Appendix: E

Reprints of some publications
Dependence of effective internal field of congruent lithium niobate on its domain configuration and stability

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Congruent lithium niobate is characterized by its internal field, which arises due to defect clusters within the crystal. Here, it is shown experimentally that this internal field is a function of the molecular configuration in a particular domain and also on the stability of that particular configuration. The measurements of internal field are done using interferometric technique, while the variation of domain configuration is brought about by room temperature high voltage electric field poling. © 2014 AIP Publishing LLC.

I. INTRODUCTION

For the last few decades, Lithium Niobate (LiNbO3) is one of the most important ferroelectrics in optoelectronics and nonlinear optics. Its properties are of vast significance to fundamental and applied optics research and are employed in several acousto-optic, electro-optic, and nonlinear optical devices such as modulators of light, beam deflector, optical frequency converters, tunable sources of coherent light, etc.1–4 While devices fabricated on stoichiometric or near-stoichiometric crystals are less prone to photorefractive damage5,6 but production of such crystals requires expensive procedures and precise control over mass production, bringing up the crystal price.7–10 So, most of the devices are made on congruent LiNbO3.

LiNbO3 crystal is characterized by its Curie temperature, which indeed reflects the congruency of the molecular organization in the crystal.11 Also asymmetry in hysteresis loop measured during forward and backward poling gives an estimation of the internal structure of the crystal. It is well known that this asymmetry in hysteresis loop is due to the existence of internal field in the ferroelectric crystal. So, a proper analysis of the asymmetry of the hysteresis loop would result in the measurement of internal field of the crystal.12,13 The presence of internal field in LiNbO3 is due to co-existence of spontaneous polarization due to inherent shifted positions of Nb5+ and Li+ ions and defect state polarization, which is due to presence of defect clusters Li+ ion vacancies and Nb-antisites.14

The strength of internal field has been studied by successive forward and reverse poling of the crystal.12,13 For inspection of the internal field in a patterned domain LiNbO3, this technique may destroy the structure. Also, the thin wafers are susceptible to damage due to high electric field. Consequently, interferometric techniques, which are non-destructive techniques, have been developed for quantitative measurement of internal field in ferroelectric crystals.15–18

The authors have also proposed19 an interferometric technique to measure internal field, which have several advantages over the methods used in Refs. 15–18.

In this work, quantitative assessment of the dependence of internal field on domain configuration and stability has been studied. For that, the internal fields in single domain LiNbO3, domain inverted LiNbO3 and unstable domain inverted or the so called frustrated domain inverted LiNbO3 crystals are measured using interferometric technique and compared. It is seen that the magnitude of internal field (IF) of single domain and domain inverted LiNbO3 are the same. Only their directions are reversed as the axes are opposite for the two cases. But in frustrated domain inverted LiNbO3, the effective internal field is considerable different. Moreover, its value also varies with time as this frustrated state is unstable, bouncing back to its initial as-bought single domain state after some time. Possible reasons for the observations are explained using the defect model.

II. MEASUREMENT SETUP AND TECHNIQUE USED

The measurement of internal field is done using the Mach-Zehnder Interferometric (MZI) setup, which is schematically shown in Fig. 1. The probe beam is obtained from a He-Ne laser source having wavelength of 632.8 nm. A beam splitter is used to split the probe beam along two mutually perpendicular paths. Two mirrors are used to

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FIG. 1. Setup for the measurement of internal field in LiNbO3 crystals.
deflect these beams and combine on a second beam splitter. A fringe pattern is, thus, produced. A microscope objective is placed along the path of output beam from the last beam splitter to magnify the output fringe pattern and, then, the resulting fringe pattern is recorded with the help of a CCD camera. The test sample, which is coated with a semitransparent aluminum (Al) coating on both faces with provision to apply high voltages across it, is placed in one arm. A similar type of sample, but without the provision for applying high voltage, is used as a reference and is kept in the reference arm of the interferometer. The aim of using reference sample is to minimize any natural or atmospheric influence that may alter crystal parameters affecting output fringe pattern. Moreover, it is used to match the intensities of test beam and reference beam. Positioning of the samples in the respective arms is critical and care should be taken such that the crystallographic c-axes of the samples coincide with the direction of probe beams to minimize the complexity of the analysis. Otherwise, the probe beam will have two sets of polarization and its effect should be considered. Photorefractive damage of the crystal does not arise as the laser beam intensity is quite low and is further lowered due to splitting of source beam by first beam splitter and subsequent reduction by the semitransparent Al-coatings on the sample surfaces. Moreover, as mentioned in Ref. 20, the absorption of He-Ne laser source at 632.8 nm is low, thus, reducing both photorefractive and photovoltaic effect. Also, Al-coating being thermally conducting, laser heating of sample surfaces is reduced; so Al-coatings can act as heat sinks here and pyroelectric effect can be avoided. The output of the interferometer is a fringe pattern, which is a function of applied voltage across the test sample. In this regard, it should be noted that no voltage should be applied across the reference sample. So any variation in the output fringe pattern is only due to the electro-optic response of the test sample.

Determination of internal field is based on the measurement of the fringe shift due to the applied field on the test sample. Due to electro-optic property of the crystal, the applied field causes a change in refractive index of the crystal (Δn), which causes a phase shift (ΔΦ) between the two interfering beams resulting in the fringe pattern. The applied field for the fringe shift due to halfwave (or 180°) phase change is called halfwave field (E_half) and can be represented as:

$$E_{\text{half}} = \frac{\lambda}{r_{13}n_o d},$$

where λ is the free space wavelength of the probe beam, d is the crystal width, r_13 and n_o are the respective electro-optic coefficients and ordinary refractive index of LiNbO_3 at that wavelength. Now, if E_{DA} and E_{DA}' are the applied field in the forward and reverse directions, respectively, for a phase change ΔΦ of the fringe pattern, the internal field (E_{int}) will be:

$$E_{\text{int}} = 2 \frac{(E_{DA} - E_{DA}')}{(ΔΦ/\pi)},$$

where z is a constant having value equal to the thickness (in mm unit). Although LiNbO_3 is also a piezo-electric material, as explained in Ref. 19, this property will not affect the internal field here.

