Depth Resolved Domain Mapping in Tetragonal SrTiO₃ by Micro-Laue Diffraction

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We present depth resolved X-ray micro-Laue diffraction experiments on the low temperature domain structure of $SrTiO_3$. At 80 K, monochromatic X-ray diffraction shows an elongated out-of-plane unit cell axis within a matrix of in-plane oriented tetragonal unit cells. Full deviatoric strain mappings from white beam diffraction show a dominance of two tetragonal domain orientations (x- and z-axis) over a large area of sample surface. This information sets an upper bound on domain wall widths and offers a method for studying 3D domain structure at low temperatures.

Keywords: SrTiO₃, tetragonal, strain, micro-Laue diffraction

Thin film oxide structures, and specifically perovskitederived materials, are of high interest to the scientific community as well as to industry due to the myriad of phenomena which have been demonstrated in them superconductivity, ferromagnetism, and ferroelectricity to name a few^{1,2}. SrTiO₃ is widely used as a substrate for many perovskite thin films, but the bulk insulating phase is interesting on its own due to its non-mean-field critical exponents³ and possible proximity to a ferroelectric quantum critical point^{4,5}. Despite interest both as a substrate and as a stand alone bulk crystal, a complete understanding of the μ m scale crystal structure and strain propagation near domain walls is still lacking.

This gap in understanding and its importance to the physical properties of $SrTiO_3$ has recently been highlighted by several papers indicating the presence of piezoelectric domain walls^{6–8} and enhanced current along domain structures⁹. A necessary first step to quantifying the importance of domain walls is measuring the intrinsic size of the domain walls and the locally induced strain field near them. Micro focused X-ray diffraction is well suited to ascertain the domain wall size due to its high resolution and lack of reliance on artificially thinned samples, that may introduce domain wall patterns which are not characteristic of single, isolated surfaces¹⁰.

SrTiO₃ undergoes a predominantly second order cubic to tetragonal phase transition at ≈ 105 K, driven by subtle rotations of the oxygen octahedra^{11,12}. The tetragonal unit cell rotates by 45° in the *x-y* plane, doubles in length in *c*-axis, and grows by $\sqrt{2}$ in each direction in the basal plane relative to the high temperature cubic unit cell. A pseudocubic convention will be used here, in which the pseudocubic axes are parallel to the high-temperature cubic axes and the tetragonality is understood as the elongation of the pseudocubic *c*-axis relative to the pseudocubic *a*-axes. The second order nature of the phase transition causes the tetragonality to saturate¹³ by ≈ 40 K to a value of $1 - c/a \approx -7 \times 10^{-4}$. The nucleation process drives a twin structure below ≈ 105 K in SrTiO₃ where, upon crossing a domain boundary, the elongated crystal axis rotates by 90°. See Fig. 1 for a schematic of these three domains and their symmetry predicted intersection angles¹⁴.



FIG. 1. Schematic diagram of the different tetragonal domains formed in $SrTiO_3$ and their domain wall intersection angles. The labels X, Y, and Z denote which pseudocubic axis is the tetragonal axis.

Historically, there have been many efforts to measure the volume averaged (on mm³ scale) domain structure below the cubic to tetragonal phase transition in SrTiO₃ using X-rays^{13,15–20} as well as other means^{6,7,11,12,21–24}, but no single method has provided both imaging and high resolution structural information necessary to quantify domain walls. This paper takes steps to tie together many of the previous X-ray structural studies and imaging results. Spatially resolved structural information, such as presented here, will be critical in understanding not only SrTiO₃'s behavior below 105 K, but also

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any heterostructures involving $SrTiO_3$; the demonstration of piezoelectric domain walls⁸ and enhanced conductivities near domain walls⁹ illustrates the importance of domain wall quantification to the detailed understanding of $SrTiO_3$ heterostructures.



FIG. 2. Diagram of the low temperature differential aperture X-ray microdiffraction (DAXM) setup: (a) chamber enclosure; (b) coldfinger; (c) sample; (d) incident X-ray window; (e) depth profiling wire; (f) outgoing X-ray window; (g) side window for dry N_2 gas exit and wire insertion.

