Domain reversal and nonstoichiometry in lithium tantalate

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Recent studies have shown that lithium nonstoichiometry has a tremendous influence on domain reversal characteristics in ferroelectric lithium tantalate. This work presents a systematic study of the domain reversal characteristics such as threshold coercive fields for domain reversal, domain stabilization times, “backswitching” phenomena, domain switching and wall pinning times, and sideways wall mobility in near-stoichiometric LiTaO3 with Li/(Li+Ta)~0.498. These properties are contrasted with those of congruent LiTaO3 [Li/(Li+Ta)~0.485]. A qualitative model is proposed based on nonstoichiometric dipolar defects to explain the dependence of threshold coercive field on defect density, and on repeated field cycling, the origin of domain backswitching, and domain stabilization times. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389525]

I. INTRODUCTION

Ferroelectric lithium tantalate (LiTaO3) and lithium niobate (LiNbO3) have emerged as key optical materials in nonlinear frequency conversion,1 electro-optics,2 and holography.3 Manipulation of ferroelectric domains into diverse shapes such as gratings, lenses, prisms, and other shapes are key to many of these applications. This is primarily achieved by application of an external electric field. Recent discoveries4,5 show that the threshold coercive fields required for domain reversal change dramatically in these crystals with changes in lithium stoichiometry. Lithium nonstoichiometry also strongly affects the optical, electrical, and elastic properties of crystal lattice near domain walls, and the dynamics of domain nucleation and growth as recently reviewed in detail elsewhere.5,7 Here we briefly describe the salient results are then contrasted with those of congruent composition crystals of LiTaO3. Finally, we propose a qualitative defect model to interpret some of the observed phenomena, such as internal fields, domain backswitching and stabilization times, and dependence of threshold coercive fields on polarization cycling.

The article is organized as follows. Sections II–IV, respectively, present experimental data on crystal growth, real-time domain studies, and polarization reversal characteristics of near-stoichiometric composition crystals of LiTaO3. Section V compares and contrasts the domain reversal characteristics of near-stoichiometric and congruent composition crystals. Section VI presents the defect model followed by conclusions in Section VII.

II. NEAR-STOICHIOMETRIC CRYSTAL GROWTH AND PROPERTIES

Stoichiometric crystals of LiTaO3 were grown by the double crucible Czochralski (DCCZ) technique as described in detail elsewhere.5,7 Here we briefly describe the salient facts. In order to grow stoichiometric crystals, a lithium rich melt (~60 mol % Li2O) is required. The double crucible geometry consists of an inner and an outer iridium crucible connected by holes in the wall of the inner crucible. This allows the growth melt to be replenished with material (in the outer crucible) in exact proportion to the weight of the crystal grown from the inner melt using an automatic weighing and powder supply system. The crystals grown along the crystallographic y axis [lying in the (1120) mirror plane] were transparent and crack-free. The Curie temperature was measured as 685±1 °C, which is very close to the Curie temperature of 690±1 °C for sintered stoichiometric LiTaO3 powder. Assuming a linear relationship between Curie temperature and crystal composition,8 the crystal composition Li/(Li+Ta) is estimated to be 0.4977–0.4992, which is quite close to the stoichiometric composition of 0.5. We will, however, show that this deviation from stoichiometry is nonetheless significant enough to introduce defect fields and influ-

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ence the physical properties of these crystals. An impurity concentration of 0.9 wt ppm Fe was measured. Copper and chromium were less than 0.1 and 0.2 wt ppm, respectively. The as-grown crystals were observed to be multidomain. The crystal was cut into a z-cut block, which was annealed in air at 750 °C, and subsequently cooled down at a rate of 2 °C/min to room temperature under a dc electric field along the z direction. These blocks were cut into z-cut plates of 10×10×0.25 mm, and optically polished, resulting in plates which were single crystal and single domain, though some microdomains of 50 μm or less size were also observed. This starting state of the crystal will be referred to in the rest of this article as the “virgin state” with a ferroelectric polarization of \(-P_s\).

III. REAL-TIME OBSERVATION OF DOMAIN WALL MOTION IN NEAR-STOICHIOMETRIC COMPOSITION

Starting from the virgin state of a 0.25 mm thick z-cut crystal, electric field is applied across the z faces to reverse the ferroelectric polarization at room temperature. Tap water is used as electrodes, with no dissolved salts, since dissolution of KNO₃ salt, for example, to any saturation level did not appear to change the observed results. The application of an electric field \(E_3\) parallel to the z axis also gives rise to an index difference \(2\Delta n_{23} = n_{o}^{3}r_{23}E_{3}\) across a 180° domain wall where \(r_{23}\) is the electro-optic coefficient and \(n_{o}\) the ordinary index. This index difference gives rise to scattering of light at the wall which is optically imaged.⁹ For example, the domain wall is not visible in Fig. 1(a), but becomes visible in Fig. 1(b), when an electric field of 10 kV/cm (which is less than the field required for wall motion) is applied along the z axis of the crystal.

Since the electric field employed for domain reversal can also aid in optically imaging the domain wall, we can study the real-time motion of domain walls under electric fields. The real-time movie was recorded using either a standard video recorder with 30 frames/s or a high-speed camera (Kodak Ektapro) with 2000 frames/s. The frames were then digitally extracted from the recorded movie using computer software.

Figure 2(a) shows a series of selected optical images showing the progression of domain wall creation and motion under an electric field. Also shown in Fig. 2(a) is the corresponding transient current, \(i\), observed during domain reversal where \(i = dq/dt = d/dt(2P_sA)\). Here \(A\) is the area of reversed domain regions, \(P_s\) is the spontaneous polarization, \(q\) the charge, and \(t\) the time. The transient currents are in the form of spikes, suggesting a very fast domain wall motion within a few milliseconds followed by no domain motion and so on. The video frames shown here, with only a resolution of 33 ms per frame, nonetheless show the net domain motion corresponding to the transient current spikes observed in the interval between two frames. F1 shows no domain walls. After one frame interval (33 ms) corresponding to F2, three small domains have nucleated, corresponding most likely to the first three main current spikes seen in Fig. 2(b). The domain merging process is observed between frames F2 and F3, and therefore frame F3 shows two big merged domains. Finally these two remaining domains merge between frames F3 and F4. It is interesting to note that even though domain reversal is complete in frame F4, a faint trace of the original domain wall position in F3 is still retained in F4. After ~33 ms this contrast disappears resulting in frame F5. This is the faint residual optical contrast at a location of a domain wall after the wall has moved away. It arises from residual strains at the domain wall which in turn arise from a small amount of lithium nonstoichiometry in the crystal and induce optical contrast through elasto-optic effect as well as through coupled piezoelectric and electro-optic effects.⁶ Though faint, and difficult to observe under bright illumination conditions [such as in Fig. 1(a)], under careful observation, this contrast is visible at a wall in near-stoichiometric crystals. The total time to reverse a domain in a given area is called the switching time, \(t_s\), which in Fig. 2(a) is 80 ms as determined from the transient current data.