### III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The experiments were performed on square shaped samples (10.0 x 10.0 mm², which are obtained by slicing them from circular (3 in. diameter), z-cut single domain LiNbO_3 crystal wafers of thickness of either 0.5 mm or 1.0 mm. The electric field is applied along the crystallographic c-axis, where the velocity of ordinary ray and that of extraordinary ray matches, so n_o = n_c = 2.28, while the corresponding electro-optic coefficient will be r_13, whose value is considered as 10 x 10^{-12} m/V. 17 Semi-transparent aluminum electrodes of rectangular shape are defined on the central portion of both the surfaces of the samples by proper masking so that they cover 50% of the sample surface. The experiment consists of measurement of electric field corresponding to halfwave phase change in both forward and reverse directions of different samples.

Initially, the test is done using as-bought single domain LiNbO_3 samples of thickness 0.5 mm. Before making any experiment using as-bought samples, they are annealed at a temperature of 200°C for about 30 min and, subsequently, cooled down to room temperature. To apply electric field along the z-axis (which is also the optic axis) of the crystal, the electrode designed at +z surface of the test sample is connected with the positive terminal of the high voltage source and the electrode designed at the −z surface of the same is connected with the negative terminal of the source. Halfwave field (E_z) is measured to be 11.0 ± 0.1 KV/mm, in this case. The fringe pattern for zero applied field is shown in Fig. 2(a), while for halfwave field (E_z), it is shown in Fig. 2(b). On comparing the two fringe patterns, a 180° phase shift corresponding to halfwave field can be clearly observed. After this measurement, the test sample is kept idle for about 1 h with its electrodes shorted and grounded, such that the sample is allowed to relax back to its initial

![FIG. 2. A typical observed fringe pattern obtained from the MZI setup for (a) zero applied field and (b) applied field for half wave phase shift. Similar fringe pattern can be obtained for different types of LiNbO_3 crystals.](image-url)
condition and any accumulation of charge in the sample may drain out. Again, the test sample is annealed at a temperature of 200 °C for about 30 min and, consequently, brought down to room temperature. Next, the polarities of the electrical connections to the test samples are interchanged so that half-wave field \( (E'_p, E'_p) \) along reverse \( z \)-direction can be determined and the value is measured to be \( 6.0 \pm 0.1 \text{ KV/mm} \). Similar shift of fringe pattern as that in Fig. 2 is observed here also. The above steps are followed again for samples of thickness 1.0 mm and nearly repeatable results are obtained.

In an attempt to test the effect of domain inversion and domain stability on internal field, the test samples, which are initially single domain, are domain inversed using room temperature high voltage electric field poling. Room temperature domain inversion generally produces complete and permanent domain inverted crystal, if the poling is done over whole surface of the sample.\(^{22}\) But stability of domain inverted structure depends on the presence of anti-parallel domains in its vicinity if poling is done over some limited region of the sample, which is the case for the sample used here. In that case, permanent inverted domains can only be obtained by thermal annealing of the poled crystal at about 200 °C for 30 min. Otherwise, the inverted domain would be unstable and return back to the initial as-bought single domain condition. As already mentioned, this is the so called frustrated domain inverted state of LiNbO\(_3\).

Stable or permanent domain inverted sample so obtained is, then, placed in the test arm of the MZI setup and its corresponding halfwave field values \( (E_p, E_p) \) are noted by observing and comparing output fringe patterns due to applied electric fields across it. Results of particular interest are the halfwave field values \( (E_p, E'_p) \) obtained for unstable (frustrated) domain inverted samples. The phase shift due to gradual increment of applied electric field in forward as well as reverse direction for single domain, permanent domain inverted, and unstable domain inverted LiNbO\(_3\) crystals is shown in Fig. 3. As the increment of phase with applied electric field along forward direction is considered positive, the increment of phase in the reverse direction is to be considered as negative. So, both positive and negative values of phases with change of magnitude of electric field are plotted in this figure.

The set-up for high voltage electric field poling, which is utilized for the production of permanent and frustrated domain inverted LiNbO\(_3\), is shown in Fig. 4. As high fields of the order of 22 KV/mm (greater than the coercive field, i.e., 21 KV/mm in case of LiNbO\(_3\)) is to be applied across the samples, they are kept insulated inside a rubber jacket so that unwanted air breakdown around the samples may be avoided to protect them from cracking down. The current meter is used here mainly to indicate the completeness of domain inversion of the test sample. After setting up the circuit shown in Fig. 4, the high voltage source is switched ON and the output voltage level is gradually increased. There will be practically no current detected by the current meter until the voltage level is greater than 10.5 KV (approximately) for samples of thickness 0.5 mm. But, at or beyond that value of applied voltage, there will be a displacement current, which can be detected by the current meter. After completion of domain inversion, the displacement current turns out to be zero again.

As given in Sec. II, the values of internal field for as-bought, stable domain inverted, and frustrated domain inverted LiNbO\(_3\) crystals are calculated using Eq. (2), from the corresponding halfwave field values. Internal fields obtained in the three cases for 0.5 mm thick LiNbO\(_3\) crystal are tabulated in Table I. It is noteworthy that in the case of frustrated domain inverted sample, the timings of measurement of halfwave fields play an important role. If immediately after domain inversion, the sample is placed in the MZI setup and the halfwave fields are measured, the magnitude of IF so achieved is much lower than that obtained for stable domain inverted sample. On the other hand, if frustrated domain inverted sample is tested in the same MZI setup after a long time interval (say about 24 h), after domain inversion it is observed that its IF comes out to be as that obtained for as-bought single domain samples.

