Highly charged 180 degree head-to-head domain walls in lead titanate

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Charged domain walls (DWs) in ferroelectric materials are an area of intense research. Microscale strain has been identified as a method of inducing arrays of twin walls to meet at right angles, forming needlepoint domains which exhibit novel material properties. Atomic scale characterisation of the features exhibiting these exciting behaviours was inaccessible with the piezoresponse force microscopy resolution of previous work. Here we use aberration corrected scanning transmission electron microscopy to observe short, stepped, highly charged DWs at the tip of the needle points in ferroelectric PbTiO3. Reverse Ti4+ shift polarisation mapping confirms the head-to-head polarisation in adjacent domains. Strain mapping reveals large deviations from the bulk and a wider DW with a high Pb2+ vacancy concentration. The extra screening charge is found to stabilise the DW perpendicular to the opposing polarisation vectors and thus constitutes the most highly charged DW possible in PbTiO3. This feature at the needle point junction is a 5 nm × 2 nm channel running through the sample and is likely to have useful conducting properties. We envisage that similar junctions can be formed in other ferroelastic materials and yield exciting phenomena for future research.
The interface is the device’ said Herbert Kroemer in his Nobel laureate speech in 2000. He was then referring to semiconductor heterostructures, however, this idea has held true for ferroic materials where domain walls (DWs) have been found to possess a high degree of functional tunability with extremely low dielectric loss. Complex domain junctions have been seen to induce exotic behaviour in ferroelectrics, from novel dipolar topologies (vortex–antivortex chains) to metallic behaviour near needle-point domains in VO$_2$ and conducting vortex cores. Hindering applications of these novel properties is the lack of knowledge of atomic-level composition. Identifying details on crystal growth and sample preparation. PTO domains (Fig. 1a) show an array of CNPs that formed in the TEM lamella cut from a single crystal of PTO. See ‘Methods’ section for details on crystal growth and sample preparation. PTO domains have a large spontaneous polarisation of 0.75 cm$^{-2}$. Four possible in-plane polarisations are allowed, which align with the major zones axes. DWs are identified by their bright intensity in the MAADF STEM image. The structural mismatch between domains causes strain at the DWs which de-channels the probe, causing additional scattering. Hence, brightness in Fig. 1a, b corresponds to increased strain. The array of stepped CNPs exhibit bright intensity at their tips. In Fig. 1b, c the reason for this becomes clear. The 180° DW is orientated along the [001] direction, 45° different to the twin DWs. This orientation causes a ~5-nm step in the twin DW boundary with an enormous resultant strain of ~29%. The stepped DW represents a 5 nm × 2 nm channel running through the sample. Figure 1c is a quantitative map of the strain measured from the atomic positions with respect to the cubic unit cell spacing. Six percent of the measured strain difference can be attributed to the rotation of the longer tetragonal c parameter in different domains. The nature of the CNP as a 180° DW is confirmed by the 6% horizontal spontaneous strain measured in both the A2 and A3 domains, perpendicular to the DW. The polarisation must be opposite in A2 and A3 to keep the longer A1/A3 DW neutral.

In PbTiO$_3$ (PTO) single crystals, needle-tip domains form due to arrays of 90° ferroelastic twin domains meeting at right angles. These regions have been highlighted by Salje et al. as potentially exciting, as they could constitute DW-based Josephson junctions in systems where some of the DW components are in the superconducting state. Recent works have focused on needle points enclosed inside another domain. In contrast, the superconducting charged needle points (CNPs) form between arrays of twin walls; two DWs bend towards each other to intersect a third, perpendicular twin DW, which results in CNP junctions. The novel properties present at CNP junctions arise from the polarisation discontinuity present, even in purely ferroelectric materials, where flexoelectric polarisation between nanoscale twin walls is significant.

Charged DWs have an energy density of one order in magnitude higher than neutral DWs, meaning they do not arise spontaneously in proper ferroelectrics. We exploit microscale elastic strain to stabilise nanoscale charged DWs. We then investigate the DW structure of the CNPs themselves, using atomic resolution polarisation mapping via aberration-corrected scanning transmission electron microscopy (STEM). Shifts in the Ti$^{4+}$ atomic columns show that the charged DW is polarised head-to-head with a high density of ionic vacancies trapped between the directly opposing electric fields.