Using differential aperture X-ray microdiffraction $(DAXM)^{25-27}$ at beamline 34ID-E at the Advanced Photon Source, we have examined the structural domains in SrTiO₃ below the cubic to tetragonal phase transition with high spatial resolution ($\approx 5 \ \mu m$ final resolution coming from a $\approx 1 \ \mu m$ beam width and a 5 $\ \mu m$ planar step size) and high reciprocal space resolution ($< 10^{-3}$ Å⁻¹). The white X-ray spectrum used ranged in energy from 7 to 30 keV with a corresponding penetration depth into SrTiO₃ of 13 to 179 $\ \mu m$, respectively. Combined resolution at this scale offers the ability to examine the structural phase transition in SrTiO₃, where subsurface structure is no longer inferred but directly measured, and local strain configurations near the surface or domain walls can be examined.

DAXM experiments at 34ID-E use white or monochromatic energy X-rays focused with a pair of Kirkpatric-Baez mirrors to a fixed spot 0.6 μ m × 0.6 μ m in size, while depth profiling wire scans provide micrometer resolution along the X-ray penetration direction²⁵. The Laue diffraction peaks are collected with a Perkin Elmer XRD1620 area detector. To allow DAXM measurements to be carried out at low temperatures, a specially designed stage was employed as illustrated in Fig. 2.

The stage temperature was controlled by a constant liquid nitrogen flow together with variable Ohmic heating. The coldfinger was contained in a custom 3D printed enclosure, which has an incident X-ray window made of a 20 μ m thick aluminum foil, as well as an outgoing X-ray window of 100 μ m thick Kapton tape. A thin tungsten rod (≈ 50 mm long and $\approx 500 \ \mu$ m in diameter) was used as a depth profiling wire. A side window was opened on the enclosure to allow the wire to be inserted into the chamber and scanned over the sample surface. The same opening also served as the outlet for the flow of dry \mathbf{N}_2 through the chamber to prevent condensation on the sample surface.

The sample used in this study was an ≈ 5 nm thick 1 at.% Nb doped $SrTiO_3$ layer grown between two 100 nm thick undoped $SrTiO_3$ layers on a (100) $SrTiO_3$ substrate (Shinkosha Co.) fabricated by pulsed laser deposition. Detailed preparation methods are described elsewhere²⁸. The sample was cut into a 2 mm \times 5 $mm \times 0.5 mm$ platelet after growth and mounted on the coldstage of the enclosure in Fig. 2 by copper paste. All sample edges were parallel to the $\langle 100 \rangle$ cubic axes. An SrTiO₃ heterostructure was chosen here to approximate the processing conditions—cutting, growth, and annealing—that a representative heterostructure might experience; the > 1000 °C growth temperature and near surface, dopant induced electric field are likely to influence domain structure and release surface strain from factory polishing present in the substrate.

The surface boundary conditions are especially important for the overall domain structure since it has been shown that the structural transformation occurs near the surface at higher temperatures than the bulk and could seed the overall domain structure²⁹. In this regard we note the surprising result that a nominally unprocessed substrate was measured in the same beam time and showed no discernible domains under the same experimental conditions as the data shown here; monochromatic X-ray scans showed it to be single domain with the tetragonal axis in plane—see Fig. 3 (b).



FIG. 3. (a) Two-dimensional distribution of out of plane lattice constant, from the (004) reflection, measured by monochromatic DAXM at 80 K. (b) Line cut at a depth of 10 μ m from the main figure. Dashed lines represent the lattice constants from literature¹³ at 85 K; dotted line represents the lattice constant from the monodomain substrate at 78 K. See Fig. S1 for an explanation³⁰ of domain wall angle, β .

