Internal fields in lithium tantalate single crystals

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ABSTRACT

An in-built internal field of 5 KV/mm was measured in Z-cut $LiTaO_3$ single crystals in the direction of the original polarization. This was reflected in the asymmetry (along the field axis) in the polarization hysteresis curve as a function of external electric field. Measurement of internal field as a function of crystal thickness revealed that the internal field is a volume effect. Using infrared absorption measurements, the spectrum of the hydroxl ions (OH^-) present in these crystals was measured at room temperature. The shape of the spectrum changes with polarization reversal in these crystals indicating a strong correlation with the direction of internal field with respect to the polarization direction. It suggests that the origin of internal field lies in point defect complexes involving OH^- ions.

Keywords: $LiTaO_3$, $LiNbO_3$, internal field, electric field poling, polarization hysteresis, infrared absorption

1. INTRODUCTION

Lithium tantalate is of interest for surface acoustic wave devices, piezoelectric devices, and in non-linear optical applications due to its large non-linear optical coefficients[1] and photorefractive damage resistance.[2,3] Here we report the presence of an in-built internal field in poled Z-cut $LiTaO_3$ crystals, which strongly influences the electric field switching of domains in these crystals.

Built-in internal fields have been reported in ferroelectric crystals such as PZT, [4,5] $BaTiO_3$,[6,7] and TGS^8. In PZT, doping experiments have shown that internal fields are of dipolar nature consisting of acceptor impurity atoms, such as K^{1+} or Na^{1+} at Pb^{2+} sites or Mg^{2+}, Fe^{3+} or Al^{3+} at $(Zr, Ti)^{4+}$ sites coupled to a neighboring oxygen vacancy. Similar effects have been observed by doping Mn^{3+}, Cr^{3+}, Al^{3+} and Ni^{3+} in Ti^{4+} sites in $BaTiO_3$ crystals where impurity atoms-oxygen vacancy defect complexes have been found responsible for internal fields in the crystal. We show that in undoped $LiTaO_3$ crystals, similar internal fields exist. The origin of these fields is experimentally shown to be a volume effect. Further, we present experimental evidence that suggests that hydroxl ions (OH^-) present in $LiTaO_3$ crystals are related to the origin of these fields.

2. POLARIZATION HYSTERESIS MEASUREMENTS

The $LiTaO_3$ crystals used in this study were obtained from Yamaju Ceramics Inc., Japan. The as-purchased "virgin crystals" were Z-cut single crystals, of congruent composition, and were single domain. The polarization of these crystals was reversed by applying a dc field across the crystal thickness.[9] Liquid electrodes (0.1 gm/mL of magnesium nitrate in water) were used as contacts and voltage was ramped at 20 V/sec.

During the poling process, the rate of change of polarization with time gives rise to a transient current of $d(2P_s A)/dt$ where P_s is the spontaneous polarization (~50 $\mu C/cm^2$), A is the poled area in the Z-plane and t the time. The hysteresis loop was obtained by the time integration of this current. If the polarization is reversed from $+P_s$ to $-P_s$, the total change in polarization is $2P_s$ and the total charge after complete polarization reversal obtained from the integrated current is $2P_s A$. Real-time integration of the transient current was thus used to detect the progress and completion of the poling process.

Figure 1 shows the polarization hysteresis curve for a virgin 0.5 mm thick $LiTaO_3$ single crystal at room temperature. The crystal was cycled from its initial polarization state I, through 180° to state II and then back to state I. For convenience we shall denote poling from state I to II as forward poling (subscript f) and from II to I as reverse poling (subscript r).

The large asymmetry in the loop about the field axis indicates the presence of an internal field, E_{int}. The magnitude of this field can be determined as $(E_f - E_r)/2 = 5$ KV/mm. This is shown schematically by an arrow in Fig. 1. In the virgin crystal, this field is aligned along the polarization direction of the crystal. Hence, the forward poling field is $E_f = E_c + E_{int}$ where E_c is the intrinsic coercive field of the crystal. At room temperature, when the polarization direction is reversed to state II, the internal field is still pointing in its original direction on the time scales of this experiment (order of minutes). Hence, the reverse poling field is given by $E_r = E_c - E_{int}$. The intrinsic coercive field can be calculated as $E_c = (E_f + E_r)/2 = 16$ KV/mm. It should be noted that the presence of internal field has been seen in all the $LiTaO_3$ crystals obtained from the manufacturer, irrespective of crystal batch or different pieces from the same wafer.

