Non-Ising and chiral ferroelectric domain walls revealed by nonlinear optical microscopy

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The properties of ferroelectric domain walls can significantly differ from those of their parent material. Elucidating their internal structure is essential for the design of advanced devices exploiting nanoscale ferroicity and such localized functional properties. Here, we probe the internal structure of 180° ferroelectric domain walls in lead zirconate titanate (PZT) thin films and lithium tantalate bulk crystals by means of second-harmonic generation microscopy. In both systems, we detect a pronounced second-harmonic signal at the walls. Local polarimetry analysis of this signal combined with numerical modelling reveals the existence of a planar polarization within the walls, with Néel and Bloch-like configurations in PZT and lithium tantalate, respectively. Moreover, we find domain wall chirality reversal at line defects crossing lithium tantalate crystals. Our results demonstrate a clear deviation from the ideal Ising configuration that is traditionally expected in uniaxial ferroelectrics, corroborating recent theoretical predictions of a more complex, often chiral structure.
Ferroelectric domain walls (DWs) have recently been shown to present unexpectedly rich and diverse physical properties beyond those of their parent materials. These include the observation of polar walls in otherwise non-polar materials, DW conductivity in insulating oxides, ferromagnetic ordering in ferroelectric antiferromagnets, and photovoltaic effects localized at the wall regions. This plethora of unusual properties has transformed the perception of DWs in ferroelectric and multiferroic materials, which are now increasingly viewed as individual nanostructures with vast applicative potential in industry rather than as unwanted defects. Similar to recent developments in nanomagnetism, DWs in ferroelectric and multiferroic materials are now considered as potential units of parameter space at the domain boundary region. The early parameter space at the wall regions separating c-domains in uniaxial ferroelectric systems. This study is conducted mainly on tetragonal Pb(Zr,Ti)O$_3$ thin films (point group symmetry 4mm). In addition, we investigate a trigonal LiTaO$_3$ bulk crystal (point group symmetry 3m) as an independent test of our approach. In spite of significant differences between these two systems, a deviation from the idealized Ising configuration is demonstrated in both cases. While we observe Néel-type DWs in tetragonal Pb(Zr,Ti)O$_3$, periodically poled LiTaO$_3$ develops mainly Bloch-type walls. Depth-resolved SHG measurements conducted in the LiTaO$_3$ bulk crystal show that the Bloch-type walls are stable across the crystal depth. However, their chirality may change at line defects, in close analogy to Bloch lines in ferromagnets. This study provides the experimental proof of a deviation from the conventional Ising-type configuration and shows the existence of chiral walls in ferroelectric materials. The functionalization of non-Ising DWs, in particular the switchable polarity of Bloch-type walls, represents promising features for the development of original nano-devices.

Results

Overview. To prove the general applicability of our approach and its ability to identify a possible deviation of ferroelectric DWs from the ideal Ising-type configuration, we focus on nominally uncharged 180° domain DWs in two fundamentally different crystals: the one is a tetragonal lead zirconate titanate thin film, the other a lithium tantalate bulk trigonal crystal. This choice is motivated by theoretical studies predicting the existence of non-Ising walls with an internal structure specific to each system. A Bloch-type configuration has been predicted for Y-oriented walls in crystals of the lithium niobate family, while Morozovska and Eliseev et al. show that Néel-type DWs are expected in PbZr$_{0.2}$Ti$_{0.8}$O$_3$. Moreover, PbZr$_{0.2}$Ti$_{0.8}$O$_3$ is often used as a stand-in system for pure PbTiO$_3$, in which Néel-type DWs are expected.