Figure 3 shows the depth resolved out-of-plane lattice constant—measured at 80 K using a monochromated X-ray beam—over a 2D section which spans 200 μ m along the sample surface (|| [100]) and 20 μ m into the sample along the X-ray penetration depth. We observe regions with an expanded out-of-plane lattice constant (Z-domains) embedded in a matrix with smaller out-ofplane lattice constant (X- or Y-domains). Figure 3 (b) demonstrates the variation of out-of-plane lattice constant at a fixed depth of 10 μ m below the surface which match closely with previous bulk experiments¹³. The heterostructure is much less than one pixel wide in these data, but its influence through seeding of domains may still be significant, as discussed previously.

A white-beam Laue study of the same 2D section seen in Fig. 3 allowed a full deviatoric strain refinement to be performed for each X-ray volume, with the results shown in Fig. 4. The refinement is performed using a non-linear least squares fitting to the entire Laue pattern collected at each spatial position based on a perturbed cubic unit cell. From the small deviations in Laue spot positions it is possible to determine the amount of deviation from a perfect cubic unit cell. This method allows for an unambiguous determination of the orientation of tetragonal domains that surround the Z-domains seen in Fig. 3. Figure 4 clearly shows that the Z-domains in the area of investigation are embedded in a matrix of X-domains.



FIG. 4. Deviatoric strain in SrTiO₃. (a) [100], [010], and [001] components of local lattice dilation. (b) Line cut of local lattice dilation at a depth of 10 μ m. A systematic error of approximately 3×10^{-4} is present in the [010] channel of this refinement from uncertainties in sample/detector positioning. The dashed line represents the expected deviatoric strain for SrTiO₃ at 85 K¹³.

Figure 4 shows that only two of the three possible tetragonal domain orientations present in this line cut of the sample: x-axis and z-axis oriented domains. The featureless deviatoric [010] strain map indicates that no y-axis oriented domains exist over the 200 μ m scan range. Other larger area scans were also taken in the surrounding areas of the crystal and in a 0.6 mm × 0.6 mm region (data not shown here) there were no detectable Y-domains. Similarly, shear components of the deviatoric

strain tensor also did not exhibit any features. Scans, not shown here, were taken at room temperature and showed no twin features, as expected for the cubic phase.

From the most naïve symmetry arguments, an equal population of X-, Y-, and Z-domains are expected to form when cooling through the cubic to tetragonal phase transition. Nonetheless, this is not what has been seen in recent literature^{8,9,31} for SrTiO₃, consistent with a lack of Y-domains in Fig. 4. The relative absence of X-domain to Y-domain walls seems very likely to be related to shape anisotropy effects¹²; it has been shown that a thinned (110) platelet exhibits only a single domain. An understanding even at the Ginzburg-Landau level that includes surface/boundary terms that might explain this phenomena is still lacking.

Furthermore, the domain walls can be seen to penetrate into the bulk of the sample at an angle close to 56° to the beam direction (45° to the surface normal as demonstrated³⁰ in Fig. S1), consistent with other cubic to tetragonal transitions in related materials^{32,33}. The single pixel changes from one domain type to the other show that there is no evidence for domain walls wider than $\approx 5 \ \mu m$ —our spatial resolution—in the *x-y* plane, nor of near surface kinks¹⁰. Such a small domain wall is in stark contrast to 25 μm wide walls which have been observed in BaTiO₃ by similar methods³². The domain walls appear to have no change in behavior within $\approx 1 \ \mu m$ of the surface, contrary to what was seen by monochromatic X-ray diffraction¹⁰ on BaTiO₃.

Arguments based on Ginzburg-Landau phenomenology predict that the domain wall width of bulk $SrTiO_3$ should be only several nanometers wide³⁴. The upper bound on domain wall thicknesses observed at 80 K is consistent with these predictions as well as with transmission electron microscopy from other similar perovskites^{35–38}.