3. THE NATURE OF INTERNAL FIELD

There are two possible origins of internal field in $LiTaO_3$ crystals: (a) surface origin, (b) bulk origin. We shall show below that the internal fields observed in $LiTaO_3$ crystals is of *bulk* origin.

The possibilty of surface charge accumulation giving rise to internal fields arises as follows: In a single domain $LiTaO_3$, depolarization charges build up at the C- and C+ surfaces. To compensate these, compensation charges must appear at the surface either from atmosphere or due to the conductivity of the sample. Thus, a space charge will build up in the crystal up to a Debye length below the crystal surfaces. The Debye length (L_D) for the space charge buildup at the surface is given by

$$L_D = \sqrt{\varepsilon . k_b . T / (2.q^2 . C_\infty)} \qquad (1)$$

where ε is the dielectric constant, k_b the Boltzmann constant, T is the temperature, q is the charge, and C_∞ is the bulk concentration of charges. In pure $LiTaO_3$ crystals, impurity defects are in the range of ppm concentration at room temperature. The Debye length is therefore of the order of nanometers. For higher defect concentrations, the Debye length is even smaller. Thus, if the internal field is of surface origin, removal of depth of the order of microns from the crystal surface (C+ or C-) should cause the internal field to disappear.

Figure 2 shows the poling voltages as a function of crystal thickness for a virgin crystal. The crystal thickness was varied from 500 μm to 250 μm by polishing the crystal surfaces using SiC and Al_2O_3 powders with water as a medium. The internal field E_{int} was found to be constant with crystal thickness as seen from the constant slope of the curve (5.2 KV/mm), which is close to the measured internal field of 5 KV/mm. This observation was independent of which surface (C+ or C-) was removed. Further, if the internal field is due to charges within a Debye length of the surface, the field should be *inversely* proportional to the thickness of the sample[10] contrary to our observations. The above discussion leads us to conclude that the internal field is a *volume* effect. We shall now discuss hydroxyl ions as a possible source of this volume effect in $LiTaO_3$ crystals.

4. HYDROXYL IONS AND THE ORIGIN OF INTERNAL FIELD

Even nominally pure crystals of closely structurally related $LiNbO_3$[11] can have up to 10^{19} /cm^3 of OH^- ions (we have observed similar internal fields in $LiNbO_3$ crystals also which shall be reported elsewhere). Here we report infrared absorption measurements of the hydroxyl ions in $LiTaO_3$ crystals, which suggest that they may be responsible for the origin of internal fields in $LiTaO_3$ crystals.

Figure 3 shows the comparison of the infrared absorption spectrum of the virgin crystal (state I in Fig. 1) of $LiTaO_3$ with the spectrum for a room temperature polarization reversed crystal (state II in Fig. 1). The spectrum was taken by transmitting an unpolarized infrared beam parallel to the z-axis of the crystal. There is a clear change in the shape of the absorption spectrum. It has been suggested in literature on hydroxyl ions in $LiNbO_3$ that this spectrum is composed of two,[12] three,[13] or even four[14] different absorption bands. Since the hydroxyl ions align along the O-O bonds in the octahedral planes, the band frequencies correspond to different O-O bond lengths and their surroundings in the octahedral plane of the $LiNbO_3$ crystals. We obtained best fits using three absorption bands, each composed of a combination of

Gaussian and Lorentzian lineshapes. The relative intensities of these bands change considerably with polarization reversal, as seen in Fig. 3.

5. DISCUSSION

From our earlier results of hysteresis measurements, it is clear that the only difference between a virgin crystal in state I and a polarization reversed crystal in state II is that (a) In a virgin crystal, the direction of internal field is parallel to the polarization direction, and (b) In a room temperature polarization reversed crystal, the direction of internal field is antiparallel to the polarization direction. This combined with the results for hydroxl ion spectra in Fig. 3 suggests that the origin of internal field is possibly related to the presence of hydroxyl ions in $LiTaO_3$ crystals.

However, it is known that the hydroxl ions are oriented perpendicular to the polarization direction in $LiNbO_3$ crystals.[13] If similar situation is expected for $LiTaO_3$ crystals, then hydroxyl ions cannot by themselves be responsible for the internal fields parallel (or antiparallel) to polarization direction in these crystals. However, they can form complexes with other point defects to give rise to internal fields. Schirmer et al.[15] conclude that in congruent $LiNbO_3$ crystals, niobium antisites $(Nb_{Li})^{4+}$ and niobium vacancies $(V_{Nb})^{5-}$ dominate. Similar situation is expected in congruent composition of $LiTaO_3$ (~48% Li and 52% Ta), where tantalum vacancies $(V_{Ta})^{5-}$ and tantalum antisites $(Ta_{Li})^{4+}$ are the dominant defects[16] at room temperature. Hence, it is proposed that the origin of internal field in congruent $LiTaO_3$ (and $LiNbO_3$) crystals at room temperature is due to defect complexes involving tantalum (or niobium) vacancies, tantalum (or niobium) antisites, and hydroxyl ions (OH^-).