180° domain walls in tetragonal lead zirconate titanate thin films. The internal structure of nominally uncharged 180° ferroelectric DWs is first investigated in a 50 nm-thick tetragonal PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) layer in which c-domains have been patterned by means of a PFM tip (see Methods section for more details), as can be seen in Fig. 1b,c. The corresponding SHG image shows a localized emission at the domain boundary regions (Fig. 1d,e). The spectral analysis of the optical signal reveals an unambiguous SHG process by demonstrating a frequency doubling combined with a quadratic dependence of the intensity with the power of the fundamental wave (Fig. 1f–h). This result is particularly surprising since, using this measurement geometry with normal incidence and back reflection detection (Fig. 1a), and moreover, given the tetragonal symmetry of the film, no SHG signal should be generated from c-oriented domains (Supplementary Fig. 9). Besides, Ising-type DWs are
centrosymmetric and they exhibit a vanishing polarization at the centre of the wall. Therefore, no SHG signal is expected at the domain boundary regions either in the case of an Ising-type DW.

Earlier studies based on observations by means of far field, near field and Cherenkov-type SHG\textsuperscript{43–45} have shown that the domain boundary regions can appear either as dark lines\textsuperscript{34,46,47}, due to destructive interference of the SHG between opposite domains (out-of-phase), or as bright regions\textsuperscript{43,48,49}. Although SHG signals at DWs have been reported in the studies mentioned above, a thorough understanding of the origin of the SHG emission remains elusive\textsuperscript{48}. The effect was first attributed to structural defects\textsuperscript{43} agglomerated at the DWs, and to the resulting loss of coherence\textsuperscript{49}. However, the detection of Cherenkov radiation at the DWs demonstrates the coherence of the generated light. The role of the defects was then dismissed in favour of other contributions such as localized d.c. electric fields induced by strain\textsuperscript{46}. In this context, we conduct a precise analysis of the SHG signal of the DWs by means of polarimetry measurements and numerical simulations based on symmetry arguments. We conclude that the SHG signal at PZT and LiTaO\textsubscript{3} DWs is not a spurious effect, but a result of the particular internal polarization structure of the DWs.

Modelling the SHG signal for Néel or Bloch-type walls requires the knowledge of the related nonlinear optical susceptibility tensor (that is, the \( \chi^{(2)} \) elements of the SHG tensor). Assuming that the optical tensor is isomorphic to the piezoelectric tensor, the same transformation operations hold for the piezoelectric tensor at a given symmetry also apply to the SHG tensor. Any new or modified tensor corresponding to an arbitrary coordinate system with a specific ferroelectric polarization of the underlying material can thus be deduced using the rotation transformation relations as they are commonly applied to piezoelectric tensors\textsuperscript{50}. For this, it is sufficient to know the reference SHG tensor \( \chi^{(2)} \), defined in the crystallographic reference frame of the parent phase. A detailed description of the transformation method as well as the resulting SHG tensors obtained in Néel and Bloch-type DWs is provided as Supplementary Note 2. Knowing the susceptibility tensors, the SHG intensity can be calculated for any wall type as a function of the polarizer angles (\( \alpha \) and \( \varphi \)) using the analytic form given in the Methods section (equations (1) and (2)).

The two-dimensional (2D) simulation of the SHG is obtained by subdividing the DWs into discrete regions, in which the ferroelectric polarization is allowed to rotate, for instance in horizontal DWs (\( || x \)-axis), within the \((yz)\)-plane in the case of Néel-type walls, and in the \((xz)\)-plane in the case of Bloch-type walls. The SHG intensity is calculated at each rotation angle assuming a small amount of experimental noise, that is, random fluctuations of the polarization angle (\( \pm 0.5 \) rad) around its equilibrium position. Fig. 2d,e displays simulated SHG images obtained for square-shaped \( c \)-oriented domains, with horizontal (HDWs \( || x \)-axis) and vertical (VDWs \( || y \)-axis) walls aligned with the cubic crystallographic axis of PZT (the laboratory coordinate system \((x,y,z)\) coincides with the crystallographic axes \((X,Y,Z)\)). The SHG images are simulated at different settings of the analyzer and polarizer angles, in the case of Néel-type (Fig. 2d) and Bloch-type DWs (Fig. 2e). A clear SHG signal is observed at the DW regions in both configurations. However, the polarimetry