**Results**

Figure 1a shows an array of CNPs that formed in the TEM lamella cut from a single crystal of PTO. See ‘Methods’ section for details on crystal growth and sample preparation. PTO domains have a large spontaneous polarisation of 0.75 cm$^{-2}$. Four possible in-plane polarisations are allowed, which align with the major zones axes. DWs are identified by their bright intensity in the MAADF STEM image. The structural mismatch between domains causes strain at the DWs which de-channels the probe, causing additional scattering. Hence, brightness in Fig. 1a, b corresponds to increased strain. The array of stepped CNPs exhibit bright intensity at their tips. In Fig. 1b, c the reason for this becomes clear. The 180° DW is orientated along the [001] direction, 45° different to the twin DWs. This orientation causes a ~5-nm step in the twin DW boundary with an enormous resultant strain of ~29%. The stepped DW represents a 5 nm × 2 nm channel running through the sample. Figure 1c is a quantitative map of the strain measured from the atomic positions with respect to the cubic unit cell spacing. Six percent of the measured strain difference can be attributed to the rotation of the longer tetragonal c parameter in different domains. The nature of the CNP as a 180° DW is confirmed by the 6% horizontal spontaneous strain measured in both the A2 and A3 domains, perpendicular to the DW. The polarisation must be opposite in A2 and A3 to keep the longer A1/A3 DW neutral.

Fig. 1 Medium and high-resolution images of the array of charged needle points. a Medium angle annular dark field (MAADF) scanning transmission electron microscopy (STEM) image of an array of charged needle-point domains. Scale bar = 40 nm. b High-resolution MAADF STEM image showing atomic-level detail of the structural changes across the 180° charged domain wall. This domain wall forms a “nanochannel” of cross-section 5 nm × 2 nm running through the sample. Spontaneous polarisation interpreted from (c) marked with yellow arrows. Scale bar = 8 nm. c Quantitative strain map of (b), measured with respect to the theoretical cubic lattice parameter at room temperature (3.929 Å). There is ~29% strain at the junction where the structure ruptures. Scale bar = 8 nm.
appears to constrain the charged wall to the vertical (100) plane, polarisation vectors in the adjacent domains. The charged state vertical A2/A3 DW in Fig.3a is almost perpendicular to the 180°

The extent of the H character at the CNP. In Fig. 4a, the contributions from de-channelling have been removed from Fig. 1b (see Supplementary Fig. 2 and Supplementary note 1 for details). Figure 4b maps out the integrated and normalised column intensities which are proportional to the number of Pb atoms present. The intensity drop of 10% is compared to Bi vacancy simulations by Rojac et al. and corresponds to the presence of ~20+/−5% Pb vacancies (VPb2−)

Figure 4 shows intensity differences of the Pb atomic columns across the CNP. In Fig. 4a, the contributions from de-channelling have been removed from Fig. 1b. In doing so it causes the needle-point A2 domain to change from a neutral H–H state into a H–H CNP.

Discussion

The extent of the H–H character at the CNP is remarkable. The vertical A2/A3 DW in Fig. 3a is almost perpendicular to the 180° polarisation vectors in the adjacent domains. The charged state appears to constrain the charged wall to the vertical (100) plane, hence creating the observed step. For the H–H DW to be stabilised the polarisation on either side must be fully screened, meaning it should contain 2 × Pe of negative charge. The charge at the PTO DW is then ae = (2)(0.75 cm−2)(0.39 nm)2 = 2.28 × 10−19 C per unit cell. Structural analysis in Fig. 2 and the de-channelling intensity in Fig. 1b suggest that the domain wall is 2 nm/5 unit cells in width but Fig. 4b suggests that vacancies are confined to 2 or 3 unit cells at the DW. Even assuming the charge is spread over 4 unit cells, the charge density p = 2.28 × 10−19 C/0.39 nm = 0.36 e− per unit cell, where e− = 1.6 × 10−19 C, elementary charge. Eighteen-percent Pb vacancies (VPb2−) would provide this charge. Examining Fig. 4b, c shows that the Pb intensity drops by ~10% at the H–H DW. Pb columns are comparable to Bi in BiFeO3, where a 10% intensity drop corresponds to 20+/−5% vacancies. Therefore, the experimental evidence supports the presence of Pb vacancies stabilising the H–H DW at the CNP.

The properties observed are very different to those at the H–H DW identified in lead zirconate titanate by Jia et al. We note that Sifuna et al. recently calculated that a 2D electron gas would be found screening PTO H–H DWs but did not take into account the 5% vacancies present intrinsically in single-crystal PTO due to Pb and O volatility. Vacancies provide a readily available source for charge screening and are energetically cheaper than creating free electrons. Indeed, in Fig. 4b, we see a variation in intensities within domains. Vacancies are clearly concentrated at the bent (and therefore charged) A1/A2 DWs that make up the needle. They are also found in the strained area in the upper left A1 domain. By contrast, the less strained, neutral A1/A3 DWs
shows no localisation of vacancies at the wall. These observations point towards a combined contribution of strain and electrostatic energy in holding vacancies at DWs around the CNP, in agreement with theoretical calculations. Thus there are likely O and Ti vacancies present too.

