Origin of internal field and visualization of 180° domains in congruent LiTaO₃ crystals

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We have observed a strong correlation between the internal fields and the infrared absorption spectra of OH⁻ ions in congruent LiTaO₃ crystals. After reversal of the direction of polarization (Pₛ) of the crystal by an electric field at room temperature, (a) the internal field is antiparallel to Pₛ, (b) the relative intensities of the infrared absorption bands of OH⁻ ions (at ~3462, ~3476, and ~3490 cm⁻¹) change, and (c) the 180° domain walls are visible under a light microscope. Annealing the domain-reversed crystal at 200 °C or above and cooling back to 25 °C has the following effects: (a) The internal field realigns parallel to Pₛ. (b) The shape of the OH⁻ spectrum returns to the shape observed before domain reversal. The time–temperature dependence of the shape of the infrared absorption spectrum of OH⁻ ions also shows the same characteristics as that of the realignment process for the internal field. (c) The optical domain wall contrast becomes extremely weak. Infrared absorption studies suggest that domain inversion as well as the heating of LiTaO₃ crystal induce structural changes that are similar in nature. It is proposed that the origin of internal fields lies in OH⁻ ions and/or nonstoichiometric point defects in the LiTaO₃ crystals. We also explain the optical 180° domain wall contrast based on internal fields. © 1996 American Institute of Physics.

I. INTRODUCTION

Lithium tantalate crystals are of interest for surface acoustic wave devices, piezoelectric devices, and in nonlinear optical applications due to their large electro-optic and nonlinear optical coefficients. Domain inversion in Z-cut LiTaO₃ and LiNbO₃ crystals has become an important tool in the fabrication of solid state lasers and electro-optic modulators. The presence of a large built-in internal field of 5 kV/mm in poled Z-cut LiTaO₃ crystals was reported recently. It was shown that this field is a volume effect and has considerable influence on the domain-switching characteristics of LiTaO₃ crystals.

In this work, we present experimental evidence and propose models which tie together three aspects of LiTaO₃ crystals, namely, internal fields, presence of OH⁻ ions, and optical contrast at 180° domain walls observed under light microscope. Accordingly, the paper is organized as follows: In Sec. II, the results of internal fields and the infrared absorption study of OH⁻ ions in congruent LiTaO₃ crystals are presented. In Sec. III, the results of optical imaging of 180° domains by internal fields and pyroelectric fields in LiTaO₃ crystals are presented. Finally, in Sec. IV, the correlations between the internal fields, OH⁻ ions, and the optical contrast at 180° walls are discussed and conclusions presented.

II. INTERNAL FIELD STUDY

A. Experimental results on internal fields

The characteristics of internal fields in Z-cut LiTaO₃ crystals have been detailed earlier. The as-purchased Z-cut LiTaO₃ crystals used in this study (obtained from Yamaju Ceramics Inc., Japan) were optical grade, of congruent composition and single domain. They shall be referred to as "virgin crystals." In our experiments described below, the polarization was reversed at room temperature by applying a dc field across the crystal thickness. Here, we summarize the significant results as relevant to this work.

1. Room-temperature measurements

Infrared absorption spectra were collected using unpolarized light transmitted parallel to the Z axis of the crystal.
Figure 2(a) shows the absorption spectrum of OH$^-$ ions in a virgin crystal (without any polarization cycling history) of single domain Z-cut LiTaO$_3$ at room temperature ($\sim$25 °C). Hydrogen gets incorporated into the virgin crystal during the crystal growth process. The spectrum was deconvoluted into three main components as shown by the solid lines in the figure. The component peaks are a mixture of Gaussian and Lorentzian functions and their centers occur at 3461.6, 3475 and 3488.7 cm$^{-1}$ wave numbers with an error of about $\pm$3 cm$^{-1}$. We shall refer to them as peaks A, B, and C, respectively.