From Table I, it is seen that the magnitude of the effective internal field in complete domain inverted crystal is approximately same as that of the as-bought single domain crystal. But, as complete domain inversion reorients the molecular configuration in the opposite direction, the sign of the internal field gets reversed. On the other hand for frustrated domain inverted sample, the magnitude of effective internal

**FIG. 3.** Phase variation with the applied field for as-bought LiNbO\(_3\) crystal (green line), stable domain inverted LiNbO\(_3\) crystal (red line), and frustrated domain inverted LiNbO\(_3\) crystal (blue line).

**FIG. 4.** High voltage electric field poling setup.
field is reduced significantly. These observed phenomena can be understood with the help of a defect cluster model suggested by Gopalan et al.\textsuperscript{14} According to this model, the presence of defects in congruent LiNbO\textsubscript{3} plays an important role for observation of internal fields in such crystals. At equilibrium, a combined effect of polarization field due to inherent molecular arrangement and depolarizing field due to defect clusters produces a resultant electric field inside the crystal, which is known as the internal field. Domain inversion by high electric field poling of the crystal creates a reorientation of the defect clusters inside the bulk crystal. If the poling conditions are controlled in such a way that all the defect clusters find stable positions inside the crystal so that no further movement of those clusters occur, the resultant crystal will be in permanent domain inverted state. A simple scheme to obtain permanent domain inversion is to anneal the poled crystal, which forces the defect clusters to move to those minimum energy positions, which should be occupied by them after complete domain inversion. On the other hand, if annealing treatment is not followed after poling of the sample, there are notable movements of those defect clusters inside the crystal and the resulting domain may return back to its initial as-bought single domain state. It should be noted that room temperature high electric field domain inversion over whole crystal generally produces permanent domain inversion without applying annealing treatment on poled samples. But here, in this work, the poling is intentionally done over some limited region (about 50%) of the sample so that unstable or frustrated domain inversion of the crystal can be done. It is shown, in this work, that subsequent annealing of the poled sample at 200°C for about 30 min can produce permanent domain inverted crystal. Also for the poled sample, where annealing is not followed, it is observed that the same has returned back to the as-bought sample condition. Time evolution of the effective IF of un-annealed or the so called frustrated domain inverted sample certainly proved that the crystal move to the as-bought single domain state from the frustrated state after some relaxation time. This observation taken 24 h after poling is also reported in Table I.

<table>
<thead>
<tr>
<th>As bought LiNbO\textsubscript{3} crystal</th>
<th>Complete domain inverted LiNbO\textsubscript{3} crystal</th>
<th>Immediately after poling</th>
<th>24 h after poling</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_i$ in kV/mm</td>
<td>10.8</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>$E_i'$ in kV/mm</td>
<td>6.0</td>
<td>11.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$E_{IF}$ in kV/mm</td>
<td>2.4</td>
<td>–2.5</td>
<td>–1.0</td>
</tr>
</tbody>
</table>

\textbf{Frustrated domain inverted LiNbO\textsubscript{3} crystal}

|                     | |
|---------------------|------------------------|------------------|
|                     | 11.0                   |

\textbf{IV. CONCLUSIONS}

Study of the dependence of IF in LiNbO\textsubscript{3} under various conditions of the domain orientation and stability inside the crystal is done. Time evolution of IF in frustrated domain inverted LiNbO\textsubscript{3} is also performed and reported. A detailed and precise work on time evolution of IF is to be carried out in future for complete understanding of unstable domain inverted LiNbO\textsubscript{3} crystals and internal mechanism of electric field domain inversion of ferroelectrics and subsequent domain stability. But still with the stated technique variation of effective IF under various domain orientation and stability is successfully measured and reported. A defect model suggested by Gopalan et al.\textsuperscript{14} is utilized here to explain the outcome of the time evolution.

\textbf{ACKNOWLEDGMENTS}

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Enhanced Electro-Optic Property in LiNbO₃ by Electric Field Domain Inversion

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Abstract—Change in the value of half-wave voltage of LiNbO₃ (z-cut) before and after high electric field domain inversion at room temperature has been reported. For verification, a Mach–Zehnder interferometric setup is used and the voltage required for phase reversal of the fringe pattern is noted for single domain and domain inverted sample. The technique of the used domain inversion process is discussed and confirmation of the domain inversion is also done. As the half-wave voltage decreases after domain inversion, it may be assumed that the overall electro-optic property of LiNbO₃ has been enhanced. This might possibly been caused by the internal field compensating the spontaneous polarization of the crystal.

Index Terms—Lithium niobate, halfwave voltage, domain inversion, Mach-Zehnder interferometer.

I. INTRODUCTION

LITHIUM Niobate (LiNbO₃) is a negative uniaxial crystal having tremendous application in integrated optics because of its ability of guided wave control via its electro-optic, acousto-optic, birefringence, non-linearity etc properties [1], [2]. Large numbers of optoelectronic devices like second harmonic generator, parametric oscillators, THz wave generator, modulators and beam scanners have been built using the control of ferroelectric domain process [3]–[6]. This control, however, requires poling of LiNbO₃ which can be done by processes like thermoelectric treatment near Curie temperature or application of very high electric field at room temperature. In room temperature electric field poling, an electric field greater than the coercive field (21 KV/mm) is applied which causes the domains to be reoriented in a specific direction depending upon the electric field direction. For all the mentioned applications, the control of the ferroelectric domain distribution in the crystal is essential and understanding the material properties is critical in order to control the corresponding electro-optical behavior. The inspection of electro-optic property of poled LiNbO₃ can be a subject of study in order to understand the effect of strain introduced by poling. Several nondestructive imaging techniques have been developed so far to study this property. Interferometric technique is one such technique which provides a simple platform for quantitative characterisation of anti-parallel domains, monitoring of poling process and inspection of optical path of the engineered reversed domains [7].