The enormous screening charge density has stabilised the array of CNPs and allowed otherwise elastically impossible properties to stabilise in the constituent DWs. Figure 2a–c offers an insight into the structural deformation by comparing profiles of the spontaneous strain, tetragonality and structural rotation across the CNP (red) and a normal, neutral twin wall (dotted, blue). The spontaneous strain $\varepsilon_{xx}$ in Fig. 2a is measured with respect to the theoretical cubic room temperature unit cell spacing (3.929 Å). The average $c$ and $a$ parameters are 5% and $-1\%$, respectively, in the areas furthest from the disruptive influence of the CNP, in agreement with theory (see Supplementary Fig. 3). Profile 2 in Fig. 2a exhibits the expected sharp transition from $a$ to $c$ spacing across the twin wall. Approaching the CNP, profile 1 in Fig. 2a drops below 2.5% at 7 nm before increasing drastically to 17% at the DW itself around 9.5 nm. There is a prolonged strain gradient away from the DW and even at 20 nm (10 nm away from the CNP) the structure has not fully relaxed back to 5%. In Fig. 1c we observe that in the A3 domain, in front of the CNP, strain extends mostly in the $x$ direction. There is a larger strain gradient in the $y$ direction, as the structure is relaxed directly above the CNP in the A3 domain.

Whilst there is only a very small difference in strain in the H–H domains (A2 and A3), Fig. 2c reveals that there is a severe rotation difference of 6° between them. The measured rotation is as high as 9° at the tip of the needle where there is an extra distortion from the ruptured structure. This can be seen clearly by inspecting the darker areas of the [001]$_{pc}$ lattice planes in Fig. 2b.

**Fig. 3** Polarisation map of domains either side of the charged needle point. a Medium angle annular dark field image of the needle-point domain structure. Boxes indicate the areas of least strain considered in polarisation mapping, and yellow arrows denote the polarisation ($P_s$) directions. Scale bar = 5 nm. b, c Unit cell polarisation maps of the highlighted areas in domains A3 (blue, dashed outline) and A2 (red, solid outline), respectively. d, e Schematics showing the unit cell deformation in tetragonal PbTiO$_3$ and the resulting polarisation in the direction opposite to the Ti shift. $\Delta$O and $\Delta$Ti refer to the displacements of the oxygen and titanium columns from their neutral positions, respectively. Scale bar = 0.5 nm.

**Fig. 4** Evidence for vacancies at the charged needle point. a Background subtracted medium angle annular dark field image of a charged needle point with overlay showing the location of the line profiles in (c). b Integrated intensity of each Pb atomic column, normalised to the maximum. c Line profiles across a charged domain wall (1, red) and across a neutral A1/A3 DW (2, blue). Scale bars = 8 nm.
Fig. 5 In situ switching narrows the charged needle point. The domain wall region (a) before and (b) after switching by the electron beam. Distance labels indicate the length of the needle tip in each case. From the initial neutral configuration in (a), the junction becomes charged in (b) after movement of the 180° (dashed yellow) domain wall to the bottom right corner. The needle point narrows from 10.6 nm to 5 nm in response. Scale bars = 20 nm.

The strain gradient extending into the A3 domain is mirrored by a 2° rotation gradient in profile 1 starting from 11 nm.

Figure 2d compares the c/a ratio of each unit cell, nominally a uniform 1.06, around the junction. Looking first at the map, this is clearly not the case. Overall, the needle domain has been compressed into a more cubic shape, while the adjacent domains have been pulled into a more tetragonal shape. Directly in front of the CNP the strain gradient into A3 means that the unit cells are highly tetragonal there, c/a = 1.08, but less tetragonal than normal at shallow angles from the CNP, close to the twin boundary, c/a = 1.05. The black lines tracing the twin DWs show their almost diagonal (110)pc plane. Large strain gradients may also lead to a 180° (dashed yellow) domain wall to the bottom right corner. The needle point narrows from 10.6 nm to 5 nm in response. Scale bars = 20 nm.

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Fig. 6 Overview of the domain structure that causes charged needle points. a Lower magnification scanning transmission electron microscopy image showing the wider domain structure with both an enclosed needle (top) and an array of charged needle points. b 3D model of the domain configuration in (a) leading to charged nanochannels at the charged needle points. The model is tilted with respect to the real viewing direction to show the 3D structure. Scale bar is 100 nm.

screen current was ~ 41 pA. Atom position finding and 2D Gaussian refinement were completed with the Atomap Python package8. Image analysis and mapping, as well as polarisation vector analysis, were completed using the TEMUL Toolkit Python package8. A walkthrough of the processing steps will be available at the TEMUL Toolkit repository (www.github.com/PinkShack/TEMUL). Strain analysis for Supplementary Fig. 1 was carried out by geometric phase analysis using the Stem Cell program9.

Data availability

The charged needle point STEM dataset and analysis can be found at https://temul-toolkit.readthedocs.io/en/latest/PTO_Junction_moore.html. Other datasets supporting the findings of this study are available from the corresponding authors upon reasonable request.

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Competing interests
The authors declare no competing interests.

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