Figure 2(b) shows the OH$^-$ absorption spectrum after the polarization direction of the crystal has been reversed at room temperature by an external electric field. The crystal polarization was reversed by a dc field applied across the crystal thickness ($\sim$0.5 mm) using liquid electrodes ($\sim$0.1 g/mL of magnesium nitrate in water). In the rest of this paper, we shall refer to these crystals as the ‘‘domain-reversed crystals.’’ The OH$^-$ spectrum in Fig. 2(b) was resolved into three components with centers ($\pm$3 cm$^{-1}$) at 3463.3 (peak A), 3475.6 (peak B), and 3495.7 cm$^{-1}$ (peak C) as shown in Fig. 2(b) with solid lines. While the peak positions are not significantly different from the virgin crystal, the ratio of integrated peak intensities $I_A/I_C$ changes from $\sim$0.25 in the virgin crystal to $\sim$3 in the domain-reversed crystal. It appears that the relative intensities of peaks A and C interchange upon domain reversal while the intensity $I_B$ of peak B remains about the same.

2. Annealing experiments

The difference in the OH$^-$ spectra between the virgin crystal (internal field parallel to polarization) and domain-reversed crystal (internal field antiparallel to polarization) at room temperature suggests that hydroxyl ions may be associated with the internal field in LiTaO$_3$ crystals. In such a case we can expect that the realignment of the internal field in a domain-reversed crystal corresponds to a time-temperature dependent evolution of spectrum 2(b) into 2(a).

Figure 3 shows the time evolution at 100 °C of the OH$^-$ spectra for a domain-reversed crystal. It can be clearly seen that the spectrum slowly evolves from a peak qualitatively similar to Fig. 2(b) to a spectrum similar to Fig. 2(a) over a time period of $\sim$1.5 h. This is the same as the time required for the internal field to realign along the polarization direction in a domain-reversed LiTaO$_3$ crystal at 100 °C.
The OH\(^-\) spectra of the virgin and the domain-reversed LiTaO\(_3\) crystals were also determined as a function of temperature. The crystal was heated at 5 \(^\circ\)C/min from 25 \(^\circ\)C up to 250 \(^\circ\)C. IR absorption spectra were collected every 25 \(^\circ\)C with the collection time lasting about \(\sim\)30 s. The evolution of the OH\(^-\) spectra for virgin crystal and domain-reversed crystals is shown in Figs. 4(a) and 4(b), respectively. For the domain-inverted crystal, the shape of the spectrum is both temperature and time dependent, as shown in Fig. 3. Thus, below 200 \(^\circ\)C, the shape of spectra in Fig. 4(b) is mainly determined by the time spent at that temperature and during temperature rampings. Above 200 \(^\circ\)C, the spectra for virgin crystals and domain-reversed crystals are identical.

C. Discussion

1. Correlation between internal field and infrared spectra of OH\(^-\)

The following features can be observed in Fig. 4: (a) The integrated intensity ratio of peaks \(I_h/I_c\) for virgin crystal in Fig. 4(a) changes from <1 at room temperature to >1 above 200 \(^\circ\)C. The crossover point where \(I_h/I_c=1\) occurs within the temperature range 150 \(^\circ\)C–200 \(^\circ\)C. This is the same temperature range in which a rapid realignment of the internal field parallel to the direction of polarization was observed in a domain-reversed crystal.\(^5\) (b) The shape of OH\(^-\) spectrum for a domain-reversed crystal at room temperature [Fig. 2(b)] has similarity (\(I_h/I_c>1\)) to the spectrum of a virgin crystal at temperatures above 200 \(^\circ\)C, suggesting that temperature-induced structural changes in a virgin LiTaO\(_3\) crystal are similar to domain reversal-induced changes in the crystal at room temperature. (c) Upon annealing the polarization-reversed crystal above 200 \(^\circ\)C for \(\sim\)30 s and then cooling back to 25 \(^\circ\)C, the shape of the OH\(^-\) spectrum returns to the shape observed before domain reversal at 25 \(^\circ\)C. The internal field also realigns parallel to the new polarization direction.\(^5\)

2. Origin of the internal field

There are three possible origins of internal field in LiTaO\(_3\) crystals: (a) Hydroxyl ions (OH\(^-\)), (b) nonstoichiometric point defects, and (c) complex of OH\(^-\) and nonstoichiometric defects. We shall now discuss each case.