In this letter, a temporary change of electro-optic property of LiNbO₃ subjected to domain inversion by application of high electric field is observed and reported. More specifically we have observed a decrease in half-wave voltage in domain inverted LiNbO₃ substrates compared to the virgin single domain LiNbO₃ substrates. For this, we examined the electro-optic effect in both virgin and domain inverted LiNbO₃ wafers. To test that, a Mach-Zehnder interferometric setup is used for inspection of the optical path difference induced by the crystal on the wave front traversing the sample due to the crystal's optical parameter variations. Work on poling inhibition [8] and refractive index modulation [9] on poled LiNbO₃ has been reported. More recently, there has been report of studies on electro-optic response of waveguides formed in LiNbO₃ [10]. But observation of this phenomenon of change of half-wave voltage by high electric field domain inversion has not been reported before, to the best of author's knowledge. Its study can be of extreme importance for the design of high quality domain engineering and electro-optic storage devices.

II. ANALYSIS METHOD

The basic idea following the observation of electro-optic effect in LiNbO₃ is that its refractive index changes with the applied electric field having strength much lower than its coercive field. Its birefringence also depends on the applied electric field. But if the field is applied along the c-axis, the velocity of the ordinary and extraordinary rays match and so no birefringence is observed along c-axis. In this letter the electro-optic behavior is evaluated using a Mach-Zehnder set-up as shown in Fig. 1. Light from a He-Ne laser (632.8 nm) is split into two parts by the beam splitter. One part passes through the sample under test and other through the reference sample. Both the sample under test and the reference are obtained from the same single crystal, single domain optical grade z-cut congruent LiNbO₃ substrates (obtained from Crystal Technology Inc.) of 0.5 mm thickness and polished on both sides. They are coated with same thickness of thin film of Aluminum deposited by thermal evaporation. For the sample under test, this Al film acts as electrode for the application of electric field. Since the electric field and the light propagation directions are the same, the thickness of the Al coating is optimized at 70 nm for each faces of the LiNbO₃ so as to allow adequate light transmission as well
as guarantee application of electric field through the sample. All the experiments are performed on small pieces of LiNbO$_3$ of size $10 \times 10$ mm$^2$ cut from a single wafer. Variation of the applied electric field on the sample will cause a change in optical path length of the light passing through it (Fig. 2). Change of this parameter, i.e. optical path length, by half of the wavelength of the light used will result a desired 180° phase shift in the fringe pattern observed by a Mach-Zehnder interferometer. The applied voltage for this to occur is termed as half-wave voltage. Since the direction of light path is along c-axis, this optical path length change is independent of the polarization of light used. If both the applied electric field ($E$) in the crystal and direction of propagation of light are along the c-axis, the refractive-index change $\Delta n_o$ is given by
\[
\Delta n_o = -\frac{1}{2}r_{13}n_o^3 E,
\]
where $r_{13} = 10 \times 10^{-12}$ m/V is the appropriate element of the electro-optic tensor and $n_o$ is the ordinary index of refraction [7]. The sign of $r_{13}$ depends on the orientation of the c-axis of the crystal which is collinear with the spontaneous polarization vector. This refractive index change translates into a phase shift
\[
\Delta \Phi = \frac{2\pi}{\lambda o} \Delta n_o d = \frac{\pi r_{13} n_o^3 V}{\lambda o}
\]
where $d$ is the crystal thickness, $V$ is the applied voltage along the c-axis and $\lambda o$ is the wavelength of the probe beam. The electro-optic phase shift in the sample is measured by monitoring the movement of the interference fringes in the output of the interferometer as a function of the voltage applied to the sample. To calculate the half wave voltage $V_{\pi}$, we put $\Delta \Phi = \pi$ and $V = V_{\pi}$, in the above equation to obtain
\[
V_{\pi} = \frac{\lambda o}{r_{13} n_o^3}.
\]

Taking $n_o = 2.28646$ for LiNbO$_3$ substrate at He-Ne laser source wavelength (632.8 nm), this value is calculated to be 5.3 KV.

### III. Experimental Results

The interference fringe pattern, obtained using the proposed Mach-Zehnder setup, shifts with the increase in applied voltage to the sample under test due to optical path length change. The corresponding phase shift is calculated and is shown in Fig. 2. In this case, the positive terminal of the source is attached to the $+z$ face of the virgin single domain LiNbO$_3$ sample and $-z$ face is grounded. The fringe pattern shows a complete phase reversal when the applied voltage is increased to $(5.4 \pm 0.05)$ KV. This is the half-wave voltage for the virgin single domain LiNbO$_3$ crystal under test. This matches very well with the theoretically predicted half wave voltage. The fringe pattern at zero voltage and voltage corresponding to 180° phase reversal are shown in Fig. 3(a) & 3(b) respectively.

Next the LiNbO$_3$ sample is domain inverted by applying a high voltage greater than its coercive field (21 KV/mm) using the domain reversal technique as described schematically in Fig. 4. The sample is placed inside a specially designed holder to prevent air breakdown at high voltage. The details of the holder arrangement are provided elsewhere. It is known [11], [12] that application of an external high electric field shifts the Li$^+$ and Nb$^{5+}$ ions to the opposite lattice positions and thus invert the direction of spontaneous polarization. It is assumed that O$^{2-}$ anions are motionless in this regard and only cations move relative to O$^{2-}$ anions. In this arrangement, the 0–10 V scale of the connected digital voltmeter corresponds to 0–20 KV of the high voltage source. When the voltage of the high voltage source is increased, the displacement current measured using the digital picoammeter increases and then after a certain applied voltage it suddenly drops to zero. This drop indicates that the domain inversion is completed. The voltage at which this occurs is found to be around 11 KV for the 0.5 mm thick LiNbO$_3$ sample. To reconfirm the occurrence of domain inversion, etching of the sample is done in a solution of HF$^+$HNO$_3$ in a 1:1 ratio as given in [13]. It is seen that there is a differential etching between
Fig. 3. (a) Fringe pattern obtained for virgin LiNbO₃ at zero voltage. (b) Fringe pattern obtained for (5.4 ± 0.05) KV applied on virgin LiNbO₃ substrate showing complete phase reversal.

