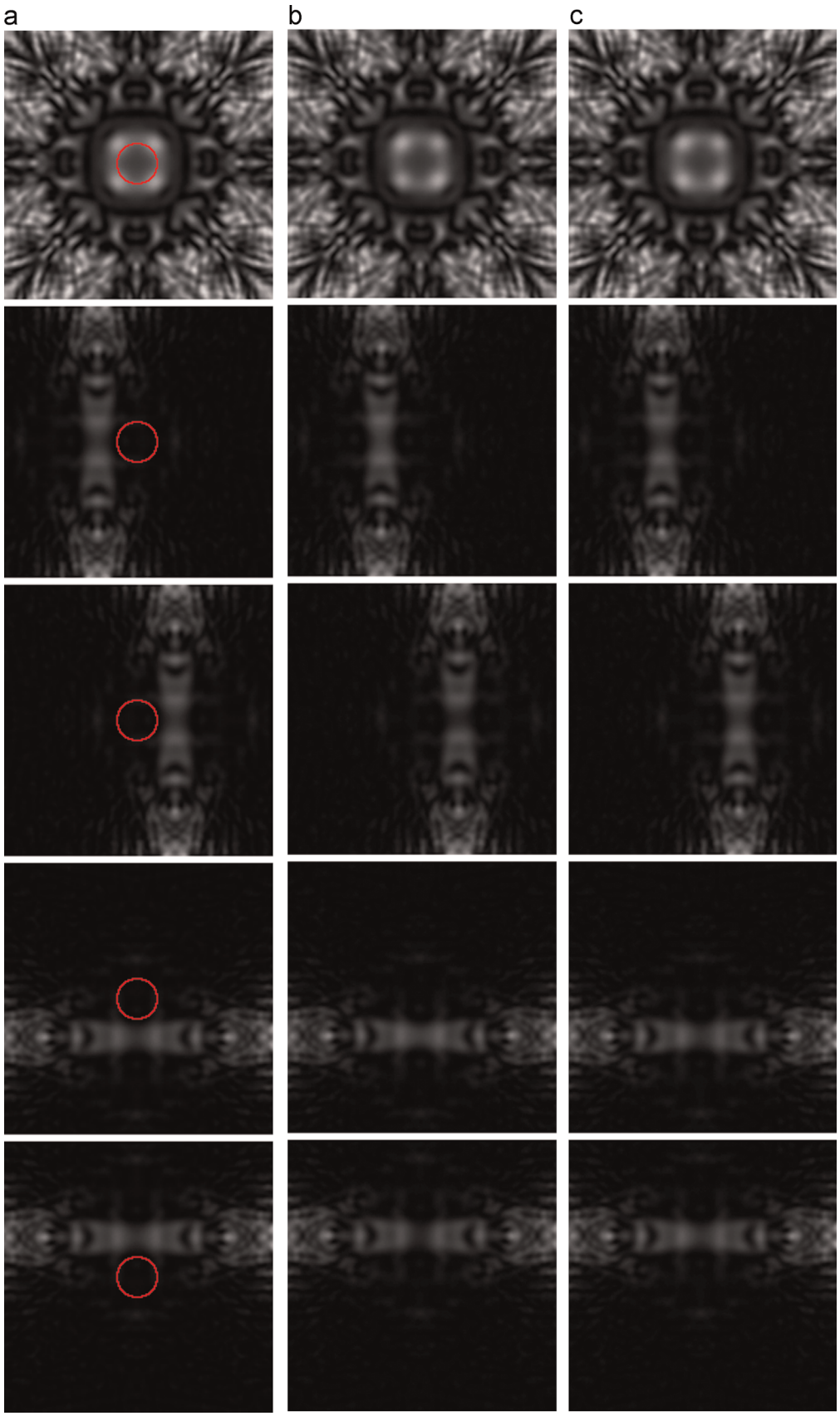

Fig. 1. Simulated CCBED patterns for 100 nm $BaTiO_3$ under different polarization conditions. All were simulated along the [100] zone axis, including 629 reflections with noise ($q = 5 \times 10^4$ incident electrons per beam tilt) at 300 keV primary energy, at 0.01° angular resolution and −1.0° to +1.0° along both the x and y axes, and a linear intensity greyscale from [0.0, 0.5]. For each pattern, the top square is the [000] reflection; under it are squares for the two ⟨002⟩ (middle) and the two ⟨020⟩ (bottom) reflections. Fig. 2 shows the differences between these patterns. (a) CCBED data for unpolarized $BaTiO_3$. The red circle depicts the maximum non-overlapping CBED disc radius. (b) CCBED data for homogeneously polarized $BaTiO_3$ with 13.9 pm Ti displacement along the [111] direction (2.0% of the diagonal). (c) CCBED data for polarized $BaTiO_3$ with depth variations ("Specimen 1" in the text); note top-bottom asymmetry. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)