6. CONCLUSIONS

Internal fields of 5 KV/mm have been measured parallel to the polarization direction in the as-purchased single domain Z-cut $LiTaO_3$ crystals. These fields has been shown to be a volume effect and independent of crystal thickness. Infrared absorption measurements indicate that the origin of these fields is related to the presence of hydroxl ions in these crystals. We propose that the origin of internal field in congruent $LiTaO_3$ crystals at room temperature is due to defect complexes involving tantalum vacancies, tantalum antisites and hydroxyl ions (OH^-).

7. ACKNOWLEDGMENTS

8. REFERENCES

1. R. C. Miller and W. A. Nordland, "Absolute signs of second-harmonic-generation coefficients of pyroelectric crystals," *Phys. Rev. B* , Vol. 2, pp. 4896- 4902, 1970 .

2. A. Ashkin, G. D. Boyd, J. M. Dziedzic, R. G. Smith, A. A. Ballman, J. J. Levinstein, and K. Nassau, " Optically induced refractive index inhomogeneities in $LiNbO_3$ and $LiTaO_3$," *Appl. Phys. Lett.* , Vol. 9, pp. 72- 74, 1966.

3. G. L. Tangonan, M. K. Barnoski, J. F. Lotspeich, and A. Lee, " High optical power capabilities of Ti-diffused $LiTaO_3$ waveguide modulators," *Appl. Phys. Lett* ., Vol. 30, pp. 238-239, 1977.

4. S. Takahashi, " Effects of impurity doping in lead zirconate titanate ceramics," *Ferroelectrics* , Vol. 41, pp. 277-290, 1982.

5. G. Arlt and H Neumann, " Internal bias in ferroelectric ceramics: origin and time dependence," *Ferroelectrics*, Vol. 87, pp. 109-120, 1988.

6. R. Lohkamper, H. Neumann and G. Arlt , " Internal bias in acceptor-doped $BaTiO_3$ ceramics: numerical evaluation of increase and decrease," *J. Appl. Phys.* , Vol. 68, pp. 4220-4224, 1990.

7. P. V. Lambeck and G. H. Jonker, "The nature of domain stabilization in ferroelectric perovskites,"*J. Phys. Chem. Solids* , Vol. 47, pp. 453-461, 1986.

8. N. Nakatani , " Temperature-independent internal bias field in L-α Alanin-doped triglycine sulfate crystals," *Jpn. J. Appl. Phys.*, Vol. 29, pp. 2038- 2040, 1990.

9. C. Baron and M. C. Gupta, to be published in *Appl. Phys. Lett.*

10. W. D. Johnston Jr. ," Optical index damage in LiNbO₃ and other pyroelectric insulators," *J. Appl. Phys,* Vol. 41, pp. 3279-3285, 1970.

11. W. Bollmann and H.-J. Stohr, " Incorporation and mobility of OH⁻ ions in LiNbO₃ crystals," *Phys. Status Solidi (a)* , Vol. 39, pp. 477-484, 1977.

12. J. R. Herrington, B. Dischler, A. Rauber and J. Schneider, " An optical study of the stretching absorption band near 3 microns from OH⁻ defects in LiNbO₃," *Solid State Commun.,* Vol. 12, pp. 351-354, 1973.

13. L. Kovacs, V. Szalay, R. Capelletti, " Stoichiometry dependence of the OH⁻ absorption band in LiNbO₃ crystals," *Solid State Commun.,* Vol. 52, pp. 1029-1031, 1984.

14. L. Kovacs, M. Wohlecke, A. Jovanovic, K. Polgar and S. Kapphan, "Infrared absorption study of the OH vibrational band in LiNbO₃ crystals," *J. Phys. Chem. Solids,* Vol. 52, pp. 797-803, 1991.

15. O. F. Schirmer, O. Thiemann and M. Wohlecke, " Defects in LiNbO₃-I. experimental aspects ," *J. Phys. Chem. Solids,* Vol. 52, pp. 185-200, 1991.

