Optical index profile at an antiparallel ferroelectric domain wall in lithium niobate

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Abstract

Unexpected optical contrast at antiparallel domain walls is observed in non-stoichiometric lithium niobate. This is imaged using near-field scanning optical microscopy. A detailed modeling of the imaging process is performed, and a comparison of the experimental and simulation images is used to extract the index profile across a single antiparallel domain wall.

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In a uniaxial ferroelectric, two ferroelectric domain orientations are possible along the uniaxial +c axis (up-domain with spontaneous polarization +P_s) and the −c axis (down-domain, with spontaneous polarization, −P_s). An antiparallel 180° domain wall separates these two domain states. Controlling and shaping domains as gratings, lenses and prisms is key to many technologies, such as quasi-phase matched second harmonic generation [1], and electro-optic focusing and scanning technologies [2–4]. The refractive index is a centrosymmetric property and is not expected to change between up- and down-domains. This would be true for ideal domain walls, where for uniaxial materials; the two indices of interest are extraordinary index, n_e (along the c-axis), and the ordinary index, n_o (perpendicular to c-axis).

However, unexpected index contrasts are indeed observed across antiparallel domain walls in congruent LiNbO_3 and LiTaO_3 single crystals using optical microscopy [5,6]. Recent studies on LiNbO_3 and LiTaO_3 also show that antiparallel domain walls have unexpected local lattice strains and variation in lattice parameters across a 180° wall, extending over many microns across a wall [7]. These contrasts have been directly correlated to the presence of non-stoichiometry in single crystals, where the composition of the congruent crystal is (Li_0.95 Nb_0.01 V_0.04)NbO_3, instead of the stoichiometric composition, LiNbO_3. This leads to non-stoichiometric defects in congruent crystals, which are presently believed to be Nb-antisites, NbLi, (which are excess Nb atoms at Li locations), and lithium vacancies denoted by V_Li. The defect equilibrium is 4[NbLi] = [V_Li]. The index and strain contrast disappears in the stoichiometric composition [6]. The same is true for LiTaO_3. As proposed by Kim et al., these defects are not random, but can possess a low energy configuration, called a defect dipole, such as shown in Fig. 1 schematically.

In a crystal grown from high temperature, all the defect dipoles have the low energy configuration, and the domain state is labeled ‘virgin state’ (labeled hereafter as V). When a domain is reversed at room temperature using electric fields, domains and domain walls are created, which are in ‘domain reversed state’ (labeled hereafter as R). Within these domains, the defects are in the ‘frustrated state’ wherein the Nb atom has moved, but the lithium vacancies are ‘stuck’ in a frustrated state, unable to move due to negligible ionic conductivity at room temperature. A domain wall at room temperature between a virgin state and a reverse state therefore represents not only a transition of the lattice polarization, P, from an up to a down state, but also from a stable to a frustrated defect state, respectively. While the lattice polarization may indeed switch over a few unit cells, the transition of defect states across a wall appears to give rise to broad index and strain change in the wall region. However, it has been shown [6] that by annealing such a crystal at >150 °C, this defect frustration can be considerably relieved.
The exact local structure of antiparallel domain walls is a fundamental property of interest. In this paper, we present a detailed measurement of the change in the optical contrast across a single domain wall in congruent LiNbO$_3$. Previous observations of an optical birefringence near the domain wall have been reported by Yang et al. [5] using cross-polarized near-field optical microscopy. In this paper, we show that a more detailed optical structure exists at the wall. There is an overall step change in ordinary index between the two domains. In addition, a more localized index contrast at the wall location itself exists, overlaying the step contrast across the wall. This information is quantitatively extracted from a careful experimental measurement of both collection and illumination mode near-field scanning optical microscopy (NSOM) images, followed by a detailed modeling of these images using a combination of electromagnetic wave propagation techniques such as beam propagation method, and finite-difference-time-domain (FDTD) method.

The essential component of NSOM is a tapered fiber tip with a sub-wavelength aperture of $\sim$40 nm at its end. Light is either forced through the fiber tip or collected through it. The tip is scanned within $\sim$20 nm over the surface of a sample, and either reflected or transmitted light is used to image the optical properties of the sample. Simultaneously, an electrical feedback circuit allows the fiber tip to follow the surface contours, and therefore provides the surface topography image as well. Based on its modes of operation, NSOM is categorized as collection mode, or illumination mode. In the illumination mode, the input laser signal is forced through the fiber tip aperture. If the desired optical signal is collected through NSOM tip aperture instead, it is called the collection mode. The spatial resolution in both illumination and collection modes is determined by size of the fiber tip aperture. To confine light inside the tapered aperture, the taper wall of the fiber is coated with $\sim$100 nm film of aluminum in this work. By using fiber-aperture NSOM, ferroelectric domains have been imaged in both collection and illumination geometries. Only collection mode results are presented.

