Separating Surface Relaxations from Bulk Structure with Multislice Ptychography

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Microscopy and Microanalysis, **30** (Suppl 1), 2024, 1513–1515
https://doi.org/10.1093/mam/ozae044.748

Microscopy AND Microanalysis

Meeting-report

Separating Surface Relaxations from Bulk Structure with Multislice Ptychography

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Surfaces of functional materials undergo structural reconstructions and could exhibit mechanical, chemical, and electronic properties being very different from those in the bulk [1-3]. The abrupt change in electrostatic boundary conditions can alter the dielectric properties of a material at the surface, making the identification and characterization of such surface reconstructions especially critical for polar materials. We will discuss such reconstructions in the context of surface relaxation of oxygen octahedral rotations (OOR) in a ferroelectric phase of sodium niobate ($NaNbO_3$).

Here, we show using multislice simulations [4] that conventional scanning transmission electron microscopy (STEM) techniques are adversely affected by the presence of surface reconstructions and will produce discrepancies if used for comparisons with other macroscopic measurements. Even a through-focal series, in addition to being dose-inefficient, fails to accurately capture the full structure of the material owing to channeling effects of the electron beam. We further illustrate that multislice ptychography [5, 6], utilizing the multislice method to address the non-linear nature of probe propagation, facilitates three-dimensional structure determination with adequate depth resolution to identify and characterize surface reconstructions from a single dataset.

Figure. 1(a) shows the schematic of a $NaNbO_3$ sample with a surface relaxation of the OOR, where the interior of the sample has an in-phase OOR with a magnitude of 7 degrees whereas the entrance and exit surfaces have a relaxed structure with no OOR. This structure is modelled on experimental observation of surface reconstruction of a similar nature in $NaNbO_3$ as shown in Fig. 2(a-c). A direct comparison of simulated annular bright field (ABF), integrated differential phase contrast (iDPC) and multislice ptychographic images of one pseudo-cubic unit cell region of this sample as a function of defocus/depth is shown in Fig. 1(b). The depth profile corresponding to the Na-O plane marked with a yellow dotted line for (c) ABF, (d) iDPC and (e) multislice ptychography is also shown for additional clarity. Away from their ideal defocus condition close to the entrance surface, the ABF and iDPC images are unable to resolve the sample structure with the requisite resolution or contrast required to unambiguously identify the relaxed surface structure. In contrast, depth sectioning with multislice ptychography from a single dataset enables retrieval of the correct sample structure throughout the depth of the sample with a clear distinction between the surface and interior sample structure. In the depth profile shown in (e), this difference appears as an offset in the position of the oxygen atom at the surfaces of the sample associated with the relaxation of OOR. We also note that the simulations assume infinite dose, no sample mistilt or probe aberrations. Deviations from this ideal situation that are practically unavoidable in an experimental setting are known to produce artifacts in ABF and iDPC images [7, 8]. Ptychographic reconstructions have been previously shown to be more dose-efficient [9] and are robust to changes in diffraction conditions.

In Fig. 2(a-c) we show the experimental reconstructions corresponding to this simulated structure. The depth profile in Fig. 2(b) for the Na-O plane marked with the yellow dotted box in (a, c) shows the offset in the position of the oxygen atoms at the surfaces. The sample structure at the surface and the interior (obtained by averaging the slices marked with the solid yellow boxes) are shown in Fig. 2(a, c) respectively and shows a significant change in the angle of the octahedral rotation. Once the surface reconstructions are identified, the structure in the interior of the sample can be isolated and used for quantitative comparisons to other bulk measurements. Ptychographic reconstructions can also reveal multiple nanoscale phases in the depth direction that would otherwise get convolved in projection. An example of such a scenario where a spatially separated region of the $NaNbO_3$ sample hosts multiple nanoscale phases in the depth direction is shown in Fig. 2(d-f). Figure. 2(e) shows the depth profile of the Na-O plane marked with the yellow dotted box in (d, f) and shows large lateral shifts in the position of the oxygen atom, even in the interior of the sample. Images averaged over the two structurally distinct regions marked with solid yellow boxes in (b) are shown in (d, f) and are seen to differ in the direction of the OOR. The short and long in-plane Nb-O bonds are marked with blue and red color respectively in both images and show that the polarization does not switch direction, indicating that the order parameters associated with OOR and polarization are decoupled [10].