The thin domain wall width as measured herein helps to interpret current mapping by Kalisky et al.⁹ in LaAlO₃/SrTiO₃ and superfluid density mapping by Noad et $al.^{39}$ in thin Nb doped SrTiO₃ layers similar to those studied here. From the X-ray work reported here, it is clear that domain walls are smaller than 5 μ m. The variations in transport properties (current and superfluid density) range from a similar resolution-limited size of several microns to many tens of μ m. It may be that the different samples have different domain structures: that the enhancement of transport properties near domain walls is driven by thin crystallographic changes sheathed in much larger electrostatic effects, such as carrier density driven dielectric constant variations⁴⁰; or that different domains have different transport properties depending on the orientation of the c-axis relative to the heterostructure. The observation of transport properties varying on much longer length scales than any crystallographic variations establishes the need for detailed macroscopic electrostatic modeling of any near surface regions; this modeling will be integral to the understanding of device physics as micro- and nanoscale processing becomes more

common.

Of special interest in the literature is the pioneering work done at SPring-8 on white beam imaging and diffraction experiments^{16,17,20} on the domain structure of SrTiO₃. The domain structure observed by Ozaki *et al.*²⁰ is generally confirmed here. Their inferred domain wall width—tens of μ m—at 30 K are several times wider than those reported here at 80 K. The X-ray micro-Laue method presented herein extends the SPring-8 work by allowing a *direct* measurement lattice strains *in three dimensions* in contrast to inferences based on intensity patterns from X-ray topography²⁰. Through the increased spatial resolution and the addition of a depth resolved technique, we are able to place a tighter upper bound on the domain wall width¹⁷ of 5 μ m at 80 K.

Depth resolved, low temperature micro-Laue measurements of SrTiO₃ have allowed the observation of 45° domain walls into the bulk of the crystal and has allowed the setting of an upper bound on domain wall width of several micrometers. Future efforts with increased spatial resolution will offer a way forward in understanding the formation and dynamics of SrTiO₃ domain walls, especially under the application of electric field^{8,41} and stress⁴². Such studies may lead to a better understanding of the longstanding problem of how shape anisotropy influences the twin structure¹² of SrTiO₃.

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- ¹H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nature Materials **11**, 103 (2012).
- ²P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, Annual Review of Condensed Matter Physics 2, 141 (2011).
- ³K. Müller and W. Berlinger, Physical Review Letters 26, 13 (1971).
- ⁴K. Müller and H. Burkard, Physical Review B **19**, 3593 (1979).
- ⁵S. E. Rowley, L. J. Spalek, R. P. Smith, M. P. M. Dean, M. Itoh, J. F. Scott, G. G. Lonzarich, and S. S. Saxena, Nature Physics 10, 367 (2014).
- ⁶J. F. Scott, E. K. H. Salje, and M. A. Carpenter, Physical Review Letters **109**, 187601 (2012).
- ⁷E. K. H. Salje, O. Aktas, M. Carpenter, V. Laguta, and J. Scott, Physical Review Letters **111**, 247603 (2013).
- ⁸M. Honig, J. A. Sulpizio, J. Drori, A. Joshua, E. Zeldov, and S. Ilani, Nature Materials **12**, 1112 (2013).