IV. THRESHOLD COERCIVE FIELDS, SWITCHING AND STABILIZATION TIMES, AND WALL MOBILITY IN NEAR-STOICHIOMETRIC CRYSTALS

Under an electric field, the first polarization reversal (or poling) of a virgin crystal from the “virgin state” to a “domain reversed state” is termed forward poling (denoted by symbol f1), and the second reversal back to virgin state is called reverse poling (denoted by symbol r1). Subsequent forward and reverse poling operations are then successively labeled f2, f3, f4,...etc. and r1, r2, r3,...etc., respectively. The polarization hysteresis loop is measured by linearly ramping the electric field and tracking the transient currents created during domain reversal. When the spontaneous polarization reverses from \(+P_s\) to \(-P_s\) (or vice versa), the total charge \(q\), observed under the transient current \(i\), is \(q = \int idt = 2P_sA\), where \(A\) is the electrode area and \(t\) the time. The threshold coercive field is arbitrarily chosen as the electric field value at which the integrated charge under the transient current peak is 1% of the total integrated charge \(q\) under the peak. The domain switching times are typically greater than 30 min at these measured threshold coercive fields. This definition was chosen over the conventional definition of coercive field at 50% domain reversed area, since we wanted to measure the lowest threshold coercive fields at which reversal begins. In order to study the effect of repeated cycling of ferroelectric polarization between \(+P_s\) and

![Optical microscope image, in unpolarized transmitted light, of a 180° domain wall in z-cut near-stoichiometric LiTaO₃. (a) No electric field applied. The wall is not visible. (b) An electric field of 10 kV/cm applied to the crystal along the z axis, rendering the wall visible through the electro-optic effect. The polarization is normal to the image plane.](http://ojps.aip.org/japo/japcr.jsp)
another experimental variable was introduced called the cycling time gap, $t_{g,j}$, where $j = f$ (for forward poling) or $j = r$ (for reverse poling). This time gap is a measure of the time gap allowed between the beginning of one domain reversal sequence (as monitored by the transient current peak) and the beginning of another. For example, $t_{g,r}$ is the time gap between the beginning of $f_1$ and the beginning of a successive $r_1$, and $t_{g,f}$ is the time gap between the beginning of $r_1$ and the beginning of a successive $f_2$. In other words, $t_{g,r}$ is the longest time period that any part of the crystal under the electrode stays in domain state $+P_s$ (after its creation) before being reverse poled into the $-P_s$ state. Similarly, $t_{g,f}$ is the longest time period that a domain stays in the $-P_s$ state (after its creation) before being forward poled into the $+P_s$ state.

A. Threshold coercive fields

Figure 3 shows the hysteresis loops of polarization versus electric field for $t_{g,j} = 300$ and $60$ s. The observed threshold coercive fields for $t_{g,j} = 300$ s are $E_{c,f} \sim 16.7$ kV/cm and $E_{c,r} \sim 14.5$ kV/cm. For $t_{g,j} = 60$ s, the threshold coercive fields decrease to $E_{c,f} \sim 13.6$ kV/cm and $E_{c,r} \sim 12.3$ kV/cm. The internal field, $E_{int} = (E_{c,j} - E_{c,r})/2 \sim 1.1$ kV/cm for $t_{g,j} = 300$ s and $0.7$ kV/cm for $t_{g,j} = 60$ s. In both cases, the offset of the hysteresis loop is along the positive (forward poling) field axis.
For \( t_{g,j} < 300 \text{ s} \) the threshold coercive field shows a sharp decrease. Figures 4(a) and 4(b), respectively, show the forward \( (E_{c,f}) \) and reverse \( (E_{c,r}) \) threshold coercive fields as a function of total cycling time \( t_{g,j} \). The data corresponding to the shortest time gap, \( t_{g,j} \), was obtained by measuring the stabilization times of \( t_{\text{stab,f}} \) and \( t_{\text{stab,r}} \) for forward and reverse poling. By the definition of stabilization time (as explained in the following section), when \( t_{g,j} = t_{\text{stab,f}} \), \( E_{c,f} = 0 \); and similarly, at \( t_{g,j} = t_{\text{stab,r}} \), \( E_{c,r} = 0 \). The solid line fits to the measurements for \( t_{g,j} > t_{\text{stab,j}'}, \) are based on a double exponential function of the form

\[
E_{c,j} = \sum_{i=1}^{2} E_{ij}[\exp(-t_{\text{stab, }j}/\tau_{ij}) - \exp(-t_{g,j}/\tau_{ij})],
\]

where \( i = 1,2 \) and \( (j,j') = (f,r) \) or \( (r,f) \), referring to forward \( (f) \) or reverse \( (r) \) poling directions. Table I lists the time constants \( \tau_{ij}, t_{\text{stab,j}'}, \) and the exponents \( E_{ij} \). Note that by definition, if \( t_{g,j} = t_{\text{stab,j}'} \), \( E_{c,j} = 0 \). The relaxation times \( \tau_{ij} \) are very similar for forward and reverse poling suggesting similar relaxation mechanisms. An important aspect of this figure is the presence of negative threshold coercive fields when \( t_{g,j} < t_{\text{stab,j}'} \).

The presence of negative threshold coercive fields in Figs. 4(a) and 4(b) appear counterintuitive, but are physically real. In this regime the negative threshold coercive field refers to the minimum baseline voltage that should be applied following the end of the original pulse of width \( t_{g,j} \), in order to prevent domain backswitching after the pulse. Such baseline voltages are often used to stabilize domains created by short pulses while fabricating domain microengineered devices.\(^1\) The behavior of threshold coercive fields with time gap, \( t_{g,j} \), appears in general to follow a different exponential time constant for time gaps shorter and longer than the stabilization time, \( t_{\text{stab,j}'} \). The functional form for this behavior for \( t_{g,j} < t_{\text{stab,j}'} \) is the same as Eq. (1). In near-stoichiometric crystals, only one data point could be obtained for the negative threshold coercive field regime due to the short times scales over which they occur. However, for congruent crystals, negative threshold coercive fields (reported in Sec. V) show a clear trend with at least one exponential \( (j = 1) \) with a corresponding time constant, \( \tau_{ij} \) (see Table I). Negative threshold coercive fields are discussed further in the following section and in Sec. V.

**B. Domain backswitching and stabilization time**

Domain backswitching and stabilization processes in congruent LiTaO\(_3\) crystals have been previously reported.\(^6\) A domain created by the application of an electric field needs a certain minimum amount of time for which the electric field that created it should remain and stabilize it. This time is called the stabilization time, or \( t_{\text{stab,j}'} \), for the domain and subscripts \( j = (f,r) \) refers, respectively, to forward or reverse poling. If the electric field is removed in a time \( t_{g,j} < t_{\text{stab,j}'} \), \( j = (f,r) \), then the newly created domain shrinks and reverts back to the original domain configuration that existed before the application of the field. This reversible domain wall motion is called domain backswitching. In reality, a range of stabilization times is found such that when, for example, \( t_{g,j} < t_{\text{stab,j}'} \) or \( t_{g,j} > t_{\text{stab,j}'} \), partial domain backswitching is observed. When \( t_{g,j} > t_{\text{stab,j}'} \), no domain backswitching is observed. In the intermediate pulse widths, partial domain backswitching is observed. The stabilization time was measured by applying square electric field pulses with varying pulse widths and electric field magnitudes and observing the transient currents.

Figure 5(a) shows the negative transient current response during domain backswitching on application of a voltage pulse of 60 kV/cm and 10 ms duration. Figure 5(b) shows the corresponding optical images of the domain walls during the backswitching process. These images were taken with a high-speed camera capable of 2000 frames/s. The time resolution was therefore 0.5 ms between frames, and the time instant starting from the beginning of the voltage pulse at \( t = 0 \) is indicated on each frame. Domain reversal takes place...
TABLE I. The fitting parameters in Eq. (1) describing the experimental dependence of coercive fields $E_{c,f}$ on the time gap $t_{s,f}$ spent in the previous domain state as given in Figs. 4 and 10.