We have shown above that there is a one-to-one correlation between the orientation of the internal field with respect to the polarization direction and the shape changes in the infrared spectrum of OH\(^-\) in LiTaO\(_3\) crystals. Further, in holographic data storage, annealing in the temperature range 100 \(^\circ\)C–200 \(^\circ\)C is done to fix the holograms in structurally similar LiNbO\(_3\) crystals.\(^8\) This is the same temperature region where a rapid realignment of internal field is observed.\(^5\) (Similar internal fields have been observed in LiNbO\(_3\) crystals, which shall be reported elsewhere).\(^9\) This has been shown to arise from movement of hydrogen in the crystal with an activation energy of 1.1 eV. However, the orientation of OH\(^-\) bond has been shown to be normal to the z axis of the crystal.\(^10\) Thus the OH\(^-\) ions can be the dipolar defects responsible for internal fields in these crystals if they either create local lattice distortions which have a net dipolar moment or form complexes with other point defects.

The second possibility is the nonstoichiometric point defects in LiTaO\(_3\) crystals. In congruent composition of LiNbO\(_3\) (~48% Li and 52% Nb), Prokhorov and Kuzminov\(^1\) concluded that lithium vacancies \((V_{Li})\) and oxygen vacancies \((V_{O})\) dominate at room temperature. More recently, Schirmer \textit{et al.}\(^12\) concluded that niobium antisites \((Nb_{Li})\) and niobium vacancies \((V_{Nb})\) are the dominant point defects and that “oxygen vacancy is present at most in negligible concentrations, except when brute force treatments such as high energy electron irradiation are applied.” Thus the literature is contradictory. A similar situation is expected in LiTaO\(_3\).\(^13\) The origin of internal fields may lie in complexes of lithium and oxygen vacancies or tantalum antisites, \((Ta_{Li})\) and tantalum vacancies \((V_{Ta})\). Changes in internal field with domain reversal at room temperature, or by heating, are then accompanied by changes in point defects in the crystal. The corresponding changes in OH\(^-\) spectra may simply be a result of these changes in point defects.

For example, based on the tantalum antisite model, a typical sequence in congruent LiTaO\(_3\) is \((...Ta Li \square V_{Ta} Ta_{Li} \square Ta Li \square...)\) where the polarization direction is from right to left. Upon domain inversion at room temperature, the sequence would become \((...Ta \square Li V_{Ta} Ta_{Li} V_{Li} Ta \square Li...)\) where the polarization direction is from left to right, and it has been assumed that point defects have not rearranged by domain reversal at room temperature due to very low mobility. This would then create additional defects of \(Ta_{Li} V_{Ta}\) and \(V_{Li}\) at room temperature. At higher temperatures, the \(V_{Li}\) would become mobile, and would realign the point defects such that at room temperature, the structure reaches a stable configuration of \((...Ta \square Li Ta \square Ta_{Li} V_{Ta} \square Li...)\). The detailed mechanism for the point defects movement at higher temperatures to achieve this configuration is presently unclear.
and may involve larger complexes of point defects moving in a coordinated fashion. A few such possible complexes with a net dipole moment have been suggested by Rauber. At higher temperatures, a tantalum antisite could also move into an adjacent tantalum vacancy, creating a mobile lithium vacancy. Thus we propose that $V_{Li}$ can be formed by two methods: (1) domain reversal at room temperature, as discussed above, or (2) heating the virgin crystal to $\sim 200 ^\circ C$ or more. This connection may also explain the similarity of $OH^-$ spectra of domain-reversed crystal at room temperature and the spectra of virgin crystal at higher temperatures as is discussed further below.

The third possibility is that the origin of the internal field lies in complexes of $OH^-$ with tantalum antisites ($Ta_{Li}$) and/or tantalum vacancies ($V_{Ta}$). The shape of the $OH^-$ spectrum has been reported to change considerably with the Li/Nb ratio in LiNbO$_3$ crystals. Since the Li/Nb ratio determines the point defect chemistry of the crystal, this suggests that the hydroxyl ions interact with point defects related to nonstoichiometry in LiNbO$_3$ crystals. Because the shape of the $OH^-$ spectra changes with domain reversal at room temperature, it suggests that the point defects in the crystal are changing with domain reversal. Thus, the origin of the internal field may lie in complexes of $OH^-$ ions and point defects in the crystal.