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**Figure 1 | Detection of localized SHG at domain walls in PZT thin films.** (a) Schematic representation of the SHG experimental set-up. Ferroelectric domains (\( c^+ \) and \( c^- \) domains) of different geometric shapes are written in the film by applying a bias voltage through a conductive PFM tip. The domain structure images by means of PFM is displayed for film regions with (b) right triangle and (c) rectangle-shaped domains. The corresponding nonlinear optical images reveal a localized optical signal at the walls surrounding the (d) triangular and (e) rectangular domains. The bars in all images correspond to a scale of 2 \( \mu \)m. (f) The fundamental wavelength is 800 nm while the localized emission (g) occurs at a wavelength of 400 nm, corresponding to the half of the fundamental wavelength. The scattered dots in (h) represent the variation of the emission intensity with the power of the fundamental wave. The error bars account for the intensity fluctuation of 10% and the continuous line is a quadratic fit of the experimental data (Supplementary Fig. 1 for more details). The SHG images represent the data recorded at a polarizer angle \( \varphi = 0^\circ \) integrated over the analyzer angles \( \alpha \). The laboratory coordinate system \((x,y,z)\) displayed in (a) coincides with the crystallographic axes \((X,Y,Z)\) of tetragonal PZT.
in the DW regions. The results are compared by assuming an average planar component of the ferroelectric polarization exists along the crystal axes. In these simulations, we assume that a non-zero polarization maximum exists across the parent material and the orientation of the wall with respect to the crystal, as well as quasi-isosceles right triangle domains and analyzer angles (φ and z, respectively) taken with respect to x-axis (schematically represented by red and blue arrows).

Figure 2 | 2D simulations of the SHG emission at PZT c-domain boundaries. The numerical simulations of the SHG emission are performed for square-shaped c-domains in tetragonal PZT as outlined in a, assuming DWs with b) Néel-type and c) Bloch-type internal structure. The variation of the SHG intensity at horizontal (HDWs || x-axis) and vertical (VDWs || y-axis) DWs is displayed in the case of (d) Néel and (e) Bloch walls at different polarizer and analyzer angles (φ and z, respectively) taken with respect to x-axis (schematically represented by red and blue arrows).
elements may be at the origin of the observed difference between the calculations and the experiment at ODWs.

180° domain walls in lithium tantalate bulk crystals. For comparison, the polarimetry analysis of the SHG signal is similarly conducted in 500 µm-thick periodically poled nearly stoichiometric LiTaO₃ (LT) bulk crystals. In this system, c-domains forming either micrometric stripes or hexagons have been produced by means of electric field poling (see Methods section for more details). To suppress spurious surface contributions to the SHG signal, the measurements were performed at a focal distance of 100–300 µm below the top optical domain walls (ODWs). Figure 3 | Polarimetry analysis of the DWs’ SHG signal in tetragonal PZT. A systematic analysis of the local SHG is conducted for different polarizer and analyzer settings, at horizontal (HDW), vertical (VDW) and oblique (ODW) domain walls, as schematically illustrated in a,b. SHG measurements conducted in c rectangular-shape c-domains exhibit maximum signal at HDWs and VDWs when the analyzer (blue arrow) is perpendicular to the walls. The same result is observed at HDWs and VDWs in d triangular-shape c-domains, while oblique walls referred to as ODW1 and ODW2 exhibit a different behaviour. The corresponding polar plots (scattered dots) of the normalized SHG intensity measured are shown in case of e rectangles and f angle triangles at a fundamental polarization angle $\phi = 0°$. The continuous lines are fits of the experimental data to the analytic expression of the SHG intensity expected for Néel-type walls with horizontal, vertical or oblique orientations. g 3D SHG polarimetry simulated in the case of a planar ferroelectric polarization along the y-axis (Néel-type), represented in cylindrical coordinates $(x = I_{\text{SHG}} \cos \phi \cos \alpha, y = I_{\text{SHG}} \sin \phi \cos \alpha, z = \phi)$. The $z$-axis has been scaled with a factor 10 to allow for a better visibility. The colour map represents the SHG intensity in a.u. and the continuous lines result from plane cuts at $\phi = 0°$ (red colour), $\phi = 90°$ and $180°$ (grey). The normalized intensity of the calculated polar plots at $\phi = 0°$ is displayed in h to facilitate the comparison with the experimental results.
surface. Figure 4a displays a clear SHG signal at the boundary regions of the alternated stripe domains. As opposed to PZT, the SHG polarimetry analysis shows maximum SHG polarization along the walls ( || y) in LT, regardless of the fundamental wave polarization. Nevertheless, a small SHG signal is still measurable when the analyzer angle of the SHG polarization is perpendicular to the walls. This result is clarified in the following analysis of the SHG polarimetry based on symmetry arguments, in particular at oblique walls in hexagonal domains.