<table>
<thead>
<tr>
<th>LiTaO$_3$ composition</th>
<th>$E_{1,j}$ (kV/cm)</th>
<th>$\tau_{1,j}$ (s)</th>
<th>$E_{2,j}$ (kV/cm)</th>
<th>$\tau_{2,j}$ (s)</th>
<th>$t_{stab,j}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>near-stoichiometric forward poling (f)</td>
<td>14.50±1.50</td>
<td>26.4±6</td>
<td>2.21±1.49</td>
<td>177.5±104</td>
<td>0.058±0.043</td>
</tr>
<tr>
<td>$t_{g,j}$= $t_{stab,j}$; (j,j')=(f,r)</td>
<td>near-stoichiometric reverse poling (r)</td>
<td>14.38±0.55</td>
<td>32.4±2.6</td>
<td>0.33±0.14</td>
<td>310.3±200</td>
</tr>
<tr>
<td>$t_{g,j}$= $t_{stab,j}$; (j,j')=(r,f)</td>
<td>congruent forward poling (f)</td>
<td>175.66±3.80</td>
<td>20.3±0.9</td>
<td>31.29±3.23</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>$t_{g,j}$= $t_{stab,j}$; (j,j')=(f,r)</td>
<td>congruent forward poling (f)</td>
<td>−37.38±1.06</td>
<td>0.0027±0.006</td>
<td>6</td>
<td>0.05±0.03</td>
</tr>
<tr>
<td>$t_{g,j}$= $t_{stab,j}$; (j,j')=(f,r)</td>
<td>congruent reverse poling (r)</td>
<td>100.37±8.25</td>
<td>26.5±3.9</td>
<td>19.80±7.82</td>
<td>316±179</td>
</tr>
<tr>
<td>$t_{g,j}$= $t_{stab,j}$; (j,j')=(r,f)</td>
<td>congruent reverse poling (r)</td>
<td>−104.06±4.19</td>
<td>0.060±0.006</td>
<td>0.7±0.2</td>
<td></td>
</tr>
</tbody>
</table>

until the first 10 ms, when the voltage pulse is on, followed by backswitching after the pulse disappears. In this case, the backswitching time was >60 ms. When the external pulse is shorter, back switching time is ~1–10 ms. If the external pulse time is close to stabilization time, back switching time increases to several hundred milliseconds. Figure 6(a) shows stabilization times ($t_{stab,j}$)$_{start}$ and ($t_{stab,j}$)$_{end}$ as a function of electric field. Many interesting aspects can be observed. The stabilization time decreases rapidly as the electric field exceeds the threshold coercive field for domain reversal. If the external field exceeds 20 kV/cm in the forward poling and 17 kV/cm in reverse poling, the stabilization times are relatively insensitive to the electric field magnitude and are approximately ($t_{stab,j}$)$_{start}$~300 ms, and ($t_{stab,j}$)$_{end}$~30 ms. The stabilization time in forward poling is ~10 times higher than in reverse poling at the same electric field. Figure 6(b) shows a logarithmic plot of the dependence of stabilization time on the electric field. An exponential dependence is found for ($t_{stab,j}$)$_{start}$ as a function of electric field for most of the field range except for fields very close to the threshold coercive field in forward poling geometry. Dropping the subscript “start” we can write this dependence as

$$t_{stab,j} = t_{stab,j0} \exp \left( \frac{\delta_{stab,j}}{E-E_{c,j}} \right),$$  \hspace{1cm} (2)

where $j=f$ or $r$, the activation values are $\delta_{stab,j}=1.72\pm0.32$ kV/cm and $\delta_{stab,r}=11.6\pm1.67$ kV/cm. The preexponents values are ln[($t_{stab,j0}$)(ms)]=5.6±0.05 and ln[($t_{stab,j0}$)(rs)]=2.08±0.53.

Referring back to the discussion of Fig. 4 in Sec. IV B, we now briefly discuss the negative threshold coercive fields when the cycling time $t_{g,j}$ is below the pulse stabilization time $t_{stab,j}$, where (j,j')=(f,r) or (r,f). As an example, let a square electric field pulse with $E>E_{c,f}$ and a pulse width of approximately equal to, but slightly smaller than, ($t_{stab,f}$)$_{start}$ be applied to the crystal in forward poling. Domain reversal (forward poling) takes place during the pulse duration, and domain backswitching (reverse poling) takes place immediately after the pulse has ended and the electric field $E$ is zero. In this situation, the external electric field required for reverse poling is zero, i.e., $E_{c,r}<0$ and $t_{g,r}$~($t_{stab,f}$)$_{start}$. This defines the zero crossing of the threshold coercive field curve in Fig. 4(b). When the pulse width of the external pulse is much less than ($t_{stab,f}$)$_{start}$, $E_{c,r}<0$ in Fig. 4(b), implying that a short electric field pulse of magnitude $>E_{c,r}$ in the forward poling direction would be needed to prevent domain reversal in the reverse poling direction from taking place during backswitching. A similar case can also be made for negative $E_{c,f}$ in Fig. 4(a) by interchanging the phrase “forward poling” (and subscripts $f$) and the phrase “reverse poling” (and subscripts $r$) in the above arguments.

C. Switching times

Figure 7 shows electric field $E$ versus switching time, $t_{s,f}$ (during forward poling) and $t_{s,r}$ (during reverse poling), respectively. Switching time here is interpreted as the total time required to switch the entire electrode area (20 mm$^2$ in this case). Two sets of data are shown, one for $t_{g,j}=300$ s and $t_{g,j}=40$ s. For $t_{g,j}=300$ s two distinct activation fields appear to be present for each of the forward and reverse domain reversal processes that follow the exponential switching time relationships given by

$$t_{s,j} = t_{s,j0} \exp \left( \frac{\delta_j}{E-E_{c,j}} \right),$$  \hspace{1cm} (3)

where $j=f$ or $r$. By this definition, when the electric field $E=E_{c,f}$ or $E_{c,r}$, the switching times $t_{s,f}$ and $t_{s,r}$ tend to
infinity. For practical purposes, the extrapolated switching times at the measured threshold coercive fields are greater than 30 min in our case. A logarithmic plot of electric field $E$ versus switching time $t_s$, as in Fig. 7, shows the different activation field regimes more clearly. Table II lists the activation fields $d_f$, $d_r$ and the preexponents $t_{fo}$ and $t_{ro}$.

Some key observations are as follows. (1) Switching time decreases with decreasing $t_g$, following a similar trend as the threshold coercive fields in Fig. 4. As already shown (see Fig. 4), decreasing time gap $t_g$ results in a decreasing threshold coercive field $E_{c_j}$. For a fixed external electric field, a decrease in threshold coercive field will result in a greater mobility of the domain wall and therefore a decrease in the switching time, which qualitatively explains this observation. (2) For $t_g=300$ s, the switching times in the forward and reverse poling regimes show two distinct slopes (activation fields) for low and high external field regimes, the slope being considerably higher in the high field regime. (3) For $t_g=40$ s, the distinction between high and low field regimes disappears, resulting in only one field regime. In this single regime, the switching times as well as the activation fields are equal for the forward and reverse poling as listed in Table II. For shorter time gaps, $t_g$ approaching the stabilization time $t_{stab}$, the difference between threshold coercive fields $E_{c_f}$ and $E_{c_r}$ become similar as seen from Fig. 4, as both of these quantities rapidly tend to zero. The switching times therefore become similar as will be seen here. The differences in forward and reverse threshold coercive fields and switching times are accentuated only for long time gaps, $t_g$.

**D. Wall mobility**

As seen in Fig. 2, the transient current shows a series of very sharp spikes on the order of milliseconds even at a constant driving field. Real-time video confirms this to cor-
respond to discrete and sporadic jumps of domain walls. In the very-low field regime close to threshold coercive field, the domain mobility is not feasible. At higher electric fields of >22 kV/cm, which lie well within the high field regime discussed in Sec. IV C, the switching times are in the millisecond range, and the transient current shows peaks which are merged into each other as shown in Fig. 8(a). The fast domain wall velocities were measured with a high speed charge coupled device camera (Kodak Ektapro) capable of 2000 frames per s in real time. Figure 8(b) shows a series of images from real-time domain motion with a time resolution of 0.5 ms between frames. It is noted that domain walls still show pinning and sporadic motion at these high fields. At all the studied fields, a single domain wall front was observed to sweep across the video screen in this particular sample area. Two parameters were measured from these real-time images: the maximum domain wall velocity of this wall, $v_{s,f}$, and the pinned time, $t_{p,f}$, spent by this domain wall in a pinned state, when it is not moving.