The portion below the electrode area and the other portion of the LiNbO₃ sample. The etched sample as seen under microscope (Carl Zeiss Axio Observer A1) in transmission mode is shown in Fig. 5.

The same interferometric experiment is again performed for the domain inverted sample. The diameter of the probe laser beam is such that it passes through the domain inverted region of the sample only. The phase-shift, corresponding to fringe shift with increasing voltages, is plotted in Fig. 6. It is seen that the phase reversal now occurs at (3.0 ± 0.05) KV. The new fringe patterns corresponding to no applied voltage and phase reversal voltage are shown in Fig. 7(a) & 7(b) respectively.

Thus it is seen that the half-wave voltage changes from a value of $V_\pi = 5.4$ KV to $V_\pi = 3$ KV after domain reversal. This experiment suggests that the electric field domain inversion of LiNbO₃ has resulted in a decrease of its half-wave voltage. This reduction may mean enhancement of the overall electro-optic conversion efficiency of LiNbO₃ after domain inversion. It is to be noted that the measurement when repeated after one day shows the same phase reversal voltage of (5.4 ± 0.05) KV as that of virgin single domain sample. Thus, using the proposed technique of application of high electric field, the domain inversion is not permanent. Study on how the phase reversal voltage increases with time, however, is not within the scope of this letter. The temporary nature is due to ineffective bulk screening [14] due to manual ramping of applied field and permanent domain inversion occurs when computer-controlled pulsed electric field is applied.
Fig. 7. Fringe pattern obtained for domain reversed LiNbO$_3$ at (a) zero voltage (b) (3.00 ± 0.05) KV showing complete phase reversal.

It is further noted that if the applied field direction is reversed, i.e., positive terminal of the voltage source is attached to $-z$ face while $+z$ face is grounded, then the phase reversal occurs at (3.0 ± 0.05) KV and (4.0 ± 0.05) KV for the virgin single domain and domain inverted samples respectively. Thus with reverse polarity, the value of phase reversal voltage increases from single domain to domain inverted sample (3.0 KV & 4.0 KV), while for the first case, its value (5.4 KV & 3.0 KV) is decreased. The difference in the value of half-wave (phase reversal) voltages for field applied in forward and reverse direction can be attributed to the internal field of LiNbO$_3$. But the positive change in one case and negative change for opposite polarity may signify that the high electric field has resulted in domain inversion. Thus this can be a non-destructive testing method to justify domain inversion by electric field instead of the traditionally used etching method.

Thus it is observed that the decrease in half-wave voltage is not permanent and is dependent on applied field direction. The effects observed could be attributed to the long relaxation time transients and direction dependence of the internal field within congruent LiNbO$_3$ produced by compensating monocharges [15]. Although the exact reason for this decrease is yet to be confirmed experimentally but it is speculated that the effect might have resulted from the internal field compensating the spontaneous polarization within the crystal.

IV. CONCLUSION

It can be concluded that a significant decrease in half-wave voltage can be observed in domain inverted LiNbO$_3$. The long relaxation time transients and direction dependence of the internal field compensating the spontaneous polarization within the crystal is suggested to be the reason for this variation. With the present setup, the effect was observed using only the $r_{13}$ coefficient. The phase shift, as seen from Eq.(1), is dependent on $r_{13}$ only, as $n_0$ is constant at a fixed temperature and chosen wavelength. Hence, it can be predicted that the internal field might have some effect on $r_{13}$. Study of this effect with other EO coefficients, mainly $r_{33}$, will be very important and can be done by fabricating waveguides on the LiNbO$_3$ samples.

REFERENCES

Interferometric measurement of the internal field of lithium niobate without high-voltage electric field poling

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Abstract. A simple interferometric technique for measurement of the internal field (IF) in a ferroelectric crystal has been proposed. This technique has several advantages over the other methods used previously for evaluation of IFs in ferroelectric crystals. Here, the electro-optic property of lithium niobate is exploited for quantitative analysis of its IF. The strength of IF obtained using this technique lies within the range given in the literature. However, at frustrated domain inversion state, the measured value of IF shows a reduced value. A possible reason for this reduction based on the defect model has been discussed.© 2014 Society of Photo-Optical Instrumentation Engineers (SPIE)

Keywords: lithium niobate; Mach–Zehnder Interferometer; halfwave field; internal field; defects; domain inversion; frustrated domain-inverted state.

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1 Introduction

Lithium niobate (LiNbO₃) is a versatile material having huge applications in photonics and optoelectronics because of its excellent optical transparency in the visible and infrared spectra and its remarkable electro-optic, ferroelectric, and nonlinear optical properties.¹,² These days, a broad range of applications, such as, e.g., nonlinear frequency conversion, photonic band-gap devices, electro-optic Bragg switches, and data storage devices, is made using LiNbO₃ by creating ferroelectric domain patterns.³–⁷ This is done by domain inversion of LiNbO₃ and achieved either by a thermoelectric process near Curie temperature or by application of a very high electric field at room temperature which may or may not be accompanied by light. In room temperature electric field poling, an electric field larger than its coercive field (E_c ≈ 21 KV/mm) is applied along the z axis of the crystal. This causes the domains and hence the polarization vector to be realigned along the applied electric field direction.⁸,⁹ In the congruent LiNbO₃, there are many defect states distributed throughout the crystal.¹⁰,¹¹ These defects and also the vacancies are generally symmetrically distributed throughout the nonstoichiometric crystal and produce a uniform internal electric field in it.¹²,¹³ This internal field (IF) influences electric field switching of domains so that polarization switching in reverse poling takes place at a smaller field strength compared to the forward poling case. So, by measuring the difference of the field required for forward and backward polings of LiNbO₃, its IF can be assessed.¹⁴ However, the said method of testing destroys the domain-inverted structures, so noninvasive techniques are preferred. An interferometric technique provides such an alternative and is used in Refs. 13 and 15–17, where Mach–Zehnder interferometry and digital holographic technique are used to evaluate the IF of congruent LiNbO₃.