C-domains with hexagonal shape patterns are obtained in LT under stoichiometric conditions as described in the Methods section. The domains are delimited by DWs along the three equivalent Y-crystallographic directions (represented by grey arrows in Fig. 4b). A typical SHG image of a hexagonal c-domain is displayed in Fig. 4b. Localized nonlinearities are clearly visible at all six equivalent Y-DWs of the hexagon. However, a larger SHG intensity is detected in HDWs ( || y-axis) when the SHG polarization is along y-axis (z = 0°), while oblique walls (ODW1 and 2) show maximum SHG polarization at +60° with respect to y-axis in the case of ODW1, and at −60° with respect to y-axis in the case of ODW2. As previously explained in the case of PZT, the SHG response depends sensitively on the probed nonlinear optical coefficients of the system. Calculations accounting for the local symmetry at the walls and their orientation are provided for trigonal LT to better clarify the SHG polarimetry response (Fig. 4c and Supplementary Movie 2). A comparison of the experimental results (Fig. 4a,b) with simulated polar plots (continuous lines in Fig. 4c) shows that in the case of trigonal LT the SHG signal at the DWs is consistent with a dominant Bloch-like configuration. On the other hand, due to the large imbalance between the nonlinear optical coefficients in the case of trigonal LT (Methods section), the SHG intensity is strongly affected by the DW types and their relative orientation with respect to the photon analyzer and polarizer angles. For example, the simulated SHG signal for horizontal Néel walls shows a low intensity as compared to the intensity expected in the case of Bloch-type wall (see the simulated 3D SHG displayed in Fig. 4c and the corresponding colour map). This means that a potential Néel component would hardly be detectable. Nevertheless, and in spite of its small value, the SHG signal related to a Néel-type component could be detected when the analyzer angle was perpendicular to the walls (right-hand column in Fig. 4a). This finding is in perfect agreement with the theoretical predictions of Lee et al.20 concerning the mixed Bloch-Néel nature of 180° DWs in trigonal lithium niobate.

The observation of Néel or Bloch-type configurations in these materials does not imply the absence of an Ising component. In uniaxial ferroelectrics, the Ising character should dominate due to electrostrictive and electrostatic effects. Therefore, a perfect Néel or Bloch-like rotation of the polarization vector is unlikely. Instead, a coexistence of Ising-Néel or Ising-Bloch configurations is expected19. In this case, the amplitude of the polarization...
LiTaO₃ crystal with stripe domains. The plane cuts represented by dotted lines correspond to the laser focus position along z-axis corresponding to the (b–g) 2D SHG datacube maps measured in the (xy) plane. The images are recorded at different depths ranging from (b) z = 300 μm up to (g) z = 400 μm in steps of about 15 μm. Here z = 0 corresponds to the top surface. The bar corresponds to a scale of 5 μm and it is common to b–g. A tomographic reconstruction showing the 3D representation of the Bloch-type DW is shown in (h). All the images are recorded at φ = 0° and α = 0°. The colour map represents the bulk SHG intensity in a.u. measured in a sample volume of 12 × 55 × 100 μm³.