3. The shape of $OH^-$ absorption spectra

We shall now discuss the possible origin of the shape of $OH^-$ spectra. Figure 5 shows a schematic of the oxygen planes perpendicular to the $c$ axis of LiTaO$_3$ with lattice parameters taken from Abrahams et al. Triangles formed by oxygen atoms (1,2,3), (1,4,5), and (1,6,7) are equilateral. The spectrum shown in Fig. 2(a) for LiTaO$_3$ is very similar to the spectra reported for LiNbO$_3$ crystals. The shape of the $OH^-$ spectra in LiNbO$_3$ has been described as composed of two, three, four, and even five separate vibrational bands. Because none of these models has been confirmed experimentally, the actual shape of the $OH^-$ spectrum is still unexplained.

We have found that fitting four or five bands to Fig. 2 results in too many possible solutions that differ substantially in relative intensities and peak positions without a significant gain in the quality of fitting as determined by mean square deviation.

We propose here a plausible explanation for the shape change from Fig. 2(a) to 2(b) upon domain reversal based on a three-band model. The sequence of atomic arrangement along the $c$ axis of LiTaO$_3$ changes from (Ta Li $\square$ Ta Li $\square$ Ta Li $\square$...) to (Ta $\square$ Li Ta $\square$ Li Ta $\square$ Li...) upon domain inversion, where $\square$ is an octahedral site. Thus polarization reversal causes the following changes in the $O$-$O$ bonds in the octahedral plane of Fig. 5: $Li$-$\square$ ($3.38 \, \AA$) $\Rightarrow$ $\square$-$Li$ ($3.38 \, \AA$), $Ta$-$Li$ ($2.72 \, \AA$) $\Rightarrow$ $Ta$-$\square$ ($2.87 \, \AA$), and $\square$-$Ta$ ($2.87 \, \AA$) $\Rightarrow$ $Li$-$Ta$ ($2.72 \, \AA$) where the arrow $\Rightarrow$ indicates the direction of change. Since the integrated intensity of peak B in Fig. 2 does not change with domain inversion, it would correspond to hydroxyl ions along the $O$-$O$ bond of length 3.38 $\AA$. If peaks A and C correspond to $O$-$O$ bonds 2.72 and 2.87 $\AA$ (not necessarily in that order), then it would explain the change of ratio $I_1/I_C$ from $\sim 0.25$ for virgin crystal to $\sim 3$ for domain-reversed crystal. However, it must be noted that this model does not follow the argument of longer $O$-$O$ bonds resulting in higher stretching frequencies.

Let us now consider the effect of nonstoichiometry in the crystals. It is known that the shape of the spectrum also changes with nonstoichiometry (Li/Nb ratio) in LiNbO$_3$. Specifically, as Li/Nb approaches 1 in LiNbO$_3$ crystals, the lowest wave-number band ($\sim 3470 \, cm^{-1}$) of $OH^-$ spectra increases in intensity. For nearly stoichiometric crystals of LiNbO$_3$, only one sharp peak at the lowest wave number (3466 $cm^{-1}$) remains. This suggests that, as the point defects due to nonstoichiometry increase, the $OH^-$ occupancy of two additional bands at higher wave numbers increases. Thus, drawing an analogy for LiTaO$_3$, the bands at $\sim 3476$ and $\sim 3490 \, cm^{-1}$ are then specifically associated with the nonstoichiometric point defects in the crystal. These bands can therefore possibly serve as a measure of the concentration of point defects in the crystal. In such a case, the model proposed earlier is true for a specific stoichiometry of the crystal. The model then predicts the following:

(1) If polarization reversal is carried out in a stoichiometric crystal of LiTaO$_3$ at room temperature, the single band at the lowest wave number ($\sim 3462 \, cm^{-1}$) would shift position to the highest wave number ($\sim 3490 \, cm^{-1}$).