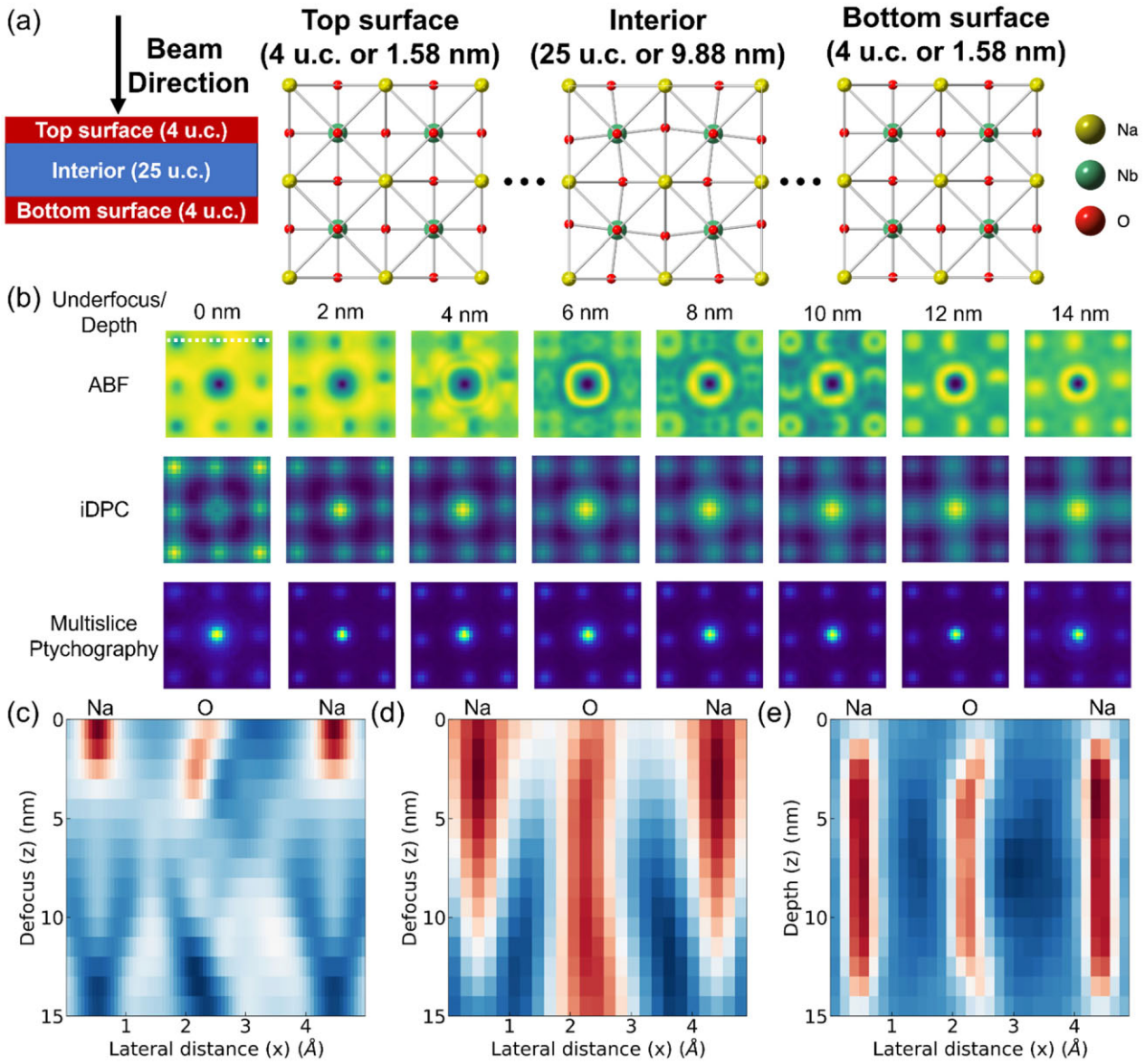

Fig. 1. (a) Schematic model for surface relaxations in $NaNbO_3$– both surface layers have no OOR, whereas the interior has a 7° OOR. (b) shows a simulated through-focal series of ABF, iDPC images and different slices from a multislice ptychographic reconstruction. (c-e), Depth profiles along the white dotted line in (b) corresponding to a Na-O plane for (c) ABF, (d) iDPC and (e) multislice ptychographic reconstruction.