Figure 5 | Depth profile of a Bloch-type chiral wall in LiTaO₃. (a) Schematic three-dimensional representation of a z-oriented periodically poled bulk LiTaO₃ crystal with stripe domains. The plane cuts represented by dotted lines correspond to the laser focus position along z-axis corresponding to the (b–g) 2D SHG datacube maps measured in the (xy) plane. The images are recorded at different depths ranging from (b) z = 300 μm up to (g) z = 400 μm in steps of about 15 μm. Here z = 0 corresponds to the top surface. The bar corresponds to a scale of 5 μm and it is common to b–g. A tomographic reconstruction showing the 3D representation of the Bloch-type DW is shown in (h). All the images are recorded at φ = 0° and α = 0°. The colour map represents the bulk SHG intensity in a.u. measured in a sample volume of 12 × 55 × 100 μm³.

Discussion
Nonlinear optical microscopy is used to probe the internal structure of ferroelectric domain boundaries. The non-Ising character of nominally neutral 180° DWs is demonstrated in two different systems. Neél-type DWs are observed in tetragonal PZT thin films and a dominant Bloch-type configuration is evidenced in quasi-stoichiometric LT crystals. This work shows that the combination of local polarimetry SHG and numerical simulations based on symmetry arguments constitutes a valuable tool for mapping polarization components at ferroelectric DWs. Little is known so far about the origin of the non-Ising structure of DWs. This deviation could be explained by localized electromechanical coupling. For example, lattice distortions caused by oxygen octahedron rotations in perovskite oxides are capable of exhibiting improper ferroelectricity (for example, at elastic twins) due to the coupling of the flexoelectric effect (polarization induced by strain gradient) and rotostriction. However, this effect should play a minor role in uniaxial ferroelectrics like those investigated in this study. Only two theoretical studies that we know of have investigated the origin of
the deviation of nominally uncharged 180° DWs from the Ising-type model.11,59. These studies have shown that the domain wall type in tetragonal BaTiO3 is determined by the competition between the depolarization and the flexoelectric fields.

We hope that our study will stimulate further experimental and theoretical interest in chiral walls. In particular, the study of strain-gradient variations could reveal exciting patterns and distinct properties that could be useful for the design of nanoferroelectric devices based on domain walls.

**Methods**

**PbZrTiO3 film preparation.** Tetragonal PbZr0.2Ti0.8O3 (50 nm) films (PZT) are epitaxially grown on SrTiO3 (35 nm)-buffered SrTiO3 (001) single crystals by means of off-axis radio-frequency magnetron sputtering, following the deposition route described in ref. 57. A single domain state (γ−) is obtained with a uniform polarization along the z-axis, out of the plane of the film. Domains of opposite polarization separated by nominally neutral 180° DWs are prepared by applying a bias voltage (±10 V) between a conductive PFM tip and the SrTiO3 base electrode. The PFM tip is scanned over a selected area to pattern the desired domains.

**Domain engineering in LiTaO3.** We used commercial (Oxide Corp) monodomain 0.5 mm-thick Z-cut 1 mol% MgO-doped nearly stoichiometric LiTaO3 crystals. Hexagonal bulk domain structures with 180° DWs aligned with the Y-crystallographic axes were fabricated by electric field poling, through the application of 1.8 kV voltage pulses of 80 ms duration via patterned metallic (Ti) electrodes deposited on the +z face58, and an uniform electric (gel) contact on the opposite side (−z). The individual hexagonal domain shape matched the preferential domain wall orientations observed in the material (six equivalent walls along the Y-axis, that is, [11−20], [−11−20] and [2−11])20. After the poling procedure, the metallic electrodes were removed by a wet-etching process in a 48% HF:H2O solution, followed by a thorough ultrasonic cleaning in organic solvents.

The same method was used to fabricate 1D arrays of 2 mm-long stripe domains aligned to the Y-axis, with a periodicity of 25 μm along X.