(2) Since the nonstoichiometry at room temperature leads to tantalum antisites, it follows that the higher the amount of this defect in the crystal, the greater will be the occupancy of the $\sim 3490 \, cm^{-1}$ band, and the lesser the occupancy of the $\sim 3462 \, cm^{-1}$ band.

The latter suggestion can also explain the similarity in the shape of infrared spectra of $OH^-$ of the domain-reversed crystal at room temperature and the virgin crystal at 200 °C or above, since in both cases, the tantalum antisites are destroyed by the creation of a lithium vacancy and hence the $\sim 3462 \, cm^{-1}$ band is stronger than the $\sim 3490 \, cm^{-1}$ band. The cross-over point (where the intensities of these two bands are equal) in the temperature range of 150 °C–200 °C also assumes significance since this may correspond to the range where tantalum antisites are destroyed to generate lithium vacancies. This is also accompanied by an exponen-
tial increase in the protonic conductivity of the crystal\(^{20}\) and a rapid increase in the rate of realignment of the internal field in a domain-reversed crystal.\(^5\)

We have thus suggested a correlation between the internal field, OH\(^+\) ions, and nonstoichiometric point defects in LiTaO\(_3\) crystals.

### III. OPTICAL CONTRAST OF 180° DOMAIN WALLS IN LiTaO\(_3\) CRYSTALS

Optical birefringence in ferroelectric crystals has been used to distinguish \(c\) and \(a\) domains under cross polarizers in a light microscope.\(^{21}\) In uniaxial ferroelectric crystals, the optical indicatrix is invariant under domain reversal. Hence, antiparallel domains cannot be imaged by this technique.\(^{19}\)

As an exception, in BaTiO\(_3\), antiparallel domains are visible between cross polarizers\(^{22}\) during the poling process. However, the wall contrast slowly disappears when the poling field used is removed. It was suggested that because of shear stresses near domain walls, a birefringence was created in the material.\(^{23}\)

We show in this work that antiparallel domains can also be imaged in LiTaO\(_3\) crystals by light microscopy after electric field-induced domain reversal at room temperature. Unlike in the BaTiO\(_3\) crystals, the domain wall contrast remains also at room temperature in LiTaO\(_3\) without any external electric fields. This contrast is destroyed by annealing the crystal at higher temperatures.

#### A. Experimental results on optical imaging

1. **Experimental setup**

   For this study, the polarization was reversed at room temperature by applying a dc field applied across the crystal thickness as detailed earlier.\(^7\) The total integrated charge from the transient poling current will be \(2P_s A\), if the spontaneous polarization \(P_s\) is reversed in the entire electrode area \(A\). Polarization reversal was done until the integrated charge obtained was \(-P_s A\). This created a uniform distribution of triangular 180° domains in the poling area. No subsequent surface treatment to the crystal was done other than cleaning in water. The sample was then placed under a regular light microscope in transmission mode. For imaging under cross polarizers, an input objective of 0.5 N.A and output objective of 0.12 N.A (magnification 5×) was used. A polarizer was placed at the input source and a rotatable analyzer was placed at the output and adjusted to get a null point (90° to input polarizer) prior to observing the crystal. For imaging in unpolarized light, an aperture was needed at the input to cut down the light intensity, which also decreased the input numerical aperture to 0.05 N.A.

2. **Imaging of 180° domains after polarization reversal at room temperature**

   Figure 6 shows a Z-cut LiTaO\(_3\) crystal with triangular regions of reversed domain. The triangles are equilateral with domain walls parallel to the crystallographic \(x\) direction. This is a typical geometry for nuleation and growth of domains observed in Z-cut LiTaO\(_3\) and LiNbO\(_3\) crystals and has the same geometry as the etch pits in LiNbO\(_3\) and LiTaO\(_3\).\(^{24}\) The contrast mainly occurs at the domain walls. Figure 6(a) shows the LiTaO\(_3\) crystal between cross polarizers. The domain wall of a triangle that is parallel to either the polarizer or the analyzer has a very weak contrast compared to the other two walls.