Analyzing video frames in Fig. 8(b) and other similar ones at different electric fields shows that the measured maximum sideways wall velocities $v_{s,j}$ increase with electric field. The maximum pinning time $t_{p,f}$ and switching time $t_{s,j}$ decrease with electric field. These are plotted in Fig. 9(a). Figure 9(b) shows the relative time fraction $t_{p,f}/t_{s,j}$ that the domain front spends not moving, as a function of electric field. It is clear that the domain wall pinning dominates the total switching time $t_{s,j}$ at lower electric fields. Based on Miller–Weinreich analysis, 10 we assume an exponential velocity dependence on electric field as

$$v_{s,j} = v_{s,j0} \exp \left(-\frac{\alpha_{s,j}}{E - E_{c,j}}\right),$$

where $j = f$ or $r$. The velocity data is replotted as a log plot in Fig. 9(c). Our experimental measurements of the velocity have very low scatter in the high field regime as compared to

<table>
<thead>
<tr>
<th>Crystal; (coercive fields)</th>
<th>Poling direction; $t_{s,j}$</th>
<th>Field regimes</th>
<th>$E_{c,j}(\text{kV/cm})$</th>
<th>$\Delta (\text{kV/cm})$</th>
<th>$\ln(t_{s,j}(\text{ms}))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near-stoichiometric LiTaO$_3$</td>
<td>forward ($f$)</td>
<td>$E_{c,f} &lt; 13.9$ kV/cm</td>
<td>26.48 ± 2.1</td>
<td>2.1 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>(E$_{c,f} = 18.7$ kV/cm)</td>
<td></td>
<td>$E_{c,f} &gt; 13.9$ kV/cm</td>
<td>5.34 ± 0.2</td>
<td>3.18 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>reverse ($r$)</td>
<td>$E_{c,r} &gt; 16.1$ kV/cm</td>
<td>33.4 ± 2.1</td>
<td>1.98 ± 0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$t_{s,r} = 300$ s</td>
<td>$E_{c,r} &lt; 16.1$ kV/cm</td>
<td>19.85 ± 1.4</td>
<td>2.2 ± 0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>forward ($f$)</td>
<td>$E &gt; E_{c,f}$</td>
<td>64.73 ± 1.3</td>
<td>1.57 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>reverse ($r$)</td>
<td>$E &gt; E_{c,r}$</td>
<td>70.05 ± 2.3</td>
<td>1.39 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$t_{s,r} = 40$ s</td>
<td>$E_{c,r} = 211$ kV/cm</td>
<td>36.93 ± 0.5</td>
<td>$-1.8 ± 1.03$</td>
<td></td>
</tr>
<tr>
<td>Congruent</td>
<td>forward ($f$)</td>
<td>$E_{c,f} &gt; 3.8$ kV/cm</td>
<td>51.4 ± 5.9</td>
<td>$-0.4 ± 1.04$</td>
<td></td>
</tr>
<tr>
<td>LiTaO$_3$</td>
<td></td>
<td>$E_{c,f} &lt; 3.8$ kV/cm</td>
<td>1.49 ± 0.5</td>
<td>11.35 ± 0.35</td>
<td></td>
</tr>
<tr>
<td>(E$_{c,f} = 211$ kV/cm)</td>
<td>reverse ($r$)</td>
<td>$E_{c,r} &gt; 2.1$ kV/cm</td>
<td>36.93 ± 0.5</td>
<td>$-1.8 ± 1.03$</td>
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<tr>
<td></td>
<td>$t_{s,r} = 300$ s</td>
<td>$E_{c,r} &gt; 2.1$ kV/cm</td>
<td>0.95 ± 0.5</td>
<td>10.44 ± 0.76</td>
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</table>
the larger scatter in the low field measurements where random pinning events dominate. A linear fit in the high field regime alone \( (E - E_{c,f} > 19 \text{ kV/cm}) \) gives \( \ln(\alpha_{s,f}) = -6.59 \pm 0.06 \) and \( \alpha_{s,f} = 22.09 \pm 2.17 \text{ kV/cm} \), which does not extrapolate well into low field regime data. Therefore we conclude that the data really represents two field regimes. For \( E - E_{c,f} < 19 \text{ kV/cm} \), the scatter in the measured velocity data is large, and therefore a range of activation fields exists, with a mean value of \( \alpha_{s,f} \sim 6.8 \text{ kV/cm} \). The fitting parameters are summarized in Table III. We assume an exponential behavior of the pinned time \( t_{p,f} \) as a function of electric field \( E \) as

\[
t_{p,f} = t_{p,f0} \exp \left( \frac{\delta_{p,f}}{E - E_{c,f}} \right),
\]

where \( \delta_{p,f} \) is the activation energy for pinning.

FIG. 8. High speed, real-time tracking of domain motion in \( z \)-cut near-stoichiometric LiTaO\(_3\) under a forward poling external field of 30 kV/cm. The transient current (a) and the corresponding optical images (b) using a high speed camera (Kodak Ektapro) capable of real-time 2000 frames/s. The time instant, \( t \) elapsed after the application of field at \( t = 0 \), is also marked in each frame.

FIG. 9. (a) Analysis of the switching time \( t_{s,f} \), the maximum pinning time \( t_{p,f} \), and the sideways wall velocity \( v_{s,f} \), analyzed from the video frames showing domain motion in Fig. 8(b). (b) The ratio of the pinning time to the switching time, \( t_{p,f}/t_{s,f} \), indicating that at lower electric fields the pinning time dominates the switching time. (c) The log plots of \( t_{s,f} \), \( v_{s,f} \), and \( t_{p,f} \) plotted according to Eqs. (3)–(5), respectively. The coercive fields \( E_{c,f} = 18.7 \text{ kV/cm} \). The fitting parameters to the linear solid line fits are given in Table III.
TABLE III. The fitting parameters for switching time \( t_{s,f} \), pinning time \( t_{p,f} \), and sideways wall velocity \( v_{s,f} \) measured from the real-time video data in Fig. 8(b) during forward poling in near-stoichiometric LiTaO₃. The results for congruent crystals (Refs. 9 and 13) are also given for comparison.

<table>
<thead>
<tr>
<th>Crystal; (coercive field)</th>
<th>( t_{s,f} ), ( v_{s,f} ), or ( t_{p,f} )</th>
<th>Electric field regimes</th>
<th>Activation fields ( \delta_{f,j} ) or ( \alpha_{s,f} ) (kV/cm)</th>
<th>Pre-exponential factors ( \ln(\tau_{fo}(s/mm)) ), ( \ln(1/\tau_{s,f}(s/mm)) ), ( \ln(\tau_{p,f}(ms)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near-stoichiometric LiTaO₃ ((E_{c,i} = 18.7 \text{ kV/cm} \ E_{c,o} = 14.4 \text{ kV/cm}))</td>
<td>( t_{s,f} ) ( E-E_{c,f} &gt; 20 \text{ kV/cm} )</td>
<td>( \delta_{s,f} = 20.86 \pm 0.75 )</td>
<td>( \ln(\tau_{fo}(s/mm)) = 3.15 \pm 0.22 )</td>
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<tr>
<td>( v_{s,f} ) ( E-E_{c,f} &lt; 20 \text{ kV/cm} )</td>
<td>( \alpha_{s,f} = 6.8 \pm 0.54 )</td>
<td>( \ln(1/\tau_{s,f}(s/mm)) = 6.99 \pm 0.06 )</td>
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<tr>
<td>( t_{p,f} ) ( E-E_{c,f} &lt; 19 \text{ kV/cm} )</td>
<td>( \delta_{p,f} = 70.5 \pm 1.78 )</td>
<td>( \ln(\tau_{p,f}(ms)) = 2.70 \pm 0.10 )</td>
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<tr>
<td>( E-E_{c,f} &lt; 18 \text{ kV/cm} )</td>
<td>( \delta_{p,f} = 4.8 \pm 0.91 )</td>
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</tr>
<tr>
<td>Congruent LiTaO₃ ((E_{c,i} = 211 \text{ kV/cm}))</td>
<td>( t_{s,f} ) ( E-E_{c,f} &gt; 3.8 \text{ kV/cm} )</td>
<td>( \delta_{s,f} = 51.4 \pm 5.88 )</td>
<td>( \ln(\tau_{fo}(s/mm)) = 11.35 \pm 0.35 )</td>
<td></td>
</tr>
<tr>
<td>( v_{s,f} ) ( E-E_{c,f} &lt; 3.8 \text{ kV/cm} )</td>
<td>( \delta_{s,f} = 1.49 \pm 0.52 )</td>
<td>( \ln(1/\tau_{s,f}(s/mm)) = 2.95 )</td>
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</tr>
<tr>
<td>( E-E_{c,f} &gt; 4 \text{ kV/cm} )</td>
<td>( \alpha_{s,f} = 42.56 )</td>
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</tr>
<tr>
<td>( E-E_{c,f} &lt; 2 \text{ kV/cm} )</td>
<td>( \alpha_{s,f} = 0.46 )</td>
<td>( \ln(\tau_{p,f}(ms)) = 10.09 )</td>
<td></td>
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</tbody>
</table>

