The role of nonstoichiometry in 180° domain switching of LiNbO₃ crystals

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We show here conclusively that the internal field originates from nonstoichiometric point defects in LiNbO₃ crystals. The switching fields required for 180° domain reversal in congruent crystals \[ C = \frac{\text{Li}_2\text{O}}{(\text{Li}_2\text{O} + \text{Nb}_2\text{O}_5)} = 0.484 \] are ~4–5 times larger than the switching fields for near-stoichiometric crystals \( C = 0.498 \). An internal field of ~2.5 kV/mm observed in congruent crystals disappears in stoichiometric crystals. The concentration of hydrogen incorporated during crystal growth has no effect on the switching or internal fields. The measured spontaneous polarization, \( P_s = 80 \pm 5 \mu \text{C/cm}^2 \) is relatively insensitive to the crystal nonstoichiometry and the hydrogen content. © 1998 American Institute of Physics. [S0003-6951(98)02416-4]

Ferroelectric lithium niobate (LiNbO₃) and lithium tantalate (LiTaO₃) have emerged as important materials in surface acoustic wave (SAW) devices and in nonlinear optical applications such as electro-optics and second-harmonic generation. A critical step in realizing many of these devices is the ability to microengineer 180° domains. Hence, understanding switching kinetics of 180° domains in these crystals is important.

Most of the reported switching kinetics in these crystals has been for the congruent composition \( C = 0.486 \), since it is easy to grow and is available as commercially as high quality wafers. The switching field for virgin crystals of Z-cut single crystal, single domain LiNbO₃ and LiTaO₃ is found to be ~21 kV/mm for both materials. Large internal fields of ~4–5 kV/mm in Z-cut LiTaO₃ and ~2–3 kV/mm in Z-cut LiNbO₃ have been reported. This internal field creates a large asymmetry in the hysteresis loop along the field axis. In a virgin crystal, it points along the original polarization direction. When the polarization direction is reversed by an external field, the internal field tends to realign parallel to the new polarization direction with time and temperature. At room temperature, the process is incomplete even after a month, while it takes less than 30 s for ~95% realignment above 200 °C.

It was postulated earlier that the origin of the internal field lies in point-defect complexes involving nonstoichiometric defects and/or hydrogen in the LiNbO₃ and LiTaO₃ crystals. We show here conclusively that the internal field originates from nonstoichiometric point defects in LiNbO₃ crystals and is independent of the concentration of hydrogen incorporated during crystal growth. The switching fields are also strongly dependent on the nonstoichiometry and suggest that the best control of selective domain switching can be achieved by chemically patterning the stoichiometry of the crystal.

In this study, LiNbO₃ single crystals were grown under nonstoichiometry control by the double crucible CZ method. Details on the crystal growth of stoichiometric LiNbO₃ are described elsewhere. The LiNbO₃ crystals were grown along the c axis at the pulling rate of 0.5 mm/h. The starting materials were high purity Li₂CO₃ (>99.99%) and Nb₂O₅ (>99.999%) powders. Growth was accomplished in an oven and nitrogen gas mixture flow with a volume ratio of oxygen to nitrogen of 5:100.

Three different stoichiometries were grown for this study, namely, the near-stoichiometric (denoted SLN), the congruent (denoted CLN), and the intermediate composition (denoted HLN), exhibiting Curie temperatures, \( T_c \), of 1200, 1139, and 1187 °C, respectively, as measured by differential thermal analysis (DTA). The nonstoichiometry, \( C(\%) = \frac{[\text{Li}_2\text{O}][(\text{Li}_2\text{O}) + [\text{Nb}_2\text{O}_5]]}{[\text{Li}_2\text{O}]} \), of LiNbO₃ was estimated from the Curie temperature using the equation proposed by O‘Bryan et al. as

\[
T_c = 9095.2 - 369.05C + 4.228C^2. \tag{1}
\]

The Curie temperatures of SLN, HLN, and CLN correspond to \( C = 49.8\%, 49.5\%, \) and 48.4%, respectively.