16. D. P. Birnie, III, " Model for the ferroelectric transition in nonstoichiometric lithium niobate and lithium tantalate," *J. Am. Cer. Soc.,* Vol. 74, pp. 988-993, 1991.
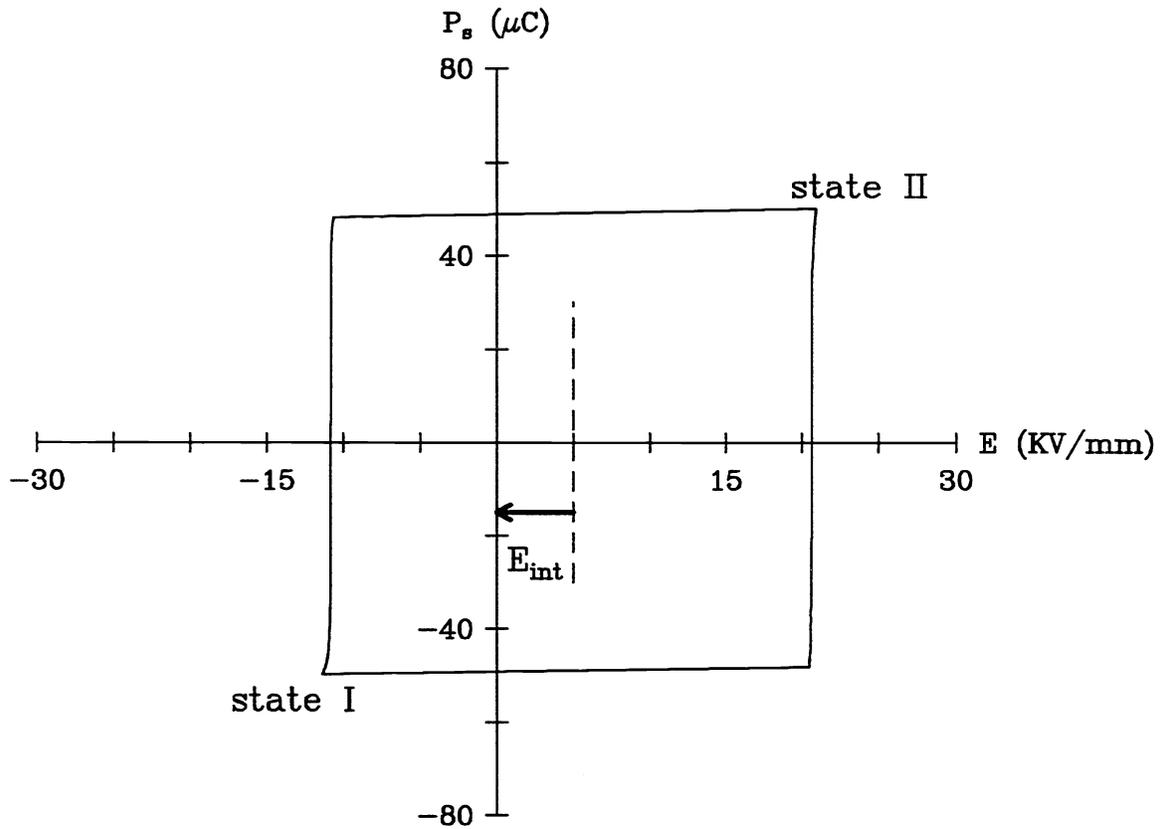
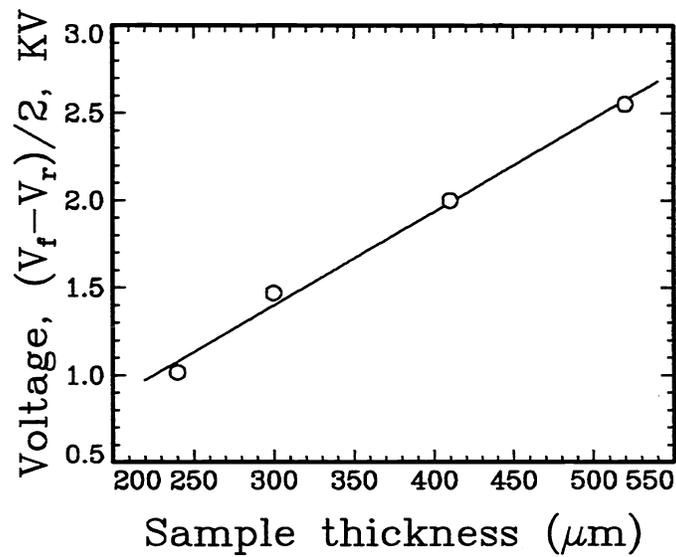Fig. 1. Experimental polarization hysteresis curve of Z-cut LiTaO₃ crystals as a function of external electric field.

