Direct Observation of Ferrielectricity at Ferroelastic Domain Boundaries in CaTiO$_3$ by Electron Microscopy

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Ever since it has been realized that interfaces and domain boundaries are not necessarily a simple structural juxtaposition of adjacent bulk materials, but contain novel structural elements which do not exist in the bulk, the chase for such “exotic” interfaces has begun. Typical examples are superconducting domain boundaries in insulating materials,[1,2] twin boundaries with high defect mobilities,[3–6] two-dimensional electron gas at interfaces,[7–10] unusual vortices near twin boundaries,[11] or multiferroicity and chirality at domain boundaries.[12–14] If such properties are exclusively related to interfaces or domain boundaries, then they qualify as objects of the emerging field of “domain boundary engineering”.[15,16] This name became popular because it embodies the hope that “active” domain boundaries can, one day, be reproduced in an engineering fashion rather than being simply observed in suitable samples. A typical example is the IBM racetrack memory based on the controlled movement of magnetic domain walls. Their movement is registered electromagnetically and their position is used as memory information. The desired breakthrough is now to use ferroelectric domain walls where the information can be written and read by simple application of electric fields. The memory is the location and the ferroelectric spontaneous polarisation of the domain wall with expected memory densities well above any current application. The wider industrial consequence of such local structures as memory devices, conductors, holographic templates, or as membranes for batteries have motivated significant research efforts during recent years.

One of the first materials, which was identified theoretically for domain boundary applications, was CaTiO$_3$. Two lines of research come together in this material: first, it was shown numerically for domain boundary applications, was CaTiO$_3$. Two lines of research come together in this material: first, it was shown that oxygen vacancies are confined to the domain boundaries. We will show that the predicted structural singularities in CaTiO$_3$ exist and that these features are mainly ferrielectric with maximum dipole moments at the wall; a small ferroelectric dipole moment was found perpendicular to the wall with alternating (antiferroelectric) dipoles between neighbouring walls. The same tendency for polar layers in CaTiO$_3$, e.g., near surfaces, was also predicted for CaTiO$_3$/BaTiO$_3$ interfaces.[21]

The great challenge for domain boundary studies is to observe the described singularities experimentally. Transport studies have made great progress in the understanding of domain wall conductivity[1–10] and atomic force microscopy (AFM) has shown that conductivity is, indeed, restricted to the domain walls.[2,4] However, in contrast to transmission electron microscopy (TEM), AFM only reveals information about near surface regions.[4] In this paper, we will show that sufficient advances have been made using aberration-corrected TEM imaging in combination with statistical parameter estimation theory[23–25] to not only visualize atomic displacements directly inside domain boundaries but also to measure their displacements, atomic layer by atomic layer, with picometer precision. This opens the door for massive advances in the investigation, design, and production of active domain boundaries and local structures that are based on small, local atomic displacements inside extended crystal lattices. We will argue that the predicted structural singularities in CaTiO$_3$ exist and that these features are confined to the domain boundaries. We will show that the dominant off-centering of Ti can be observed while all other structural deformations, such as, shifts of the Ca atomic positions, remain too small to be seen.

Twin boundaries in CaTiO$_3$ have been imaged using aberration-corrected TEM in combination with exit wave reconstruction.[26] The insertion of multipole aberration-correcting elements in the electron optical column has significantly improved the direct interpretability of TEM images. A FEI Titan$^3$ 50–80 operated at 300 kV has been used in this study providing direct structural imaging at a sub-Å resolution level. Further improvement of the resolution up to the information limit of the microscope can be achieved by reconstructing the so-called exit wave, which is in fact the complex electron wave when leaving the specimen. The idea is to invert the image formation process so that all residual lens aberrations can be
eliminated. This requires post acquisition processing of multiple images recorded under varying imaging conditions. Here, we used the through-focal series reconstruction method in which the exit wave is reconstructed from a set of images taken at different defocus values. The present observations relate to a (110) type twin boundary formed in the orthorhombic Pnma CaTiO$_3$ phase after cooling from the cubic high temperature phase and imaged along its [001] zone-axis in order to maximize the visibility of any expected atomic displacements. The imaging conditions are schematized in Figure 1, also noting the respective definitions for the further discussion. The experimental focal series comprised 20 images separated by a focal increment of –2.4 nm with the series centred around the zero defocus condition (starting defocus +27 nm) with a spherical aberration coefficient of +50 μm (see the Experimental Section for a full list of experimental parameters). The actual reconstruction of the exit wave is carried out using the TrueImage software. After reconstruction the residual aberrations are corrected using the standard techniques in TrueImage. The amplitude and phase of the reconstructed exit wave are shown in Figure 2a and b, respectively, with a resolution equal to 0.8 Å. An example of a low-magnification image of the relevant area is given in the Supporting Information (Figure S1) including a fast Fourier transform (FFT) revealing the spot splitting confirming the twin nature of the interface.