   The contrast in Fig. 6(a) arises from a birefringence between refractive indices between crystallographic \(x(n_x)\) and \(y(n_y)\) directions in a region adjacent to the domain walls. The schematic of Fig. 7 explains the mechanism of the observed contrast between cross polarizers in Fig. 6(a). Two birefringent axes \(x_1\) and \(y_1\) \(i\!=\!1, 2,\) or 3 can be defined, respectively, parallel and perpendicular to each domain wall \(i\) in the plane \(x-y\) of the crystal. If the cross polarizers are parallel to axes \(x_3\) and \(y_3\), then the incident polarization will be rotated by the axes \((x_1, y_1)\) and \((x_2, y_2)\), thus making the corresponding domain walls visible. The axes \((x_3, y_3)\) will not rotate the polarization, thus not revealing that domain wall. This is the situation observed in Fig. 6(a). If the crystal is rotated such that now the cross polarizers are parallel to \((x_1, y_1)\), then the corresponding domain wall contrast disappears and that of the other two walls becomes strong. This was indeed observed experimentally. The domain walls are also revealed under transmitted unpolarized light as shown in Fig. 6(b), suggesting that light is also being scattered by these walls.

3. **Annealing studies**

   To investigate the possible role of internal fields in domain imaging, the crystal in Fig. 6 was annealed at 350 °C...
for 12 h. This process realigns the internal field in the domain-reversed regions to become parallel to the polarization direction. Following annealing and slow furnace cooling (5 °C/min), the sample was washed in running water to remove any pyroelectric charges. Figure 8(a) shows the same crystal after annealing as observed between cross polarizers. The contrast has almost disappeared. The domain walls are also visible under unpolarized light with similarly diminished contrast, as shown in Fig. 8(b).

4. Pyroelectric imaging of 180° domains

The imaging contrast can be recovered in the annealed crystal by generating pyroelectric fields. To that end, the crystal is placed on a thin glass slide on a hot plate preheated to 100 °C–150 °C and open to atmosphere. After 5 min, the glass slide with the sample is removed from the hot plate, placed on a metal block and allowed to cool in air. Typically, at this stage, the domains are even visible to the naked eye under reflected room light. Without touching the surface of the sample, the glass slide is then transferred to a light microscope for observation. Figures 9(a) and 9(b) show the crystal as imaged between cross polarizers and in unpolarized light, respectively. Excellent contrast of the domain walls is observed. The higher the temperature gradient, the larger the pyroelectric field upon cooling, and the stronger the contrast of the domain walls both under polarized and unpolarized light. However, contrary to the observation in Fig. 6, the contrast of all the domain walls is equally strong, irrespective of their relative orientation with the input and output polarizers. If the sample is now washed in water and then observed again, the contrast returns to that of the annealed sample (Fig. 8), thus conclusively proving that the origin of improved contrast in rapidly cooled samples (Fig. 9) are pyroelectric fields.

5. Imaging in reflection mode

All the domain imaging techniques described above can also be done in the reflection mode. However, at high magnifications (>50×), the focus depth decreases to a few microns. Since this imaging technique depends on the interaction of light through the bulk of the crystal, the image is lost at higher magnifications in the reflection mode. Focusing on either surface of the crystal in reflection mode at high magnifications showed no surface topographical changes between domain-reversed and virgin crystal regions, indicating that the imaging process is a bulk optical effect.

B. Discussion

1. Origin of optical contrast after room temperature domain reversal

The schematic of Fig. 10 summarizes the proposed model to explain the above observations. Figure 10(a) shows the case of an unannealed domain-reversed crystal at room temperature. The change in ordinary index \( \Delta n_0 \) across a domain wall is \( n_0^3 \cdot r_{13} \cdot E_{\text{int}} = 4.35 \times 10^{-4} \) where \( E_{\text{int}} = 5 \text{ kV/mm} \) and \( r_{13} = 8.4 \text{ pm/V} \). This will give rise to scattering of light at the wall, thus making it visible in transmitted light [see Fig. 6(b)]. However, since \( r_{13} = r_{23} \), the \( E_{\text{int}} \) will not give rise to a birefringence between the \( x \) and \( y \) axes. The origin of birefringence \( (n_x - n_y) \) in Fig. 6(a) can arise from three possible sources: (a) distribution of \( \text{OH}^- \) ions and other point defects, (b) stresses near the domain wall, and (c) nonvertical, 180° domain walls.