and overlay this plot as well in Fig. 9(c). In addition, for comparison we plot the switching time \( t_{s,f} \) obtained from the video data on the same plot. The fitting parameters for switching time [Eq. (3)], sideways wall velocity [Eq. (4)], and pinning time [Eq. (5)] are presented together in Table III. All three physical properties show a discontinuity around the field range of \( E-E_{c,f} = 18-20 \text{ kV/cm} \). In the higher electric field regime \((E-E_{c,f} > 19 \text{ kV/cm})\) the activation fields \( \alpha_{s,f} (~22 \text{ kV/cm}) \) for the sideways domain wall velocity and the activation field \( \delta_{f} (~21 \text{ kV/cm}) \) for the total switching time are similar, while that for pinning time \( \delta_{p,f} (~70.5 \text{ kV/cm}) \) is significantly higher, indicating that sideways domain wall motion dominates the switching time \( t_{s,f} \) in this field regime. In the low electric field regime \((E-E_{c,f} < 19 \text{ kV/cm})\), the activation fields \( \delta_{p,f}, \alpha_{s,f}, \) and \( \delta_{f} \) are all similar. However, the magnitude of switching time is dominated by the pinning time in this regime as seen in Fig. 9(b).

V. COMPARISON OF NEAR-STOICHIOMETRIC AND CONGRUENT COMPOSITION CRYSTALS

Many of the polarization reversal properties depend strongly on the lithium nonstoichiometry in LiTaO₃ and LiNbO₃. This section compares and contrasts the congruent \([\text{Li}/(\text{Li} + \text{Ta}) = 0.485]\) and near-stoichiometric \([\text{Li}/(\text{Li} + \text{Ta}) = 0.4977-0.4992]\) compositions of LiTaO₃.

The most dramatic difference is that the threshold coercive field required for domain reversal in congruent LiTaO₃ is \( 210-220 \text{ kV/cm} \) for forward poling and \( 110-120 \text{ kV/cm} \) for reverse poling direction at room temperature. The internal field is therefore \( E_{int} \approx 45-50 \text{ kV/cm} \). This contrasts with threshold coercive fields of 17 kV/cm for forward and 15 kV/cm for reverse poling directions, and therefore an internal field \( E_{int} \approx 1 \text{ kV/cm} \) in the near-stoichiometric crystals studied here. In lithium niobate similar large changes are observed, and the variation of threshold coercive fields with lithium concentration, \( C = \text{Li}/(\text{Li} + \text{Nb}) \), is found to be approximately linear in this composition range. This linearity, though not strictly confirmed in isostuctural LiTaO₃, is also expected.

Another clear difference is the domain wall contrast under optical microscope at room temperature. In congruent crystals, domain walls are easily observed under an optical microscope without any external field. The region adjacent to these walls has been shown to possess optical birefringence of \( 10^{-5} \) to \( 10^{-4} \), lattice strains, and local electric fields.

On the other hand, in near-stoichiometric crystals, optical birefringence is significantly lower (estimated well below \( 10^{-6} \)), and strains can hardly be observed even with x-ray synchrotron imaging. Therefore there is a close relationship between lithium nonstoichiometry and domain wall structure. The local relaxation of point defect dipoles arising from nonstoichiometry in the region of the domain wall leads to the observed strains, fields, and optical birefringence.

The variation of threshold coercive fields with repeated polarization cycling shows similarities and differences in congruent and near-stoichiometric composition crystals. Figure 10 shows the threshold coercive field \( E_{c,j} \) versus time gap \( t_{g,j} \) for congruent LiTaO₃. Like near-stoichiometric crystals, congruent crystals also show large negative threshold coercive field when the time gap is shorter than its stabilization times. Again, the data point for the zero crossing of the field axis was obtained from the stabilization time \( t_{stab,j} \) where \( (j,j') = (f,r) \) or \( (r,f) \). Similar to the measurements on near-stoichiometric crystals shown in Fig. 4(a), this measurement on congruent crystals can be fit to multiple-exponential curves given by Eq. (1). However, one clearly notes that the fit for the negative threshold coercive fields is different from that for positive threshold coercive field, with a discontinuity of the derivative at the zero field crossing corresponding to the stabilization time. In Table I the parameters for this fit are shown, with the caveat that the zero time gap intercept for the fit to negative coercive fields has large uncertainty due to the very small time gaps involved. Both stoichiometric and congruent crystals show an abrupt de-
increase in threshold coercive field at $t_{g,fr} \sim 5$ min. For time gaps longer than stabilization time, near-stoichiometric compositions exhibit time constants of $\tau_{f,fr} = 26$ s and $\tau_{r,fr} = 177$ s, while congruent compositions exhibit $\tau_{f,fr} = 29$ s and $\tau_{r,fr} = 523$ s. The time constants $\tau_{i,fr}$ are very similar for both compositions even though the magnitudes of threshold coercive fields show an order of magnitude difference. This implies that even though the defect densities in the two compositions are very different, the relaxation mechanism occurs by the same underlying physical phenomenon. In Sec. VI we propose such a mechanism based on slow reorientation of defect dipoles following polarization reversal.

The switching times for congruent and stoichiometric compositions exhibit similarities and differences as well. The switching time $t_{s,fr}$ as a function of external electric field $E - E_{c,fr}$ for congruent crystals is shown in Fig. 11. Shown overlapped are the switching times for stoichiometric crystals as well. Note that these measurements for congruent crystals were reported before in literature, but were plotted as a function of $E - E_{\text{int}}$.\textsuperscript{13,14} However, based on the exponential relationship between switching time and electric field [see Eq. (3)], at $E = E_{c,fr}$ the switching time goes to infinity. This is physically more realistic than assuming the same thing at $E = E_{\text{int}}$ as was done in Refs. 13 and 14. Both congruent and stoichiometric crystals exhibit two distinct electric field regimes of $E - E_{c,fr}$, where the activation fields $\delta_{j}$ are different. These activation fields are listed in Table II. Note that in the high field regime, the activation fields for both congruent and near-stoichiometric LiTaO$_3$ are similar indicating again a similar mechanism for domain wall motion. In the low electric field regime, the domain wall pinning dominates the switching time as shown earlier in Fig. 9(b). This is true for both near-stoichiometric and congruent compositions. However, since the nonstoichiometric defect density is lower in the near-stoichiometric crystals, the pinning process and hence the switching time is quite random and varies drastically from one area of the same sample to another. With higher defect density in congruent LiTaO$_3$ this variance from area to area decreases. The difference in the switching time behavior with field in the low field regime between the near-stoichiometric and congruent compositions is a direct result of this process. Note that implicit in this argument, we are proposing that the pinning sites are also correlated with nonstoichiometric defects or defect aggregates. This proposition is supported by the fact that the threshold coercive field in congruent crystal appears to be a pinning–depinning transition. Small reversible pinning and bending of a domain wall locally on micrometer length scales has been observed\textsuperscript{11} in congruent crystals at fields of $E < 20$ kV/cm which is an order of magnitude lower than the threshold coercive field of $\sim 210$ kV/cm. Since the threshold coercive field also changes drastically with point defect concentration, the process of pinning and the actual pinning sites themselves must be correlated with point defects. We propose below that the point defect complexes have an electrical dipole, which prefer to orient parallel to the lattice polariza-

FIG. 10. The dependence of coercive field $E_{c,fr}$ as a function of the cycling time gap $t_{g,fr}$ for forward and reverse poling for $z$-cut congruent LiTaO$_3$, where (a) $j = f$ and (b) $j = r$. The time axis crossings at $E_{c,fr} = 0$ is equal to the measured stabilization time of $t_{stab,j}$, where (a) $(j,j') = (f,r)$ and (b) $(j,j') = (r,f)$. This crossing and the negative coercive fields are shown more clearly in the insets. The solid line is a double exponential fit for $t_{g,fr} > t_{stab,f}$ and a single exponential fit for $t_{g,fr} < t_{stab,j}$, as described by Eq. (1). The fitting parameters are given in Table I. The inset schematic describes the meaning of negative coercive field as a minimum baseline voltage following the main pulse needed to prevent domain backswitching after the end of the pulse.