- ⁹B. Kalisky, E. M. Spanton, H. Noad, J. R. Kirtley, K. C. Nowack,
- C. Bell, H. K. Sato, M. Hosoda, Y. Xie, Y. Hikita, C. Woltmann, G. Pfanzelt, R. Jany, C. Richter, H. Y. Hwang, J. Mannhart, and K. A. Moler, Nature Materials **12**, 1091 (2013).
- ¹⁰M. Holt, K. Hassani, and M. Sutton, Physical Review Letters 95, 085504 (2005).
- ¹¹K. Müller, W. Berlinger, and F. Waldner, Physical Review Letters **21**, 814 (1968).
- ¹²K. A. Müller, W. Berlinger, M. Capizzi, and H. Granicher, Solid State Communications 8, 549 (1970).
- ¹³A. Okazaki and M. Kawaminami, Mat. Res. Bull. 8, 545 (1973).
- ¹⁴J. Sapriel, Physical Review B **12**, 5128 (1975).
- ¹⁵T. Koga, Z. Lu, K. Munakata, M. Hatakeyama, Y. Soejima, and A. Okazaki, Phase Transitions 54, 109 (1995).
- ¹⁶T. Ozaki, I. Fujimoto, K. Mizuno, S. Iida, K. Kajiwara, T. Taira, J. Yoshimura, T. Shimura, and Y. Chikaura, Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms **199**, 81 (2003).
- ¹⁷K. Kajiwara, T. Ozaki, H. Sakaue, Y. Taketomi, and Y. Chikaura, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 238, 248 (2005).
- ¹⁸N. Ohama, H. Sakashita, and A. Okazaki, Phase Transitions 4, 81 (2006).
- ¹⁹M. Sato, Y. Soejima, N. Ohama, A. Okazaki, H. J. Scheel, and K. A. Müller, Phase Transitions 5, 207 (2006).
- ²⁰T. Ozaki, K. Kusunose, H. Sakaue, H. Okamoto, K. Kajiwara, Y. Suzuki, and Y. Chikaura, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **238**, 255 (2005).
- $^{21}\text{E.}$ Courtens, Physical Review Letters $\mathbf{29},\,1380$ (1972).
- ²²J. Slonczewski, Physical Review B 2, 4646 (1970).
- ²³F. Kuchar and P. Frankus, Physical Review B 16, 874 (1977).
- ²⁴M. A. Geday and A. M. Glazer, Journal of Physics: Condensed Matter 16, 3303 (2004).
- ²⁵B. C. Larson, W. Yang, G. E. Ice, J. D. Budai, and J. Z. Tischler, Nature **415**, 887 (2002).
- ²⁶G. E. Ice, B. C. Larson, W. Yang, J. D. Budai, J. Z. Tischler, J. W. L. Pang, R. I. Barabash, and W. Liu, Journal of Synchrotron Radiation **12**, 155 (2004).
- ²⁷G. E. Ice, J. D. Budai, and J. W. L. Pang, Science **334**, 1234 (2011).
- ²⁸Y. Kozuka, Y. Hikita, C. Bell, and H. Y. Hwang, Applied Physics Letters **97**, 012107 (2010).
- ²⁹U. Höchli and H. Rohrer, Physical Review Letters 48, 188 (1982).
- ³⁰See supplemental material at [URL will be inserted by AIP] for detailed experimental angles.
- ³¹Z. Erlich, Y. Frenkel, J. Drori, Y. Shperber, C. Bell, H. K. Sato, M. Hosoda, Y. Xie, Y. Hikita, H. Y. Hwang, and B. Kalisky, Journal of Superconductivity and Novel Magnetism 28, 1017 (2015).
- ³²R. C. Rogan, N. Tamura, G. A. Swift, and E. Ustundag, Nature Materials 2, 379 (2003).
- ³³K. S. Lee, J. H. Choi, J. Y. Lee, and S. Baik, Journal of Applied Physics **90**, 4095 (2001).
- ³⁴W. Cao and G. Barsch, Physical Review B **41**, 4334 (1990).
- ³⁵S. Stemmer, S. K. Streiffer, F. Ernst, and M. Ruhle, Philosophical Magazine A **71**, 713 (1995).
- ³⁶S. J. Lloyd, N. D. Mathur, J. C. Loudon, and P. A. Midgley, Physical Review B 64, 172407 (2001).
- ³⁷N. Floquet, C. M. Valot, M. T. Mesnier, J. C. Niepce, L. Normand, A. Thorel, and R. Kilaas, Journal De Physique III 7, 1105 (1997).
- ³⁸C. L. Jia, K. Urban, M. Mertin, S. Hoffmann, and R. Waser, Philosophical Magazine A 77, 923 (1998).
- ³⁹H. Noad, E. Spanton, K. Nowack, H. Inoue, M. Kim, T. Merz, C. Bell, Y. Hikita, A. Vailionis, H. Y. Hwang, and K. Moler, unpublished.
- ⁴⁰M. A. Saifi and L. E. Cross, Physical Review B **2**, 677 (1970).
- $^{41}\mathrm{G.}$ Schmidt and E. Hegenbarth, Phys. Stat. Sol. 3, 329 (1963).
- ⁴²T. S. Chang, Journal of Applied Physics **43**, 3591 (1972).