Although the combination of exit wave reconstruction with aberration-corrected TEM significantly improves the visual interpretability, quantitative numbers for the atomic column positions are still lacking. Therefore, techniques such as statistical parameter estimation theory need to be included in order to properly interpret the experimental data. This allows position measurements of all atomic columns with a precision of a few picometers without being restricted by the information limit of the microscope. For a further quantitative analysis we will use the phase of the reconstructed exit wave since it is directly proportional to the projected electrostatic potential of the structure. First, the atomic column positions are estimated using statistical parameter estimation theory (see the Experimental Section for a full list of experimental parameters). The actual reconstruction of the exit wave is carried out using the TrueImage software. After reconstruction the residual aberrations are corrected using the standard techniques in TrueImage. The amplitude and phase of the reconstructed exit wave are shown in Figure 2a and b, respectively, with a resolution equal to 0.8 Å. An example of a low-magnification image of the relevant area is given in the Supporting Information (Figure S1) including a fast Fourier transform (FFT) revealing the spot splitting confirming the twin nature of the interface.

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interatomic column distances between neighbouring Ca–Ca and Ti–Ti columns are determined. In Figure 3b, the distances perpendicular to the twin wall are presented in terms of their mean values, averaged in the direction parallel with the twin wall, together with their 90% confidence intervals. The vertical red line corresponds to the overall mean Ca–Ca interatomic distance. Note the deviations from this line for particular Ti–Ti atomic column distances close to the twin wall (arrows).

c) Mean interatomic Ca–Ca and Ti–Ti column distances parallel with the twin wall, averaged in the direction parallel with the twin wall, together with their 90% confidence intervals. The vertical red line corresponds to the overall mean Ca–Ca interatomic distance. No deviations from this line are observed for the Ca–Ca or the Ti–Ti atomic column distances.

d) Mean displacements of the Ti atomic columns from the center of the four neighbouring Ca atomic columns and indicated by green arrows. e,f) Displacements of Ti atomic columns in the x- and y-directions averaged along and in mirror operation with respect to the twin wall together with their 90% confidence intervals.

The previous analyses clearly indicate shifts in the Ti atomic positions whereas any shifts in the Ca atomic positions are too small to be identified. Therefore, in the following, we will focus on the off-centering of the Ti atomic positions with respect to the center of the neighboring four Ca atomic positions. As these displacements are largely random and small as compared to the experimental measurement precision, we will extract the systematic fluctuations related to the twin wall using the following filtering. First, we average all displacements in planes parallel to the twin wall. Next, we average the results in the planes above with the corresponding planes below the twin wall. This second operation identifies the overall symmetry of the sample with the twin wall representing a mirror plane. The

resulting displacements along and perpendicular to the twin wall are shown in Figure 3e and f together with their 90% confidence intervals. In the x-direction (perpendicular to the wall), we find systematic deviations for Ti of 3.1 pm in the second closest layers pointing toward the twin wall. A larger displacement is measured in the y-direction (parallel to the wall) in the layers adjacent to the twin wall. The averaged displacement in these layers is 6.1 pm. In all layers further away from the twin wall, no systematic deviations in x- or y-direction are observed. The significant shifts are schematically shown in Figure 3d.

