Direct Imaging of Polarization Gradients by Atomic Resolution Differential-Phase Contrast STEM

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In the last years, differential-phase contrast (DPC) technique in scanning transmission electron microscopy (STEM) has attracted a great attention for allowing phase-contrast imaging at the very high spatial resolution typical of probe-corrected transmission electron microscopes. With respect to conventional phase-contrast TEM techniques, which allow for reconstructing the phase of the electron beam, in DPC-STEM the local electric-fields in the specimen plane induce a displacement of the center of mass of the transmitted electron beam that can be detected by means of a segmented detector. In this way, the electric-field can be directly retrieved in both its amplitude and phase by measuring the differential signals between pairs of opposite quadrants. Recently, Shibata and coworkers [1,2] successfully employed DPC-STEM to map the atomic electric-fields in unperturbed structures like bulk $SrTiO_3$, $BaTiO_3$ and single Au atoms.

In this work, we demonstrate that atomic resolution DPC-STEM is capable of detecting local atomic electric-field fluctuations in ferroelectric materials, thanks to its sensitivity to charge redistribution [3]. The investigation was carried out on a $Bi_{0.8}Ca_{0.2}FeO_3$ thin film grown on $SrTiO_3$ (001) substrate, which shows a spontaneous layering of the Ca dopant along the growth direction. The dopant layering, occurring together with an ordering of oxygen vacancies, was investigated by combined high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging. The gradient in Ca concentration is responsible for a vertical polar superstructure in which paraelectric Ca-rich regions are periodically alternated to Ca-poor regions, as obtained from HAADF-STEM polarization analysis (Fig. 1). Noteworthy, the polar pattern exhibits a giant polarization gradient of ~70 μC cm^{-2} across 30 Å thick domains.

Acquiring atomically resolved DPC signals, we are able to map the atomic electric-field over this polar structure (Fig. 2). In particular, the asymmetries in the field components are analyzed and correlated to the ordering of the $6s^2$ lone-pair of Bi cations (occupying the A-site of the perovskite structure). Our results show that the anisotropic polarization obtained by mapping the atomic displacements is strictly related to the Ca doping gradient, which actively alters the ordering of the lone-pair of Bi atoms. In the ferroelectric regions, in fact, the localized lone-pairs on Bi cations are visible in the electric field maps as a color unbalance and they are responsible for the displacements of the oxygen octahedrons and the Fe cations (B-site) that generate the polar field. On the contrary, the higher amount of substitutional Ca dopant in the paraelectric regions is effective in breaking the lone-pair ordering, inducing a quenching of the ferroelectric instability.

The results prove that the polar state of ferroelectric thin films can be tailored at the nanoscale by controlled doping, generating complex polar patterns and creating strong polarization gradients that can be useful for the design of complex ferroelectric structures. Furthermore, the presented findings demonstrate that DPC technique is sensitive to the local charge redistributions at the origin of polar fields, opening new perspectives and challenges in advanced material characterization by transmission electron microscopy.

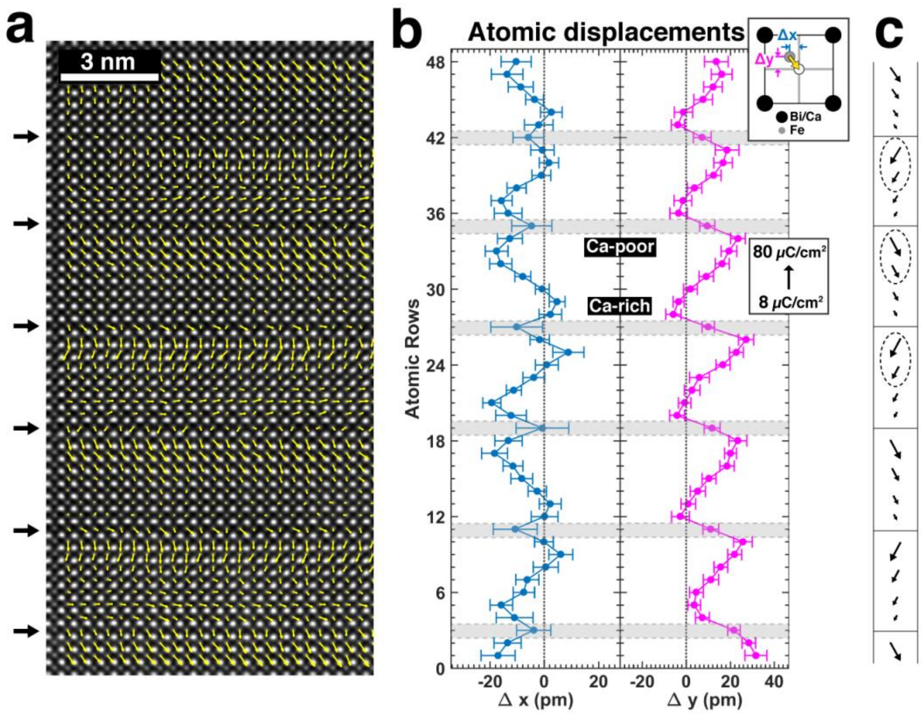

Figure 1. Analysis of the polar state of the $Bi_{0.8}Ca_{0.2}FeO_3$ thin film by HAADF-STEM imaging. (a) Polarization map superimposed to HAADF signal, (b) quantitative analysis of the atomic displacements, (c) scheme of the polar pattern.

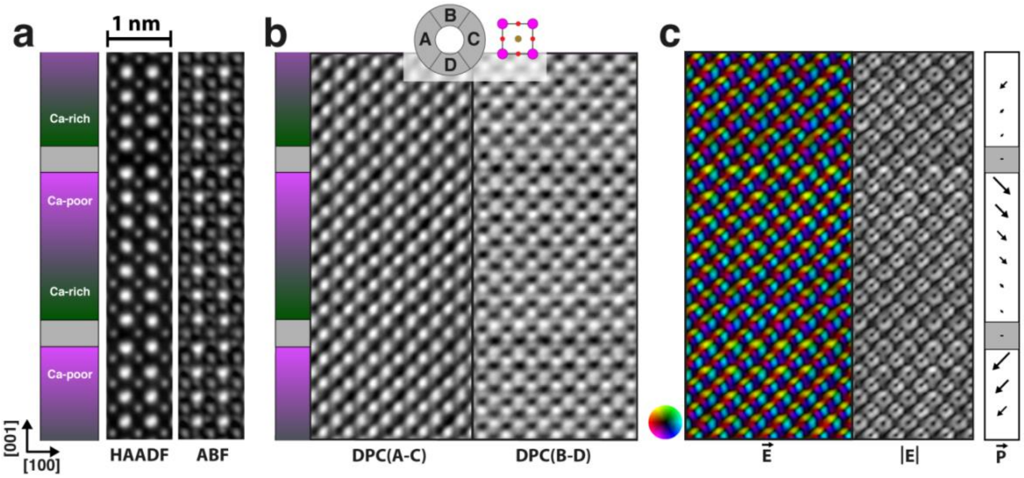

Figure 2. DPC-STEM analysis of the polar structure. (a) HAADF and ABF signals, (b) DPC signals, (c) electric-field vector and amplitude maps.

[1] N. Shibata et al., Nat. Phys. 2012, 8, 611-615.

[2] N. Shibata et al., Nat. Commun. 2017, 8, 15631.

[3] M. Campanini et al., Nano Lett. 2018, 18, 2, 717-724.

M.C. thanks NCCR-MARVEL project funded by the Swiss National Science Foundation (SNSF) for the financial support.