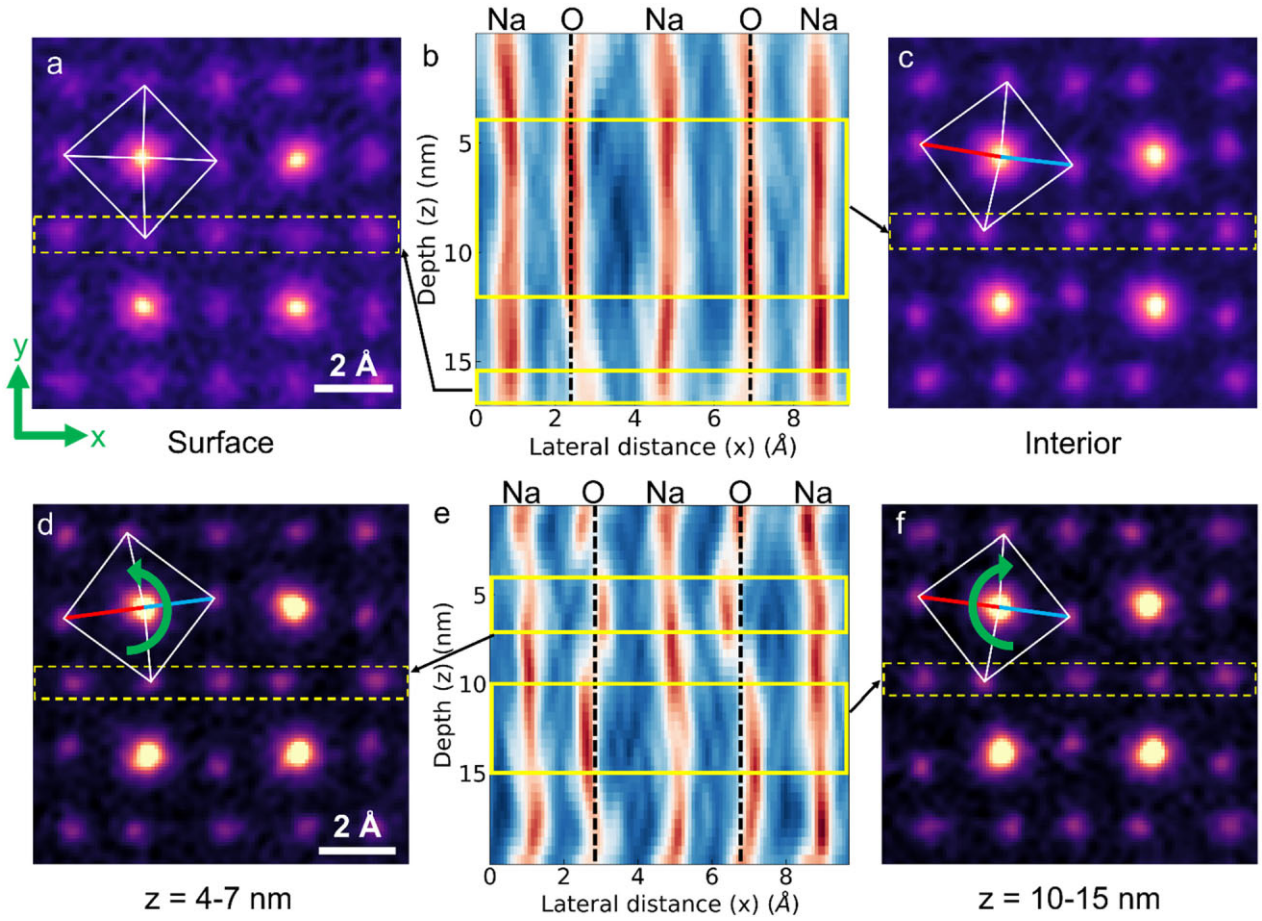

Fig. 2. Ptychography reconstruction of a 2x2 pseudo-cubic unit cell region of $NaNbO_3$ showing the (a) surface and (c) interior structure of the sample. (b) Depth profile along the Na-O plane marked with a yellow dotted box in (a, c). The slices summed to get the images shown in (a, c) are also labelled in (b). (d-f) Ptychographic image of $NaNbO_3$ spatially separated from the region shown in (a-c). (e) Depth sectioning along the Na-O plane labelled with a yellow dotted box in (d, f) show multiple nanoscale phases present in the projection direction arising from large shifts in the position of the oxygen atoms. These phases differ in the sense of oxygen octahedral rotation as shown in (d, f) obtained by summing the slices corresponding to the two different phases. Blue and red solid lines are used to label the short and long in-plane Nb-O bond lengths.

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10. The authors acknowledge funding from the Army Research Office under the ETHOS MURI via cooperative agreement W911NF-21-2-0162 and the AFOSR Hybrid Materials MURI award # FA9550-18-1-0480. Facilities supported by the National Science Foundation (DMR-1719875, DMR-1429155, DMR-2039380, DMR-1719875).

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