FIG. 11. The domain switching times for $z$-cut congruent LiTaO$_3$ crystals in forward for time gaps $t_{g,fr} = 300$ s. The linear solid line fits are according to Eq. (4). The coercive fields $E_{c,fr} = 211$ kV/cm for congruent LiTaO$_3$. The activation field and preexponents from the fit are listed in Table II. Also overlapped for comparison are the switching times for $z$-cut near-stoichiometric LiTaO$_3$ crystals from Fig. 7(b). The electrode area was 20 mm$^2$ for both cases.
tion. Simple electrostatic calculations then show that there is an energy barrier associated with a domain wall having to cross a defect dipole in its path, which is the precise role of a pinning site.

The concept of stabilization time also is closely related to the presence of point defect dipoles in the crystal. At room temperature, the stabilization times for forward and reverse poling in congruent LiTaO$_3$ are $t_{\text{stab},f} = 1.4 - 2$ s and $t_{\text{stab},r} = 0.1 - 0.3$ s, respectively. On the other hand, the near-stoichiometric composition exhibits stabilization times of $t_{\text{stab},f} = 0.25 - 0.9$ s and $t_{\text{stab},r} = 0.015 - 0.1$ s. Both compositions show an order of magnitude difference between $t_{\text{stab},f}$ and $t_{\text{stab},r}$. In addition, the stabilization times for congruent compositions are an order of magnitude larger than that for stoichiometric crystals in both forward and reverse poling directions. In the following section we present a model where the origin of domain stabilization time is proposed to be directly related to the time taken for the slow reorientation of the electrical dipole moment associated with the movement of Ta$_{\text{Li}}$ defect ions through close packed oxygen planes. Longer stabilization times in congruent crystals suggest that this movement of the defect ion is slower in congruent crystals as compared to near-stoichiometric crystals. The difference in forward versus reverse stabilization time in each composition arises from the fact that the lithium vacancies $V_{\text{Li}}$ surrounding a Ta$_{\text{Li}}$ defect ion do not rearrange around the new Ta$_{\text{Li}}$ position after domain reversal at room temperature, thus creating a frustrated defect dipole. These are explained in greater detail in the following section.

Figure 12 shows the sideways wall velocity $v_{s,f}$ as a function of electric field $E - E_{c,f}$ for congruent LiTaO$_3$. The wall velocity of independently growing domains is an order of magnitude lower than merged, serrated domain fronts as reported earlier due to preferential nucleations at the serratons at the domain walls. We note that the behavior of switching time $t_{s,f}$ and sideways wall velocity $1/v_{s,f}$, as a function of electric field $E - E_{c,f}$, show similarities in both congruent and stoichiometric compositions. Both switching times $t_{s,f}$ and inverse sideways wall velocity $1/v_{s,f}$ show two electric field regimes where the activation fields $\delta_f$ and $\alpha_{s,f}$ change from one regime to another. These electric field regimes are similar, as are the activation fields $\delta_f$ and $\alpha_{s,f}$ for the switching times and the sideways wall velocities, respectively. In congruent composition, the high electric field regime is $E - E_{c,f} > 3.8$ kV/cm for switching time and $E - E_{c,f} > 4$ kV/cm for sideways wall velocity. The activation fields are $\delta_f \sim 51$ kV/cm and $\alpha_{s,f} \sim 43$ kV/cm in the high field regimes and $\delta_f \sim 1.5$ kV/cm and $\alpha_{s,f} \sim 0.5$ kV/cm in the low field regime. In the near-stoichiometric composition, the high electric field regime is $E - E_{c,f} > 14$ kV/cm for switching time and $E - E_{c,f} > 17$ kV/cm for sideways wall velocity. The activation field values are $\delta_f \sim 26$ kV/cm and $\alpha_{s,f} \sim 22$ kV/cm in the high field regime and $\delta_f \sim 5.4 - 6.8$ kV/cm and $\alpha_{s,f} \sim 6.8$ kV/cm in the low field regime. [The $\alpha_{s,f}$ in the low field regime is very approximate due to a large scatter in the velocity data in Fig. 9(c).] These comparisons show that while the actual magnitudes of the threshold coercive fields and wall velocities are very different in the congruent and the stoichiometric compositions, there are strong similarities. Above the threshold coercive field, the electric field shows at least two distinct ranges in both cases, which we denote as low and high electric field ranges. The domain wall pinning is dominant in the low field regime, and wall velocity is dominant in the high field regime in both compositions.

VI. DEFECT DIPOLES AND DOMAIN REVERSAL

In this section we present a defect model based on non-stoichiometric dipolar defects in LiTaO$_3$. This model is based on the basic concept of bulk dipolar defect complexes giving rise to domain stabilization and internal fields in ferroelectrics as has been detailed in the works of Arlt, Lambeck, and Warren. The model provides a qualitative explanation of the domain reversal processes such as the dependence of threshold coercive field on defect density and on repeated cycling at different frequencies, the phenomena of domain stabilization time, and that of domain “backswitching” in lithium niobate and tantalate.

A. Nonstoichiometric dipolar defects

A comparison of stoichiometric and congruent crystals makes it clear that nonstoichiometry in LiTaO$_3$ is intrinsically related to the domain wall structure and kinetics. The above discussion raises the question as to what the exact nature of nonstoichiometric point defects or defect complexes is. Below we will discuss defect models in isostructural congruent LiNbO$_3$ which has been more extensively studied. We will then draw a parallel between defect models in LiNbO$_3$ and LiTaO$_3$ based on the fact that they have the same lattice structure, threshold coercive fields, switching times, internal fields, domain wall contrast, and phenomena of domain wall pinning and stabilization, differing only in the magnitudes of these effects.