Z-cut plates, 10×10×0.27 (or 0.51) mm in size, were cut from the as-grown crystals (the polarization, \( P_s \), normal to the plate surface). For each stoichiometry, the hydrogen content in the crystal was varied by annealing at 1000 °C for 24 h with a gas flow of dry oxygen (resulting in low hydrogen content) or humid oxygen (resulting in high hydrogen content). To obtain a qualitative measure of the OH⁻ content, the infrared transmission spectrum was measured by a Hitachi U3200 spectrophotometer over a wavelength range of 2700–2900 nm, at a scanning rate of 120 nm/min. This is shown in Fig. 1. The sample notation is as follows: SLND is a stoichiometric crystal annealed in dry oxygen and SLNW is a stoichiometric crystal annealed in humid or wet oxygen. The suffix notation is similar for HLN and CLN crystals.

The as-grown SLN and HLN crystals were automatically single domain. However, the as-grown CLN crystals were poled into single domain configuration at ~1100 °C after growth. The starting crystals for switching experiments were thus single crystal, single domain Z-cut LiNbO₃. The 180° domain switching experiments were done at room temperature by applying a dc electric field across the crystal thickness using liquid electrodes (saturated KNO₃ solution in

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The voltage was ramped at 15 V/s. The switching field was determined by measuring the width of the transient current peak during domain reversal. This was taken as the voltage range where current spikes greater than the 0.01 μA (which is the measurement sensitivity of our setup) were observed. The infrared transmission spectra of the OH\(^-\) ions were measured again in dry samples after performing the switching experiments. The spectra were the same as at the start, thus making sure that the hydrogen content had not changed during the application of an electric field with water based electrodes. The starting crystals will be called the virgin crystals. The first domain reversal of the virgin crystals will be called forward poling and the second reversal back to its original state will be called reverse poling. The switching fields for forward and reverse poling will be denoted \(E_f\) and \(E_r\), respectively.

Figure 2 shows the switching and internal fields for the three stoichiometries with low hydrogen content (SLND, HLN, and CLND) as a function of Curie temperature, \(T_c\). For clarity, Fig. 3 separately shows the switching and internal fields for the three stoichiometries for crystals with high concentration of hydrogen (SLNW, HLNW, and CLNW). The top axis is the composition, \(C\), calculated from the approximate expression \(C(%) = 17.37 + 0.02725 T_c\) (°C) given in Ref. 10. The following important observations can be made: (1) Both \(E_f\) and \(E_r\) decrease linearly with increasing Curie temperature. The forward and reverse poling fields for congruent crystals are five times and four times higher than the respective fields for stoichiometric crystals. (2) The asymmetry between the forward and reverse poling fields indicates the presence of internal fields, \(E_{int}\), calculated as \(E_{int} = (E_f - E_r)/2\). The internal field also decreases linearly with increasing Curie temperature as shown in Figs. 2 and 3. (3) Within error bars, the results are the same for both low and high hydrogen concentration in crystals. Thus switching and internal fields are independent of the hydrogen content. (4) Multiple measurements for the same stoichiometry in both Figs. 2 and 3 represent data from two different crystal thicknesses: 270 and 510 μm. The switching and internal fields are thus independent of crystal thickness.

Combining the results of both Figs. 2 and 3, we can write the following relations for the switching and internal fields (in kV/mm) at room temperature as a function of Curie temperature (in °C) in LiNbO\(_3\) crystals:

\[
E_f = 335.9(\pm 45.7) - 0.277(\pm 0.039)T_c, \tag{2}
\]

\[
E_r = 249.0(\pm 46.6) - 0.204(\pm 0.040)T_c, \tag{3}
\]

\[
E_{int} = 42.3(\pm 25.9) - 0.035(\pm 0.022)T_c. \tag{4}
\]