In this work, a similar interferometric technique has been used to measure the IF of single domain LiNbO₃. But, the Mach–Zehnder interferometer used in this case has the sample under test in one arm with a provision for application of the electric field across it and a similar sample as a reference in the other arm. By placing a similar sample at the reference arm of the interferometer, any effect other than that resulting from the application of the electric field to the sample under test can be cancelled out. This technique, apart from being noninvasive, has several advantages over the methods used earlier. First, this method does not require domain inversion of LiNbO₃ as in Refs. 14 and 15. So there is no need for handling very high voltage or making a domain inversion setup. Also, the use of hysteresis loops can be avoided, which, indeed, is a source of errors as the poling is never fully under control.¹⁸–²⁰ Second, a separate arrangement for analysis, like recording a reference hologram in the digital holography technique used in Refs. 13 and 15–17, is not required here. Last, this method gives quantitative assessment of the IF of LiNbO₃ by exploiting its electro-optic property, unlike the qualitative analysis done in Ref. 16.

2 Experimental Procedure

The experiments are performed on optical grade, congruent z-cut LiNbO₃ crystals (obtained from Crystal Technology Inc., Palo Alto, California). The starting crystals are single crystal, single domain, and in the form of 76.2-mm diameter wafers, which are 0.5-mm thick and polished on both sides. Small pieces of size 10 × 10 mm² are cut from this single wafer. All the experiments described here are performed on samples cut from the same wafer. The samples are cleaned properly by a standard cleaning procedure followed by drying using a nitrogen jet. Both z faces of the LiNbO₃ samples are coated with considerably thin semitransparent aluminum films in order to apply an electric field along the z axis for the evaluation of the IF of the crystal. The measurement setup used is schematically illustrated in Fig. 1. This is basically a Mach–Zehnder interferometer where Al-film-coated z-cut LiNbO₃ samples are placed in both the arms, perpendicular
to the path of the probe beam. In one arm, the LiNbO₃ sample is electrically connected with the high voltage source, whereas in the other arm, the LiNbO₃ sample acts as a reference only. Since the electric field and the light propagation directions are the same, the thickness of the aluminum coating is optimized (≤70 nm for each faces) to allow sufficient light transmission as well as guarantee application of a high electric field. Change in the optical path length by half the wavelength of the light used will result in a desired 180-deg phase shift in the fringe pattern observed by the Mach–Zehnder interferometer. The applied electric field for this to occur is termed as a halfwave field (Eₚ) and a high voltage source (obtained from Glassmann Inc., Japan) is employed for this purpose. The positive terminal of the source is connected to the electrode on the +z face while the electrode on the other side is grounded and the halfwave field along the z-axis is measured. It is noteworthy that the halfwave fields are measured by observing the fringe shift at the output of the interferometer such that the position of a black strip of the initially obtained fringe pattern (i.e., with no applied field) is totally replaced by a white strip of the final fringe pattern (i.e., with the said halfwave field). The polarities of the electrodes are then reversed and the halfwave field is similarly measured again. The IF of LiNbO₃ is calculated from these two measured values of halfwave fields using the analysis technique discussed in Sec. 3. Although the halfwave fields are considered here, it is interesting to note that quarter-wave fields and even lower fields can also be used in this technique. In fact, the IF of any type of transparent ferroelectric crystal can be obtained by applying very small electric fields across the sample provided the interferometer output is within the resolution limit of the detector. It is to be noted that, here, the interferometric setup has been used for assessment of the optical path difference introduced by the crystal on the wavefront traversing through the sample due to the application of a field much lower than the coercive field of LiNbO₃.

The experiment is carried out with the as-bought samples after annealing them at 200°C for 30 min. Next, the same sets of experiments are also repeated with single-domain LiNbO₃ crystal wafers of thickness 1 mm. Finally, the experiment is carried out to determine the IF of unannealed and annealed domain-inverted samples. The domain inversion of the samples is done using a high-voltage electric field poling technique whose arrangement is shown in Fig. 2. For applying a high voltage across the sample for poling, the previously mentioned high voltage source is used. The output of the high voltage source is computer controlled or mechanically controlled with high precision. LiNbO₃ samples are housed in an airtight rubber jacket such that there is no air-gap inside the structure to prevent air breakdown due to the application of the high field. Since LiNbO₃ is dielectric there is no current flowing through the samples for moderately high fields. But, at the time of domain reversal, there is a notable current flow called a displacement current, which is measurable by the picomammeter. The output voltage indicator is attached externally to the high voltage source to point out the output voltage precisely. As found in the literature, domain inversion of the samples can be claimed by noting a sudden increment of displacement current followed by a reduction of its value to zero. Domain inversions were obtained over large areas covering over 50% of the sample surfaces. Finally, IFs of the unannealed and annealed domain-inverted samples are measured with the same interferometric setup.

3 Results, Analysis, and Discussions

LiNbO₃ being a nonlinear electro-optic birefringent crystal, its index of refraction and hence its birefringence depends on the applied electric field. When an electric field is applied along the z axis, birefringence is observed along all directions except along the z direction, since along this direction, the velocity for both ordinary ray and extraordinary ray matches. As both the applied electric field in the crystal and the direction of the propagation of the probe beam (polarized in the XY-plane) are along the z axis, the refractive index change Δnₒ due to the electro-optic property of LiNbO₃ is given by

$$\Delta n_o = -\frac{1}{2} r_{13} n_o^3 E,$$  (1)

where $r_{13} = 10 \times 10^{-12} \text{ m/V}$ is the appropriate element of the electro-optic tensor and $n_o$ is the ordinary index of refraction. $E$ is the applied electric field directed from the +z face to the −z face of the crystal. This refractive index change gets translated into a phase difference between the
two beams passing along two-different arms of the interferometer. The electro-optic phase shift in the sample is measured by monitoring the movement of the interference fringes in the output of the interferometer as a function of the applied electric field across the sample. The halfwave field \( E_0 \) can be obtained from Eq. (1) and is given by