Fig. 2. Difference in poling voltages for "forward" (V_f) and "reverse" (V_r) poling as a function of crystal thickness for a Z-cut LiTaO₃ crystal. The slope of the linear fit (solid line) to experiment (circles) gives the internal field (~5.2 KV/mm).
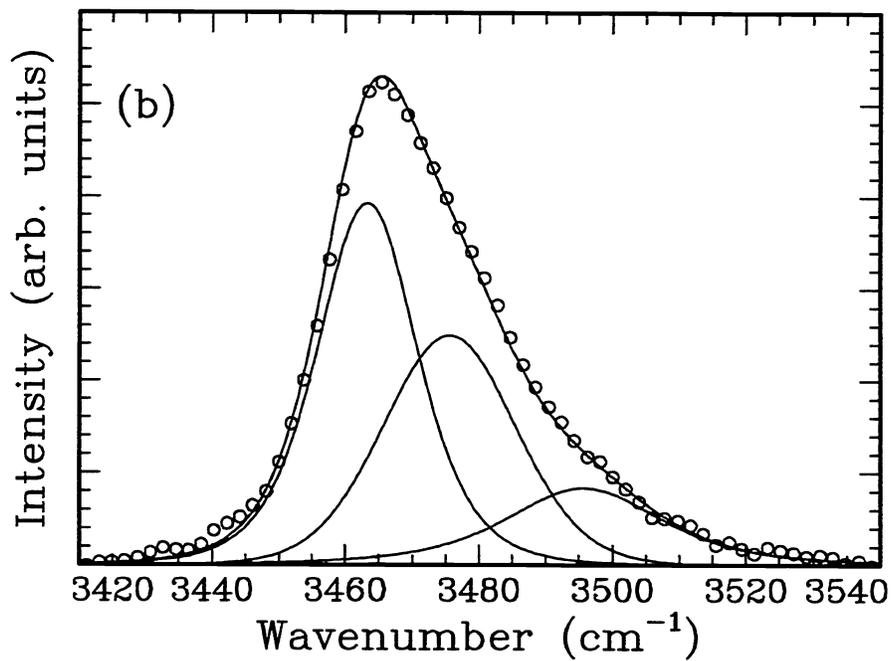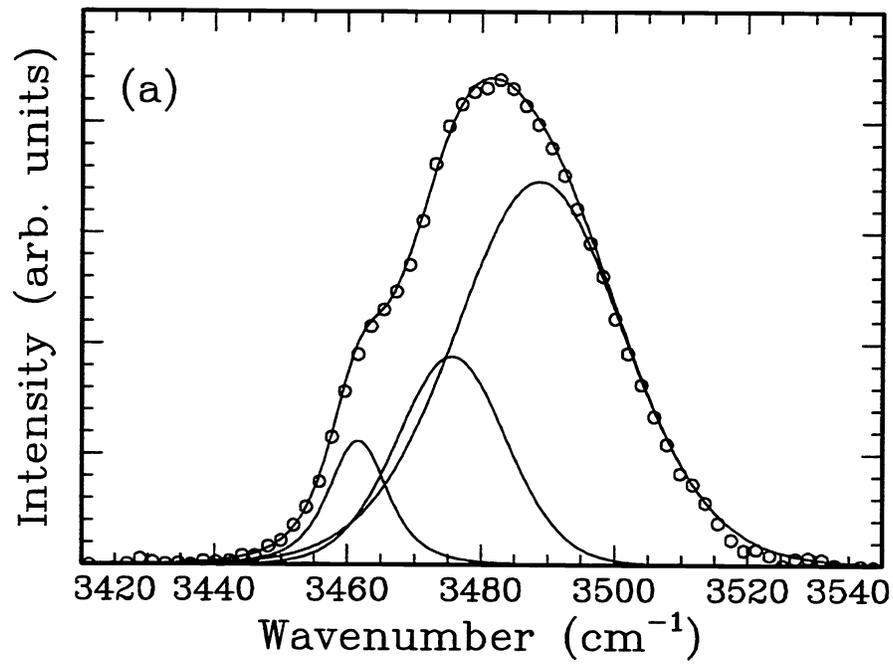
Fig. 3. Infrared absorption spectra of hydroxyl ions (OH⁻) in Z-cut LiTaO₃ for (a) as-purchased "virgin" crystals (b) room temperature polarization reversed crystals. The circles are experimental points and solid lines are fits based on three sub-bands model.