We have shown above that the infrared absorption spectrum of \( \text{OH}^- \) ions in \( \text{LiTaO}_3 \) crystal changes with domain reversal in \( \text{LiTaO}_3 \) at room temperature. Hence, across a 180° domain wall, the shape of the hydroxyl ion spectra...
should change. If the changes in the OH\(^-\) spectra are related to a lattice distortion in the oxygen–oxygen bonds or the creation of new point defects (such as \(V_{1\alpha}, Ta_{1\alpha}\), etc.), then a birefringence can be created in the crystal near the domain wall.

Let us next consider the stresses. As already noted, the shape of domain-inverted triangles is exactly the same as that for etch pits in LiTaO\(_3\).\(^{24}\) These etch pits have been observed to form at the intersection of dislocations in the crystal with the crystal Z surface. The domain walls would, therefore, also preferably nucleate along these defect sites on the surface. We have also observed a network of lines in the domain-inverted regions both under crossed polarizers and in unpolarized light. Figure 11 shows the crystal after it was etched in HF+H\(_2\)O\(_3\). These lines correspond to regions where domain inversion did not occur under electric field application, indicating that they correspond to defects (dislocations and low-angle grain boundaries).\(^{26}\) While these regions have also been observed to eventually get domain inverted with the application of higher fields, in the initial nucleation stage, they act as preferential nucleation sites for new domains in the regions around them. These lines are very faint in Figs. 6(a) and 6(b) and become strongly scattering after a high-temperature anneal (Figs. 8 and 9). These defects are associated with stresses\(^{27}\) that, through the piezoelectric effect, give rise to anisotropic electric fields in the crystal that can cause birefringence through the electro-optic effect. Another possibility is that the stresses caused by defects can give rise to structural anisotropy, causing \(r_{13}\neq r_{23}\). The internal field \(E_{\text{int}}\) can then create a birefringence through the electro-optic effect.

Let us now consider the possibility of nonvertical 180° domain walls. Because of the divergence of polarization across the walls, a 180° wall at an angle \(\theta\) to the c axis would have an associated electric field normal to the wall of \(\sim (P_{\parallel} / \epsilon_0) \cos^2 (90 - \theta)\). Etching the crystal in HF+H\(_2\)O\(_3\) mixture followed by observing the y face in cross section revealed that most domains extend through the entire thickness of the crystal and were estimated to be within 1° of the crystallographic c axis of the crystal, giving a field of \(\sim 0.3\) kV/mm normal to the wall and a \(\Delta n \sim 3.3 \times 10^{-5}\). However, in our experiments, the contrast by pyroelectric field imaging [Figs. 9(a) and 9(b)] is destroyed if the surface pyroelectric charges on \(C^+\) and \(C^-\) faces are removed (washed away by water). Therefore, it rules out nonvertical, 180° domain walls in thickness direction as the main source of domain imaging, since the fields caused by these walls are inside the crystal and not removed by water on the crystal surfaces.

2. Loss of optical contrast after annealing

After the sample is annealed at 350 °C for 12 h, the internal field in the domain-reversed regions realigns completely parallel to the polarization direction as shown in Fig. 10(b).\(^{3}\) This would explain the loss of optical contrast at the domain walls in Fig. 8(b). The birefringence is also destroyed as seen in Fig. 8(a) under cross polarizers. This may be because above 200 °C, the crystal conductivity increases exponentially,\(^{3}\) resulting in ionic charges (lithium vacancies or hydrogen) screening the electric fields that give rise to the birefringence at room temperature. Annealing can also recover any structural anisotropy near the domain walls causing the birefringence.