The starting sample in virgin state was congruent composition of LiNbO$_3$ single crystals in a single domain state. Partial domain reversal in the samples was performed by applying electric field of $\sim$21 kV/mm to the samples by using water electrodes at room temperature. Random hexagonal shaped-domains were created in the crystal. The walls naturally prefer to be parallel to the crystallographic $\gamma$-$\zeta$ plane in the crystal.

In the collection mode geometry, the tiny fiber aperture of the NSOM tip collects the He–Ne 632 nm laser. The NSOM signal is build up by the incident beam propagating through a 500 $\mu$m thick crystal. An input laser beam of 5 mm is focused with an 80 cm focal length lens through the sample at or near the fiber tip to $\sim$500 $\mu$m spot diameter. In the collection geometry, NSOM tip can collect significant evanescent wave signal because of close tip and sample distance. If the sample surface has a topological variation, it creates a strong evanescent wave near the surface. The surface topological variation can change the NSOM image significantly. Therefore, both topological information and optical signal should be collected simultaneously to extract the pure optical image. In LiNbO$_3$ ferroelectric domain walls, topological structure is very small (less than 2 nm). We can therefore assume that observed NSOM optical images do not include topological effects.

Fig. 2(a) shows transmission-collection mode images of 180$^\circ$ domain walls in LiNbO$_3$. The first surprising observation is that any optical contrast is present at all, since 180$^\circ$ domains must ideally possess the same refractive index. However, the contrast indicates that a refractive index gradient exists at the domain wall, and perhaps even between these two domain states. The matrix domain in the images is the virgin state (V), and the inside of the hexagonal or triangular regions is the electrically reversed domain state (R) at room temperature.

To show that the non-stoichiometric defect dipoles are responsible for the observed optical contrast, the following experiment is performed. First a virgin LiNbO$_3$ crystal (state V) is completely domain-inverted at room temperature, such that the starting matrix domain can now be considered to be in a domain-inverted state (R). Starting with this state, an applied field partially creates hexagonal domain regions that have the same orientation (state V$_1$) as the original virgin crystal (V), with the exception of having some domain reversal history. Now, the domain region inside these hexagons has a more stable defect configuration, as compared to the outside matrix domain. Therefore, the internal field is opposite to the outside domain matrix and the electro-optic effect would therefore be expected to increase the index in the matrix domain. This would result in a brighter matrix domain than the interior of the hexagonal domain regions. Thus, the NSOM image contrast will be expected to be reversed in this case as compared to Fig. 2(a). This is indeed observed, as shown in Fig. 2(b).
Fig. 2. Collection-mode near-field scanning optical microscopy images of ferroelectric domain walls in congruent LiNbO₃. Domain state V and R refer to 'virgin' and 'domain reversed' states at room temperature. The contrast reverses when the domain states exchange positions.

The bright and dark fringes indicate that the light is bending while it is propagating along the domain wall. Based on the Eikonal theory, light bends from the low index region to the higher index region. One can therefore guess that the bright side of the domain walls has a higher refractive index than the darker side. In addition, we note that in Fig. 2a and b, there is a dark rib-like line contrast going across the domain wall. We first start with the conjecture that this corresponds to an additional localized change in refractive index at the domain wall. Based on these initial ideas, we construct several possible index distributions across the wall throughout the crystal thickness.

In comparing experimental and simulated NSOM images of domain walls, the approach we have adopted is to first make an educated guess for the refractive index profile across the domain wall. Using this profile as a starting point, a combination of Fast Fourier transform-beam propagation method (FFT-BPM) and finite difference time domain (FDTD) method is used to calculate the expected NSOM images. Incident beam on the sample is considered a weakly focused Gaussian beam. Light propagation through the assumed index profile inside a 500 µm thick crystal is calculated using the FFT-BPM method in a MATLAB based code. In the proximity of the near-field tip, where dimensions approach sub-wavelength features, the more versatile and accurate FDTD technique is used. However, in the vicinity of the near-field tip, where dimensions approach sub-wavelength features, the more versatile and accurate FDTD technique is used. The primary drawback is the calculation domain size, which is practically limited to regions of the order of 100 × 100 wavelengths of light. To calculate larger areas of optical wave propagation, other methods such as BPM should be linked with FDTD. In this work, a hybrid code was developed that seamlessly integrates BPM and FDTD techniques. Starting from a trial index profile, the simulated images are then compared with experimental images and the original index profile refined to achieve convergence between the two. Uniqueness of the index profile is determined by finding agreement between experiments and modeling in both collection and illumination geometry images. Therefore, this is a trial and convergence process in determining the optimum refractive index profile.