\[
E_0 = \frac{\lambda_0}{r_{13} n_0 d}.
\]

where \( d \) is the crystal thickness and \( \lambda_0 \) is the wavelength of the light wave. Using this equation, the halfwave field directed from +\( z \)- to −\( z \)- face is calculated to be 10.8 KV/mm for a He-Ne laser source of wavelength 632.8 nm. Although LiNbO\(_3\) is a piezomaterial, the piezo-electric effect has a negligible effect in this experiment. It has been pointed out by Grilli et al.\(^{22}\) that the phase retardation of the light wave due to the piezo-electric effect occurs at the domain boundary. In this experiment, the probe beam passes entirely through the central portion of the Al-coated sample where they are obviously single domain. So, in this case, due to the piezo-electric effect, the test sample may expand or compress along the applied field direction. Consequently, the crystal density [as well as the refractive index (n.r.)] will change in a reciprocal manner along the same direction. The optical path before and after the application of the electric field will, therefore, not change due to the piezo-electric property of LiNbO\(_3\).

The interference fringe pattern obtained using the setup shown in Fig. 1 is now used for determination of halfwave fields along the forward and reverse \( z \)-axes of the LiNbO\(_3\) samples. Fig. 3(a) represents the fringe pattern when no electric field is applied to the sample under test. As stated earlier, the +\( z \)- face of the sample is connected with the positive terminal of the voltage source, and the −\( z \)- face is connected with the negative terminal of the same source. Then, the field across the sample is slowly increased by adjusting the voltage controller of the controlling system attached to the source. It is noticed that a 180-deg phase shift of the output fringe pattern occurs when a field of the order of \((11.0 \pm 0.1) \text{ KV/mm}\) is applied across the sample and is designated as \( E_{\pi 12} \). This is almost in agreement with the calculated value and is clearly observed from the shifted fringe pattern shown in Fig. 3(b) in comparison to Fig. 3(a). This halfwave field is much lower than the coercive field required for domain reversal of LiNbO\(_3\). After that, the electrodes on both faces of the test sample are electrically shorted and kept for about an hour so that the sample gets back to its initial condition by discharging any possible accumulated charges and the crystal also gets sufficient time to relax. Now, keeping all the arrangements intact, the polarity of the applied voltage is altered so that the electric field is applied along the reverse \( z \)- direction through the LiNbO\(_3\) sample. In this situation, at zero applied field, the fringe pattern is adjusted so that they look exactly like that of Fig. 3(a). The field is then increased slowly and the halfwave field is detected now to be \((6.0 \pm 0.1) \text{ KV/mm}\), which is expressed as \( E_{\pi 21} \). The corresponding fringe pattern is shown in Fig. 3(c). Repeatable results are also obtained when the experiment is performed with different sets of similar sample and/or reference materials. Here, for any electric field \( E_{\pi i j} \), “\( i \)” represents the face at which the positive terminal of the source is connected, keeping face “\( j \)” grounded. In the as-bought single domain LiNbO\(_3\), the subscripts 1 and 2 represent the +\( z \)- face and −\( z \)- face of the sample, respectively. So, the field represented by subscript 12 means that the source is connected to the +\( z \)- face while the −\( z \)- face is shorted to ground. Similarly, the field represented by subscript 21 means the converse.

Measured values of phase shift with an applied electric field in the two opposite directions give linear fit curves and are shown in Fig. 4. From the figure, it is seen that the slope of the two straight lines are not the same. A possible reason for this asymmetry is the presence of an internal

![Fig. 3 Fringe pattern obtained for as-bought single domain LiNbO\(_3\) due to (a) zero applied field (b) applied field of \((11.0 \pm 0.1) \text{ KV/mm}\) from its +\( z \)- face to −\( z \)- face (c) applied field of \((6.0 \pm 0.1) \text{ KV/mm}\) in reverse direction.](image-url)
Fig. 4 Phase variation with the applied field for as-bought LiNbO₃ wafer.

electric field in the said crystal. A relation between the IF with the measured field values is thus proposed, which is given by

\[ E_{\text{int}} = \alpha (E_{\Delta \phi_{12}} - E_{\Delta \phi_{12}^*})/ \Delta \phi \pi \],

where \( \alpha \) is a constant having a value equal to the thickness of the substrate in millimeters and \( \Delta \phi \) is the phase change for the applied field. As halfwave fields of the crystal of thickness 0.5 mm are considered in Fig. 3, in that case, \( \alpha = 0.5 \) and \( \Delta \phi = \pi \) are to be put into the above equation. The term \( \alpha \pi / (\Delta \Phi) \) being constant, Eq. (3) is similar to that as mentioned in Refs. 11 and 16, as in both the cases the fields are measured along the forward and backward poling directions. So it is proposed here that the differences between the halfwave field values must be due to the presence of an IF in the crystal. Using the above equation, the IF of LiNbO₃ can be calculated as \( E_{\text{int}} = 2.5 \) KV/mm. This value is within the range of values given in Refs. 15, 23, and 24, where IFs are obtained from the difference of the electric field during forward and reverse poling directions. Similarly, for a quarter wave field or, in general, for any value of an applied field, the corresponding value of phase change is to be put into Eq. (3) to get the IF of the crystal. The experiment is repeated with the as-bought LiNbO₃ substrates of thickness 1.0-mm annealed at 200°C for about 30 min. The halfwave voltages measured using the interferometric set-up used here is almost the same as that of the previous cases, which is quite obvious and can be cross-verified from Ref. 25. However, the halfwave field will decrease to half its values of the previous sets of experiments due to the doubling of the substrate thickness. The IF is calculated using halfwave field values in Eq. (3). Thus a new and simple technique to determine the IF is proposed based on the measurement of halfwave fields along the positive and negative directions of the z axis of the crystal. This technique can be applied to any ferroelectric crystal to determine its IF. The method of determination of the IF thus requires handling voltages and fields much lower than that required for electric field poling of the congruent LiNbO₃ crystal and it does not require domain inversion of the same or a generation of reference holograms.