In congruent composition of LiNbO$_3$, Prokhorov and Kuzminov concluded that lithium vacancies ($V_{\text{Li}}$)$^+$ and oxygen vacancies ($V_{O}$)$^{2+}$ dominate at room temperature, corresponding to a congruent defect structure of [Li$_{0.94}$(O$_{2.97}$)$^{0.028}$][Nb$_2$O$_{9}$] which we refer to as model I.
However, the density of LiNbO₃ increases with increasing lithium deficiency which is incompatible with the oxygen vacancy model.²⁶ Schirmer et al. concluded that niobium antisites (NbₐLi)⁴⁺ and niobium vacancies (VₐNb)⁵⁻ 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.²⁰ The chemical formula for this defect model suggested by Abrahams and Marsh is [Li₉.₉₄Nb₀.ₐ₅Jₙ] ×[Nb₀.₉₅₂₆O₃₋₀.₀₄₇]O₅, to be referred to as model II. However, Donnerberg et al.²¹ showed that the formation of a niobium vacancy was found to be energetically unfavorable as compared to the formation of a lithium vacancy. The third proposed defect model (model III) is the presence of niobium antisites (NbₐLi)⁴⁺ and lithium vacancies (VₐLi)⁻.²² The neutron diffraction studies by Iyi et al.²³ and Zotov et al.²⁴ support this defect model with a chemical formula of [Li₉.₉₅O₃₋₀.₄₇Nb₀.₀₅]O₅. Schirmer et al.²⁵ point out that the niobium vacancy model and the lithium vacancy model can be reconciled if it is assumed that there are ilmenite type stacking faults in the regular LiNbO₃ crystal structure. However, a different suggestion has come from Ivanova and Yatsenko et al.²⁵,²⁶ who have recently interpreted the nuclear magnetic resonance (NMR) spectra in congruent LiNbO₃. They conclude that at room temperature, a combination of models I and III in a ratio of 1.1:1.0 would provide a “rather good qualitative and quantitative agreement with the NMR ⁷Li spectra.” However, the authors assert that only the model III (with allowance for mobility of Li⁺ ions in LiO₆ octahedra) can explain the temperature dependence of the experimental NMR ⁷Li and ⁵⁹Nb spectra from 77 to 4.2 K. Accordingly, the authors propose the structure of a defect complex as comprising of a niobium antisite surrounded by three Li⁺ vacancies in the nearest neighborhood, plus one independent Li⁺ vacancy along the polar z direction. Yatsenko²⁷ has also reported that the preliminary analysis of the structural distortions caused by a NbₐLi antisite defect reveals a contraction of the nearest three oxygen atoms, and a displacement from the c axis of the nearest three Nb⁹⁺ nuclei. This defect complex comprising of one NbₐLi with four VₐLi certainly possesses an electrical dipole moment, arising primarily along the z axis from antisite NbₐLi itself as well as from the relative arrangement of VₐLi around the antisite. This defect model is also supported by x-ray and neutron diffuse scattering of congruent LiNbO₃ reported by Zhdanov et al.²⁸ Ivanov et al.²⁹ and most recently by Zotov et al.³⁰ These studies conclude that the diffuse lines in scattering arise from a one-dimensional (1D) displacive and substitutional disorder in the three pseudo-cubic directions along the Li–O–Li· · · chains. These directions correspond to pseudo-cubic directions [24.1], [22.1], and [42.1] (in orthohexagonal notation) which are related to each other by the threefold symmetry axis (polarization c axis) and are inclined at 52° to the c axis. Diffuse maxima around the Bragg positions reflect some three-dimensional (3D) short-range order of the defect elements and the homogeneous part of the diffuse planes indicate random distribution of the defect clusters. Since each niobium antisite requires four lithium vacancies in the neighborhood for overall charge neutrality, Zotov et al.³⁰ suggest chains such as Li–NbₐLi–□–Li, Li–□–NbₐLi–□, Li–□–□–NbₐLi, etc. as possible combinations.

Figure 13 shows a possible schematic of the equilibrium states of a defect complex for an up and a down domain. Upon domain reversal, the niobium antisite defect moves to the neighboring octahedron by movement of NbₐLi through the close-packed oxygen plane. The lithium vacancies around the original defect in Fig. 13(a) need to rearrange around the new antisite position to reach the stable defect equilibrium state of Fig. 13(c). At room temperature, a lack of lithium mobility can result in the frustrated state of defect complex as shown in Fig. 13(b), which can be relieved into state (c) after a high temperature anneal. However, as pointed out by Nassau and Lines,³¹ the presence of two niobium ions in adjacent oxygen octahedra can be energetically unfavorable due to dense positive charge around the cluster. They propose extended stacking fault defects in the structure. Zotov et al.³² however, restrict the size of such clusters to ~11.4 Å (about four cation sites) in order to match the correlation length L₅ ~ 13 Å along the chains calculated from the full width at half maximum of the diffuse streaks in x ray.
The average spacing between defect clusters along the chains is estimated to be ~76 Å. The temperature dependence of diffuse x-ray streaks\textsuperscript{30} suggest that at low temperatures, the lateral correlations between defect clusters become quite substantial. With increasing temperature, these correlations decrease, resulting in more random 1D disorder. The changes in the threshold coercive and internal fields with temperature as reported by Battle \textit{et al.}\textsuperscript{32} also point to the breaking up of the 3D clusters with heating followed by reformation of the defect dipole in an energetically favorable orientation upon cooling down to room temperature.

\section*{B. Backswitching and internal fields}

Following the approach and interpretation of Arlt and Neumann in Ref. 15 we propose a qualitative defect model for explaining internal fields and stabilization times in LiTaO\textsubscript{3} and LiNbO\textsubscript{3}. Drawing an analogy between LiNbO\textsubscript{3} and LiTaO\textsubscript{3} we will assume a simple defect model primarily based on a tantalum antisite defect and lithium vacancies in lithium tantalate as depicted in Fig. 13. With this physical basis we will now proceed to build a model for domain reversal in LiTaO\textsubscript{3}.

The process of domain reversal in LiTaO\textsubscript{3} involves movement of lithium atoms, Li\textsubscript{Li}, through the adjacent close-packed oxygen planes into the neighboring vacant oxygen octahedra. This is accompanied by a simultaneous motion of the tantalum atom, Ta\textsubscript{Ta}, from its acentric location within its octahedra. This is accompanied by a simultaneous motion of packed oxygen planes into the neighboring vacant octahedra. This is accompanied by a simultaneous motion of packed oxygen planes into the neighboring vacant octahedra.

At room temperature, the lithium vacancies around a tantalum antisite defect Ta\textsubscript{Li} has moved into the adjoining octahedron under electric field induced domain reversal. This configuration has higher energy, which can be only lowered by rearrangement of lithium vacancies in a new configuration, achieved by heating and cooling, for example, which yields the final stable configuration of Fig. 13(c).

The defect complex in Fig. 13 is assumed to comprise of a dipole moment, which has two contributions. These are (a) the contribution to the electrical dipole arising only from the Ta\textsubscript{Li} antisite defect, and (b) the contribution to the electrical dipole arising from the relative arrangement of the lithium vacancies V\textsubscript{Li} around a tantalum antisite defect Ta\textsubscript{Li}. Upon domain reversal at room temperature, the electric field can move the Ta\textsubscript{Li} antisite defect through the neighboring oxygen triangle and therefore reverse the component (a) of the electrical dipole moment associated with only Ta\textsubscript{Li}. However, the component (b) of the electrical dipole moment associated with the arrangement lithium vacancies is not reversed by the electric field. This results in the frustrated domain state shown in Fig. 13(b). This requires thermal activation at >150 °C for a few minutes followed by cooling to rearrange lithium vacancies to achieve the low energy domain state shown in Fig. 13(c).

Figures 14(a)–14(e) show a schematic of the potential energy diagram at room temperature for the forward switching process at various instants of time \( t \) on application of a voltage pulse of width \( t_{p,r} \). The energy diagram represents the electrostatic energy of the lattice polarization, modified by the interaction energy resulting from the interaction between defect polarization and bulk lattice polarization, and due to external field contributions to the total lattice energy. For a first order ferroelectric phase transition, the difference

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{fig14.png}
  \caption{A schematic describing the process of forward domain reversal and domain backswitching in the presence of dipolar defects shown in Fig. 13. Each of the five schematics (a)–(e) shows the voltage pulse \( V \) and the transient current \( i \) (top), followed by the corresponding potential energy well (below) for the lattice polarization in the presence of defects at the time instant \( t \) denoted by a gray circle in the voltage pulse schematic. The notations are lattice polarization \( P_i \) (denoted by \( \uparrow \) or \( \downarrow \)), defect dipole associated with Ta\textsubscript{Li} antisite defect (denoted by \( \prec \) or \( \succ \)), defect dipole associated with the arrangement of V\textsubscript{Li} (denoted by \( \bullet \) or \( \circ \)), the time gap \( t_{p,r} \) that domain spends in the \(-P_i\) state before being forward poled to the \(+P_i\) state, and stabilization time \( t_{stab} \).}
\end{figure}
between the free energy \( G \) per unit volume in a ferroelectric state and that in the paraelectric state \( G_o \) can written as\(^{15}\)

\[
G - G_o \mid _{P_s} = -\frac{A}{2} P^2 + \frac{B}{4} P^4 - E_D(t)P - EP,
\]

where \( P \) is the lattice polarization, \( A \) and \( B \) are positive physical constants, \( E_D(t) \) is the effective time dependent defect field, and \( E \) is the external field applied. Note that the above equation is applicable near the \( \pm P_s \) states only. Here \( P_s \) indicates spontaneous lattice polarization at the minimum energy state. Before any external field is applied \([E=0 \text{ at } t=0; \text{ see Fig. 14(a)}] \), the \( -P_s \) lattice polarization state (indicated by \( \downarrow \)) is stabilized by the defect polarization by an amount of \( \Delta w^- \) per defect dipole, with respect to the \( +P_s \) state. If all the defect dipoles are aligned parallel to the \( -P_s \) direction in Fig. 14(a), then the magnitude of the defect field \( E_D \) at time \( t=0 \) is given by\(^{15}\)

\[
E_D(0) = \frac{N\Delta w^-}{2P_s},
\]

where \( N \) is total number of defect dipoles per unit volume. As Arlt and Neumann point out,\(^{15}\) this effective defect field is not an existing electric field in the material. Rather, it is a formal equivalent to the energetic difference between the two polarizing states.