Fig. 3a shows the refined index distribution model and the resultant BPM simulation of the light intensity after the light has travelled through a 500 µm thick crystal with a single domain wall. The refined index profile consists of a wide step index profile of index change, Δnₒ = nₒ,R − nₒ,V ∼ 1 × 10⁻³ with a step transition range of ∼20 µm across the wall. The ordinary refractive index is higher (nₒ,R ∼ 2.288) in the domain-inverted region (R) as compared to index of the matrix domain (nₒ,V ∼ 2.287) in the virgin state (V). This essentially explains why the domain-inverted region is brighter than the matrix domain. In addition, a sharp index profile kink of Δnₒ ∼ ±3 × 10⁻³ and localized at the center of the wall.
over a width $\leq 2\mu m$ (upper limit) is also assumed as shown in Fig. 3(a). Fig. 3(b) shows three experimental line scans across the domain wall in LiNbO$_3$ with the numerically simulated fit (solid thick line). The agreement between the two is excellent.

However, this agreement, we note, is not sufficient to determine the uniqueness of the refined index profile in Fig. 3(b), particularly with respect to the magnitude of the unusual kink in the refractive index profile near the wall center. In order to confirm uniqueness, the measurement and simulation of the optical image in the illumination mode is used. These experiments and simulations performed similarly were used to confirm the index profile shown in Fig. 3.

For a virgin crystal, defect dipoles have the most stable configuration such as those shown in Fig. 1. On the other hand, domains created by an external electric field at room temperature consist of frustrated defect structures, which make this domain state relatively less stable than the virgin state. It can be seen from the polarization hysteresis loops, that the electric field of $\sim 21$ kV/mm required to create the reversed domains from a virgin state is much higher than the $\sim 15$ kV/mm to re-invert this domain state back to a virgin domain state. This difference in the coercive fields gives rise to internal fields that are effectively parallel to the virgin state. This defect field of $\sim 6$ kV/mm in LiNbO$_3$ is biased antiparallel to the domain-inverted state (R), indicated by the negative sign. In addition, using X-ray synchrotron studies and symmetry arguments, local strains in the vicinity of the domain wall were measured to be $\varepsilon_2 \sim 4 \times 10^{-3}$, where the negative sign indicates a larger lattice parameter of the (300) plane in the R state with respect to the V state. Further, strain component $\varepsilon_3 \sim 5 \times 10^{-3}$. This leads to a rise in the surface of the +P$_s$ end of a hexagonal R domain matrix. The domain wall lies in the y-z plane, and therefore by symmetry, one expects $\varepsilon_2 \sim 0$. The internal strains and electric fields are related through the piezooptic and electrostrictive effects.

The strains give rise to a change in the ordinary index, $n_0 (\varepsilon_2 = n_2)$ directly through the direct elastooptic effect, given by $\Delta(1/n_0^2) = n_2 E_1$. The strains also give rise to electric fields, $E_j$ through the piezoelectric effect, $\varepsilon_j = \varepsilon_{pj} E_p$, which in turn give rise to a secondary index change through the electro-optic effect, given by, $\Delta(1/n_0^2) = \varepsilon_{pj} E_p$. The sum total of the primary and secondary effects can be summarized for LiNbO$_3$ (with 3m symmetry), as:

\[
\Delta \left( \frac{1}{n_0^2} \right) = (p_{12} - p_{11})\varepsilon_2^2 + (p_{13}d_{31} + r_{13} + 2p_{32}d_{32})E_3 + \varepsilon_{14} \varepsilon_4 \tag{1}
\]

Here the relations $\varepsilon_1 = 2d_{31}E_3 - e_2$, and $E_3 \sim e_3/d_{33}$ hold. Substituting for the appropriate values using bulk LiNbO$_3$ values, we estimate the ordinary index change, $\Delta n_0 = \Delta n_1 \sim 4.5 \times 10^{-3}$ in the domain state R with respect to the domain state, V. This is a factor of 2 lower than the index change measured and simulated in Fig. 3(a) between the two domain states. This discrepancy may arise from many possible reasons. The piezooptic, electro-optic and piezoelectric coefficients in the vicinity of a wall may not be the same as the bulk values away from the wall. There may be local changes in symmetry around a defect that may give rise to additional strains and index changes not normally allowed in the original point group. Further, the sharp highly localized kinks in the simulated refractive index at the domain wall (Fig. 3(a)) may arise from highly localized strains or distortions within the wall, that are not experimentally known at present.

In summary, we present a detailed local structure of the index contrast at a single antiparallel domain wall in ferroelectric LiNbO$_3$ single crystals. The index change arises from organized non-stoichiometric defects in single crystals that can exist in a stable state on one side of the wall and in a frustrated state on the other side. This leads to local strains, index changes, and electric fields. These features tend to disappear when either the defect frustration is removed by high temperature annealing, or in stoichiometric crystals with no defects.

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References