**Second-harmonic generation measurements.** Local SHG measurements are conducted by means of a scanning confocal microscope. The fundamental wave is provided by a Spectra Physics Ti:Al2O3 laser (Millennium/Tsunami combination), which generates 100 fs pulses with a repetition rate of 80 MHz and a wavelength centred at 800 nm. The laser beam is directed at normal incidence to the sample, and focused with a ×40 magnification objective lens (numerical aperture N.A. = 0.66). The SHG images are obtained by scanning the sample with respect to the incoming beam using computer-controlled stepping motors with a minimum step of 100 nm, and recording the SHG signal at each scan step with a typical exposure time of 20–40 ms per step at a power of 100–150 mW. The output intensity was spectrally filtered and collected into a photomultiplier box. Polarity measurements are performed by recording the images at different polarization and analyzer angles (φ and ζ, respectively). See Supplementary Note I for more details about the data acquisition and processing procedures.

**SHG modelling.** The SHG emission involves the coupling of two incident photons at frequency ω to produce a dipole characterized by a polarization P(2) oscillating with the double frequency. The leading term in the frequency doubling process is the second-order nonlinear optical susceptibility tensor χ(2). The elements of the susceptibility tensor are usually replaced by a contracted d-tensor, following the Voigt notation (contracted tensor elements d,1 = 1−3 and j = 1−6)59.

where φ is the polarization angle of the fundamental wave. The complete polarization representation of the SHG polarization as a function of the analyzer angles φ and ζ, respectively, is obtained using the Jones formalism:

Equations (1) and (2) allow for a complete description of the SHG intensity I(φ,ζ) = |P(2)(φ,ζ)|2, provided that the symmetry of the material (that is, the d element of the susceptibility tensor) is known, and vice versa. By choosing the set of polarizations (φ and ζ) properly aligned with respect to the crystal orientation, the elements of the χ(2) tensor can be directly accessed through polarity measurements (polar plots). Quantitative evaluations tend to be difficult as they require relative measurements with respect to a reference system (for example, quartz or ammonium dihydrogenphosphate) and specific measurement geometry. Nevertheless, the qualitative probe of the χ(2) elements provides valuable information on the symmetry and on the ferroic domain structure.

SHG polarity data (polar plots) were fitted at a given polarization of the fundamental wave (φ constant) using the analytic model deduced from equations (1) and (2) by assuming various DW types. The agreement with the data or lack thereof allowed us to uniquely infer the structure of the observed DWs. The susceptibility tensor in equation (1) is specified in Supplementary Tables 1 and 3 for each domain wall type and geometry (horizontal, vertical and oblique walls).

The 2D simulations of the SHG images were obtained by subdividing the DWs into discrete regions, in which the ferroelectric polarization is allowed to rotate. The χ(2) SHG tensor is calculated at each rotation angle. The result is then inserted as input parameter in equations (1) and (2). This allows the calculation of the SHG intensity at any position in domains and domain wall regions for given analyzer angles. The numerical value of the SEG tensor elements used in the simulations are d,33 = −11.09 pm V−1, d,31 = −11.09 pm V−1 and d,22 = −18.34 pm V−1 for tetragonal PZT50 and d,33 = 1.54 pm V−1, d,22 = 0.46 pm V−1 and d,33 = 12.9 pm V−1 in trigonal LT91. The SHG intensity is calculated by taking ε0εr = 1 and it is presented in arbitrary units.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

S.C.-H. designed the study and directed the project. The SHG measurements were performed by G.T. and S.C.-H. in collaboration with K.D.(H.D). The 2D simulations of the SHG have been conducted by H.B. with H.B. from S.C.-H. The data processing procedures and the 3D simulations were developed and conducted by S.C.-H. and R.H. The ferroelectric domain lithography in thin PZT films and the related PFM measurements were performed by J.G., I.G. and P.P. The 1D (strips) and 2D (hexagons) periodic domains were poised in LiTaO$_3$ ferroelectric photonic crystals by K.G. S.C.-H. wrote the manuscript with contributions from R.H., K.G. and P.P. All authors discussed the experimental results and models, commented on the manuscript and agreed on its final version.

Additional information

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