3. Origin of optical contrast by pyroelectric fields

When the annealed crystal is heated to 100 °C–150 °C and then cooled down rapidly, pyroelectric fields are created. Their distribution is shown schematically in Fig. 10(c) across a domain wall. The magnitude of the pyroelectric fields \(E_p\) across the sample for a \(\Delta T\) change in temperature is \(E_p \approx p \Delta T / \epsilon\), where \(p\) is the pyroelectric coefficient \((p_3 = 2.3 \times 10^{-4} \text{ C K}^{-1} \text{ m}^{-2}\) for LiTaO\(_3\)),\(^{28}\) and \(\epsilon\) the dielectric constant \((\epsilon_3 = 44\) for LiTaO\(_3\)).\(^{29}\) For \(\Delta T \approx 50\) °C, the theoretical pyroelectric field is \(\sim 30\) kV/mm, which is higher than the coercive field of 21 kV/mm. However, no noticeable change was observed in the domain microstructure after generating the pyroelectric fields in open atmosphere. Thus we conclude that the pyroelectric fields in our case were less than the coercive field. Also, due to surface mobility, some pyroelectric charges across the domain walls will compensate each other, resulting in a field distribution passing through zero at the domain wall, as shown schematically in Fig. 10(c). This provides a net increase in the refractive index in the bulk and a decrease in the index close to the walls, giving the strong domain wall contrast in Fig. 9. However, since all domain walls seem equally visible under cross polarizers, it is concluded that incoherent scattering of light at the domain walls is more predominant than a coherent rotation of the input polarization, as in Fig. 6(a).

4. Other possible origins of optical contrast

Another possibility for imaging the domains is the change in the transmission coefficient of the virgin vs domain-reversed crystals. The transmission spectrum of virgin and domain-reversed crystals (with no annealing) was measured by spectrophotometer. The two spectra were identical within the error of our measurements (0.5%), thus ruling out this possibility. Preliminary experiments indicate that the domain wall contrast can also be modified by an externally applied electric field during the imaging process. An electric field of \(\pm 2–6\) kV/mm was applied across the
domain-reversed sample (shown in Fig. 6) while observing the crystal under an optical microscope between two cross polarizers. The optical contrast at the domain walls seemed to significantly sharpen with applied external fields of either polarity. While these observations are qualitative and preliminary, they demonstrate the role of electric fields (internal or external) in the optical domain wall contrast. Preliminary results using atomic force microscopy also indicates that there is no surface discontinuity across a 180° domain wall in Figs. 1(a) and 1(b) within an error of ±10 Å. Further work is required in these studies.

IV. CONCLUSION

In conclusion, we show that infrared absorption spectra of OH\textsuperscript{−} ions in congruent LiTaO\textsubscript{3} crystals change with (a) domain reversal at room temperature, and (b) time and elevated temperature. The similarity of the OH\textsuperscript{−} spectra for a domain-reversed crystal at room temperature and a virgin crystal annealed above 200 °C suggests that temperature-induced structural changes in a virgin LiTaO\textsubscript{3} crystal are similar to domain reversal-induced changes in the virgin crystal at room temperature. The OH\textsuperscript{−} spectrum and the built-in internal fields change in the same temperature range (150 °C–200 °C). This is evidence for a strong correlation. We propose that the origin of the internal field in congruent LiTaO\textsubscript{3} lies in OH\textsuperscript{−} ions and nonstoichiometric point defects (tantalum antisites, tantalum vacancies) in LiTaO\textsubscript{3} crystals. The possible connection between internal fields and nonstoichiometric point defects is important since properties such as dielectric constant\textsuperscript{30} and fatigue\textsuperscript{31} are also stoichiometry-dependent in LiNbO\textsubscript{3} and LiTaO\textsubscript{3} crystals and hence will be affected by internal fields.

We have also shown that 180° domains can be imaged by light microscopy in Z-cut LiTaO\textsubscript{3} either by using unpolarized light or between cross polarizers. We present evidence that the optical contrast at 180° domain walls has a strong correlation to the internal fields in the crystal. They behave similarly upon annealing. A model is proposed to explain this optical contrast as a result of electric fields (both internal and pyroelectric fields), which act through the electro-optic coefficient to give rise to index variation across 180° domain walls. Further, the LiTaO\textsubscript{3} crystal exhibits birefringence near domain walls, suggesting structural changes in the crystal after domain reversal.

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