The defect that stabilizes the \( -P_s \) polarization is thought of as being comprised of two components: one arising from \( \text{TaLi} \) (indicated by \( \downarrow \)) and the other arising from the relative arrangement of lithium vacancies around the antisite defect (indicated by \( \uparrow \)).

The application of an external electric field, \( +E \), decreases the energy of the \( +P_s \) state by \( -EP \) and increases the energy of the \( -P_s \) state by a corresponding amount. This results in the reversal of the lattice domain state from \( -P_s(\downarrow) \) to \( +P_s(\uparrow) \) state as shown in Fig. 14(b). However, at a time instant \( t=t_{stabh,f} \), the defect polarizations \( \downarrow \) and \( \uparrow \) have not reversed from their original state in Fig. 14(a).

We now consider three cases.

(i) When the applied voltage pulse width \( t_{g,r} \) is less than the stabilization time \( t_{stabh,f} \). At the end of the pulse (time instant \( t=t_{g,r}<t_{stabh,f} \)), domain backswitching occurs as shown in Fig. 14(c). This is directly due to the fact that the external field related energy contribution \( E\cdot P \rightarrow 0 \) on removal of the voltage pulse, and the system returns to the \( -P_s \) state, stabilized by defect polarization.

(ii) When the applied voltage pulse width, \( t_{g,r} \), is just equal to or greater than \( t_{stabh,f} \) (Fig. 14[d]), no backswitching occurs. In this case the defect polarization component \( \downarrow \) reverses to the \( \downarrow \) state, corresponding to a movement of \( \text{TaLi} \) through close-packed oxygen planes. Referring to Table I, the time constant for the realignment of defect polarization relating to \( \text{TaLi} \) movement is proposed to be of the order of \( \tau_{1,f}\sim 20.3 \text{ s} \) for congruent and \( 26.4 \text{ s} \) for near-stoichiometric \( \text{LiTaO}_3 \) during forward poling. The stabilization time \( t_{stabh,r} \) in this interpretation would approximately correspond to the time taken for the \( \text{TaLi} \) atoms to cross the close-packed oxygen plane. The new defect polarization component stabilizes the polarization state \( +P_s(\uparrow) \), thus preventing the back-switching. Note, however, that the defect polarization component \( \uparrow \) still does not reverse due to the lack of rearrangement of \( \text{V}_L \) around the new \( \text{TaLi} \) position at room temperature.

(iii) When the applied voltage pulse width \( t_{g,j} \gg t_{stabh,f} \) (Fig. 14[e]), no backswitching occurs as in case (ii). In addition, a slow time-dependent relaxation of the lattice polarization takes place in the presence of a frustrated defect dipole (a combination of \( \downarrow \) and \( \uparrow \) in Fig. 14), in reaching a final equilibrium state as shown in Fig. 14(e). Referring to Table I, the time constant for this slow relaxation is attributed to \( \tau_{2,f}\sim 399.6 \text{ s} \) (congruent) and \( 177.5 \text{ s} \) (near-stoichiometric) time constants observed from Eq. (1). The final effective defect field \( E_D \) in Fig. 14(e) is given by

\[
E_D(t\gg t_{stabh,r}) = \frac{N\Delta w^+}{2P_s}.
\]

Note that the effective defect fields \( E_D \) in Eqs. (7) and (8) are not equal, a direct consequence of the frustrated defect dipole component \( \uparrow \) related to lithium vacancies in Fig. 14(e).

The threshold coercive field \( E_c \) can be written as \( E_c(t) = E_D(t) + E_{intrin}(t) \), where \( E_{intrin} \) is the intrinsic threshold coercive field of exactly stoichiometric \( \text{LiTaO}_3 \) with no defects present. This immediately suggests many qualitative features of domain reversal. First, changes in the threshold coercive field with time (see, for example, Figs. 4 and 10) are directly related, in part, to the time dependent changes in the effective defect field \( E_D \) arising from the reorientation of the defect dipole denoted by \( \downarrow \) in Fig. 14. Second, since the magnitude of the effective defect field \( E_D \) is directly proportional to the density of defects \( N \) [Eqs. (7) and (8)], the threshold coercive field \( E_c \) is directly proportional to defect density \( N \). This has indeed been confirmed in \( \text{LiNbO}_3 \) where the threshold coercive field varies linearly with the ratio \( \text{Li}/(\text{Li+Nb}) \) between congruent and stoichiometric compositions.\(^5\) Third, the internal field, \( E_{int} \), given by the offset in the hysteresis loop along the field axis arises directly from the difference in the defect fields \( E_D \) between times \( t=0 \) [Eq. (7)] and \( t\gg t_{stabh,f} \) (Eq. 8). Assuming that magnitude of the intrinsic threshold coercive field, \( E_{intrin} \), does not change between domain state in Figs. 14(a) and 14(e), we can write the internal field\(^{4-6} \) \( E_{int}[=\{E_D(t=0) - E_D(t\gg t_{stabh,f})]/2 \) for slow polarization cycling \( t_{g,j} \gg t_{stabh,f} \) as

\[
E_{int} = \frac{N(\Delta w^- - \Delta w^+)}{4P_s}.
\]

Again, the internal field clearly depends linearly on the density of defect dipoles as is also experimentally observed.\(^6\)

As mentioned before, it must be emphasized that the defect and internal electric fields discussed above are not to be thought of actual electric fields, but as energy equivalents to the differences in the energy levels between different states. These energy differences can include not only electrostatic energy differences but elastic energy differences as well due to lattice distortions. The electrical dipoles associated with defect complexes can therefore also have elastic dipole components.\(^{15}\)
VII. CONCLUSIONS AND SUMMARY

The central message of this article is that the presence of nonstoichiometry in ferroelectric LiTaO₃ gives rise to large changes in the polarization reversal properties of this material. In particular we have presented real-time studies of domain motion in near-stoichiometric composition \( C = \text{Li}/(\text{Li}+\text{Ta}) \approx 0.4977–0.4992 \) crystals. We have directly imaged and tracked the domain backswitching process in lithium tantalate. We have systematically investigated polarization hysteresis loops, threshold coercive fields, stabilization times, switching times, and wall velocities of these crystals at room temperature. These results are then compared and contrasted with those for congruent compositions \( C = 0.485 \).

The threshold coercive field for domain reversal and domain stabilization time increases by an order of magnitude with increasing lithium deficiency from near-stoichiometric to congruent compositions. The presence of lithium nonstoichiometry also introduces internal fields, which increase with increasing lithium deficiency. The sideways domain wall velocities are two orders of magnitude higher in nearstoichiometric crystals as compared to congruent crystals. There are similarities between the dependence of switching times and wall velocities with electric field in both nearstoichiometric and congruent compositions as discussed in Sec. V. In both compositions the domain wall motion is dominated by wall pinning at electric fields close to threshold coercive fields, and by wall velocity in the high field regime.

We propose a physical defect dipole composed of lithium vacancies and tantalum antisites. Based on the concept of domain stabilization by bulk dipolar defects, this model qualitatively predicts many of the observed features of domain reversal such as the dependence of threshold coercive field on defect density and on time spent in a domain state after its creation, the phenomenon of domain stabilization time, domain backswitching, and internal fields. The experiments and modeling results in this article can be applied to lithium niobate (LiNbO₃) as well, which shows very similar domain reversal properties.⁶

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