These results can now be compared with the predictions for the displacements in the literature. Goncalves-Ferreira et al.\textsuperscript{[17]} found large displacements of Ti with much smaller values for Ca. They also showed that the main Ti displacements occur inside the twin wall, by which displacements parallel to the twin wall are implied, with only a small component perpendicular to the wall (their Figure 2). The thickness of the domain wall is ca. two octahedra, which is the same length scale as in the present experiments. The displacement pattern can be seen as a combination of ferroelectric and antiferroelectric/ferrielectric components. The ferroelectric component is the smaller one and has effect both parallel as well as perpendicular to the wall. This is the only component which we can observe in our experiment because the anticipated larger antiferroelectric movement of Ti atoms displaces pairs of Ti in an antiparallel fashion at the wall. Averaging over the wall along the viewing direction thus yields no resulting displacement which would be visible in the electron microscope. Nevertheless, simulations\textsuperscript{[17]} show a very strong coupling between the ferroelectric and antiferroelectric movement so that our observations imply that antiferroelectricity concurs with ferroelectricity in the domain walls. We may now compare the observed and predicted displacement amplitudes: the theoretical predictions are based on empirical potentials and vary somewhat with the model parameters. The largest amplitude of some 2 pm was found along the c-direction with an antiferroelectric displacement pattern. The ferroelectric component along the y-axis is anticipated from the simulations to be slightly below 1 pm amplitude. In the calculations this displacement is not maximum in the centre of the wall but shows two peaks on either side of the centre; this however might be an artifact of the model which would lead in Landau coupling to displacements of some 1.5 pm. All amplitudes depend on the actual model parameters with variations of 30% within the same model but different energy minimizing conditions. The only visible displacement in the y-direction in the present experiment is 6 pm, i.e., 4 times bigger than the largest value anticipated by model calculations. Nevertheless, calculations in their present version can only give rough orders of magnitude for the displacements but we expect that they predict correctly that the displacements are finite in the twin wall and lead to ferroelectricity in CaTiO$_3$.

Finally, let us comment on the magnitude of the spontaneous polarization of the wall. In the model calculations it was found that, depending on the chosen model, the wall polarization is between 0.004 and 0.02 Clb m$^{-2}$. Using the experimental value for the displacement of 6 pm we expect the polarization to be as big as 0.04–0.2 Clb m$^{-2}$. This value is comparable with the bulk spontaneous polarization of BaTiO$_3$ (0.24 Clb m$^{-2}$) and confirms the tendency of interfacial structures to enhance the spontaneous polarization.\textsuperscript{[30]} Important progress is presented in this paper: we do not enhance ferroelectricity, we generate it! This means that ferroelectricity is indeed confined to twin boundaries in a paraelectric matrix. In addition, we can now observe such localized effects experimentally. Moreover, the density of these defects can be controlled by slow cooling through the cubic-to-orthorhombic transformation temperature while their position can be changed by external stress applied using a micromanipulator. Devices can then be imagined where each domain wall acts as a memory element, which can be switched electrically. The pixel density is then as high as the domain wall density and can surpass all known ferroelectric devices known so far. Recent developments in electron microscopy have advanced our resolution to the point that we can now measure small atomic displacements inside domain boundaries which opens the door for using such domain boundaries as active elements in such device applications.

### Table 1. List of experimental parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting defocus</td>
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<tr>
<td>Number of focal images</td>
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<tr>
<td>Focal increment</td>
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<tr>
<td>Spherical aberration constant</td>
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<td>Focal spread</td>
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<td>Convergence angle</td>
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<td>Pixel size</td>
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</tr>
</tbody>
</table>

### Experimental Section

The CaTiO$_3$ single crystals were grown by the floating-zone technique with powders of CaCO$_3$ and TiO$_2$ (99.9% purity) as starting materials.\textsuperscript{[31]}

All electron microscopy, including through focal series reconstruction of the complex exit wave of the (110) twin boundary region, was performed on a FEI Titan\textsuperscript{5} 50–80 microscope operated at 300 kV acceleration voltage. The parameters used for the through-focal series reconstruction are summarized in Table 1.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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