Now, if the sample is domain inverted and the same experiments are repeated, it is expected that the magnitude of the IF of the crystal will remain same. For the domain-inverted LiNbO₃, the faces will be interchanged with respect to the as-bought single-domain LiNbO₃ crystal, i.e., face 1 will now be referred to as the \(-z\) face and face 2 as the \(+z\) face of the domain-inverted LiNbO₃. The field represented by subscript 12 will now mean that the positive terminal of the source is connected to the \(-z\) face of the domain-inverted sample while its \(+z\) face is grounded. The opposite will happen for the field in the reverse direction (i.e., the field represented by subscript 21). The kinetics of ferroelectric domain during the domain inversion process are explained in detail by Gopalan et al. 12 based on the defect model and by Shur. 26 The domain inversion by a high electric field is stabilized to a steady state by a high-temperature annealing. In the room temperature process, the kinetics of the ferroelectric domain structure essentially depend upon effectiveness of the screening processes, which are time dependent. Thus, the room temperature process can be referred to as a macroscale domain reversal process. Here, the domain inversion of LiNbO₃ with a high electric field (\( \approx 22 \) KV/mm) exceeding the coercive field strength (\( \approx 21 \) KV/mm) is done using the arrangement shown in Fig. 2. The high electric field is ramped up manually for a certain time duration until the current shown in the current monitor jumps to zero. This signifies that the polarization switching is complete, i.e., domain reversal has occurred. The high electric field domain inversion is done on two sets of samples. Immediately after domain inversion, the experiment to determine the IF is performed on one set of samples, while the other set is annealed at 200°C for 30 min before performing the same experiment. As suggested by Gopalan et al., 12 the unannealed domain-inverted state in LiNbO₃ is the so-called frustrated state and the annealed domain-inverted state is the stable state.

For the annealed domain-inverted samples, the halfwave fields \( E'_{\Delta \phi_{12}} \) and \( E'_{\Delta \phi_{12}^*} \) are measured to be \((6.0 \pm 0.1) \) KV/mm and \((11.0 \pm 0.1) \) KV/mm, respectively. The prime (‘) sign in the expressions for the halfwave field mean that they represent the parameters for the domain-inverted LiNbO₃ crystal. The IF \((E'_{\text{int}}) \) calculated using Eq. (3) comes out to be \(-2.5 \) KV/mm, which is same as that for the single-domain samples. The negative sign, however, is due to the direction convention used in the calculation and also suggests the occurrence of domain inversion of the LiNbO₃ sample.

For the unannealed domain-inverted samples (the so-called frustrated domain-inverted LiNbO₃), the measurement of the halfwave field for determining IF is done immediately after domain inversion. Some interesting observations are obtained in this case. Here, the halfwave fields are \( E'_{\Delta \phi_{12}} = (6.0 \pm 0.1) \) KV/mm and \( E'_{\Delta \phi_{12}^*} = (8.0 \pm 0.1) \) KV/mm. The variation of phase at the output of the interferometer with the applied field for the two opposite directions is plotted in Fig. 5. The calculated IF \((E'_{\text{int}}) \) thus comes out to be \(-1.0 \) KV/mm. Thus, a reduction in the value of the IF is observed in the frustrated domain-inverted LiNbO₃.

In congruent LiNbO₃, point defects arising from nonstoichiometry are not randomly distributed, but are organized as
defect clusters. These defect clusters possess a defect polarization $P_D$ that is different from the lattice polarization $P_S$. In a stable defect state, the $P_D$ is assumed to be parallel to the $P_S$. Upon domain reversal at room temperature, the niobium antisite defect moves to the neighboring octahedron by the movement of $\text{Nb}_\text{Li}$ through the closely-packed oxygen plane. At the same time, the lithium vacancies around the original defect are unable to rearrange around the new antisite position to reach the stable defect state of the domain-inverted LiNbO$_3$ sample owing to a lack of lithium mobility at room temperature. This state is termed as the frustrated defect state, where the defect polarization $P_D$ is in the opposite direction to the lattice polarization $P_S$. The IF is, however, directed toward the direction of effective polarization of the crystal, which is stable state is $(P_S + P_D)$, while in the frustrated state it is $(P_S - P_D)$. This will, therefore, cause a reduction in the effective IF of the sample in the frustrated state, as observed here.

The measurement of the halfwave fields of this frustrated domain-inverted LiNbO$_3$ sample is repeated after 24 h and their values in the two opposite directions are obtained to be same as that of the as-bought single-domain samples. This signifies that the proposed domain inversion process by application of a high-electric field alone at room temperature does not produce a stable domain inversion and the sample has shifted back to its initial stable single-domain state after some relaxation time. The measurement of the time evolution of the IF, and hence the relaxation time, gives some interesting results. However, its discussion is beyond the scope of this work. The present process can give a stable domain inversion after high temperature annealing. However, at room temperature, a macroscale domain reversal process can create a stable domain inversion. A comparative study between the domain inversion process at room temperature and at elevated temperature will be reported elsewhere.

4 Conclusions

Thus, it can be concluded that using the electro-optic property of LiNbO$_3$, its IF can be measured. The technique used for this measurement is noninvasive and does not require high-voltage electric field domain inversion of the samples. With the present setup, the maximum applied voltage is 5.5 KV for a 0.5-mm-thick sample. The applied voltage level may be further reduced provided the output is within the detection limit of the detector. It is also simple in the sense that it is not a two-step measuring process as no separate analysis of the reference is required. Moreover, in this method using the electro-optic property, a quantitative measurement of IF of LiNbO$_3$, and not a qualitative analysis as reported before, can be done. It can also be used to find the IF of any type of transparent ferroelectric crystal. The applicability of this technique has been verified with single domain and domain-inverted LiNbO$_3$ samples of two different thicknesses at both annealed and unannealed conditions. For the frustrated domain-inverted state of LiNbO$_3$, the IF is reduced. An explanation for this effect using a defect model has been tried.

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References


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