Using Eq. (1) with Eqs. (2), (3) and (4), one can obtain the switching and internal fields as a function of nonstoichiometry, \(C\). We note that these equations are valid for only the first cycle of domain reversal in a virgin LiNbO\(_3\) crystal. The effect of changes in switching and internal fields with multiple cycling is not included in this study.
The spontaneous polarization, \( P_s \), as a function of crystal stoichiometry and hydrogen content is shown in Fig. 4. It is important to note that the measurement of \( P_s \) needs care in LiNbO\(_3\) crystals. The transient current during switching is in the form of discrete and very sharp (\(< 1\) ms) spikes spread over 50–100 ms depending on the applied field. Thus, depending on the sampling rate of data collection, one may completely miss many current spikes or the peak of a spike. This would, upon integration, give a lower estimate of \( P_s \), ranging anywhere from 50m to 70 \( \mu \)C/cm\(^2\). In order to avoid this artifact, we built an analog integration circuit using a capacitor in series with the sample, thus collecting all the current pulses. Upon domain switching, the final voltage across the capacitor gives the total charge \( Q \), and spontaneous polarization, \( P_s = Q/(2A) \), where \( A \) is the electrode area. A high input impedance (1 G\( \Omega \)) multimeter was used to read the capacitor voltage to avoid any charge leakage. The electrode area, \( A \), was measured carefully from the images of the switched region under a polarized light microscope.\(^7\) Within the error bar of our measurements, \( P_s = 80 \pm 5 \mu \)C/cm\(^2\) and is relatively insensitive to the stoichiometry or the hydrogen content of the crystal.

It was postulated earlier that the origin of internal field lay possibly in a combination of nonstoichiometric point defects and/or hydrogen in these crystals.\(^7\) From the results presented here, it is clear that the origin of the internal field is the nonstoichiometry of the [Li]/[Li+NB] ratio in LiNbO\(_3\) crystals. Since the switching and internal field characteristics for LiTaO\(_3\) are similar to LiNbO\(_3\) crystals,\(^5\) we expect a similar effect of nonstoichiometry on switching fields in LiTaO\(_3\) crystals.

The most plausible physical picture of the origin of internal fields is the presence of point-defect complexes at room temperature arising from nonstoichiometry. There are currently two point-defect models for LiNbO\(_3\): (1) Lithium vacancy model:\(^1\)\(^2\) \( V_{Li} \)\(^{2+}\) and \( (Nb_{Li}L_{Li})^{4+}\); (2) Niobium vacancy model:\(^3\)\(^4\) \( V_{Nb} \)\(^{3+}\) and \( (Nb_{Li}L_{Li})^{4+}\). While evidence for the lithium vacancy model has recently been gaining ground,\(^1^4\) the issue is yet to be completely resolved. One suggestion is that the presence of ilmenitelike defect stacking in an otherwise regular LiNbO\(_3\) structure would render the two models equivalent.\(^1^5\) However, experimental evidence for this suggestion is still pending.

The hydrogen, on the other hand, does not play any active role in determining the switching or internal fields. A strong correlation between the time-temperature behavior of internal fields and the absorption spectrum of \( \text{OH}^- \) ions in both LiNbO\(_3\) and LiTaO\(_3\) crystals was reported earlier.\(^7\) This could be explained if we assume that at least a fraction of the hydrogen is preferentially associated with the nonstoichiometric point defects. The \( \text{OH}^- \) spectrum in LiNbO\(_3\) is composed of at least three distinct bands,\(^6\) centered around 3467.5, 3478.5, and 3489 cm\(^{-1}\) wave numbers, where the two bands at higher wave numbers are associated with nonstoichiometry in the crystal, since they disappear in a stoichiometric crystal. The domain reversal process would, in principle, change the nature of point defects due to nonstoichiometry,\(^6\) and hence correspondingly change the \( \text{OH}^- \) spectra.

A plausible reason for the drastic increase in the switching fields with nonstoichiometry may be as follows. Upon 180° domain reversal in LiNbO\(_3\), the Li ion has to move into the neighboring vacant oxygen octahedra by passing through the close packed oxygen plane. With a niobium antisite defect such as Nb\(_{Li}\), the Nb will have to pass through the oxygen plane, which may be more difficult.

In summary, it is shown that the origin of internal fields in LiNbO\(_3\) crystals lies in nonstoichiometry of the [Li]/[Li+NB] ratio. The magnitude of switching fields in stoichiometric composition are lowered by 4–5 times from that for congruent composition. Hydrogen incorporated during crystal growth plays no active role in the switching or internal fields in LiNbO\(_3\) crystals.

\(^{1}\) V. V. Lemonov and Yu. V. Lislavsky, Ferroelectrics 47, 77 (1982).