Time dependence of ferroelectric coercive field after domain inversion for lithium-tantalate crystal

Shiuh Chao[a)]
Electrical Engineering Department, National Tsing Hua University, Hsin-Chu, Taiwan, Republic of China

William Davis, David D. Tuschel, Ronald Nichols, Mool Gupta, and Hsing C. Cheng[b)]
Research Laboratory, Eastman Kodak Company, Rochester, New York 14650

(Received 6 April 1995; accepted for publication 8 June 1995)

We found the ferroelectric coercive field of $LiTaO_3$, both in forward and reverse direction, vary with time after the domain is inverted. The coercive field drops when the domain is inverted, then gradually recovers. This phenomenon is light sensitive. The existence of a net time-varying internal electric field after domain inversion is hypothesized. The internal field is composed of the depolarization field, which is due to the spontaneous electric dipole moments, and an opposite direction time-varying space-charge field which is due to the redistribution of free-carriers transport under the influence of the depolarization field. Electro-optical effect caused by the internal electric field has been observed by means of an *in situ* optical monitoring technique for the domain inversion process. The *in situ* optical monitoring technique is based on using the $LiTaO_3$ thin-plate crystal as a low finesse Fabry–Perot interferometer. © *1995 American Institute of Physics.*

Quasi-phase matching (QPM) by periodical inversion of the nonlinear optical coefficient can achieve high conversion efficiency for second-harmonic generation (SHG).[1,2] Periodically inverted ferroelectric domain for achieving this purpose has been demonstrated on laminated[3] and waveguide[4,5] $LiNbO_3$ crystals. $LiTaO_3$ is known for its large nonlinear susceptibility, short wavelength transparency, and better resistance of photorefractive effect.[6] Intensive studies on fabrication, characterization, and performance of SHG device for blue and green lasers on periodically inverted ferroelectric domain $LiTaO_3$ are taking place,[7,8] but studies on basic material properties of $LiTaO_3$ in the domain inversion process are lacking. In this letter, we report our findings and analysis on time dependence of the ferroelectric coercive field after domain inversion of the $LiTaO_3$ crystal.

In this work, we used 0.5 mm thick SAW grade *z*-cut $LiTaO_3$ crystals. Electric field poling method was used to invert the domain. The external field was applied to the crystal plate along the crystallographic *c* axis through transparent liquid electrodes that were in direct contact with the crystal plate sur faces. The external electric field started from 0 V and ramped up at a rate of 16 V per second. Displacement current was measured during the ramping-up period of the external field. The external field was turned off after the displacement current reached its maximum value and dropped back to zero. The external field strength at which the maximum displacement current occurred was taken as the coercive field. It is known, for $LiTaO_3$, the ferroelectric hysteresis loop is asymmetric, and the crystallographic *c* axis is the easy axis. We shall call the direction along which the external field inverts the domain at higher strength the ''forward'' direction, and the opposite direction along which the external field inverts the domain at lower strength the ''reverse'' direction. The procedure for measuring the coercive field in forward direction is described as follows: The sample is first inverted in the reverse direction, the time at which the maximum displacement current occurs is recorded as t_r. After inversion in reverse direction, wait for a certain period of time, then apply the external field in the forward direction, record the time at which the displacement current reaches its maximum value as t_f, the difference between t_f and t_r, Δt, is defined as ''time interval.'' The external field strength at t_f is recorded as the coercive field in the forward direction at Δt. Repeating the same procedure for different Δt, we can obtain the relationship between the forward coercive field and Δt as is shown in Fig. 1(a). The same procedures, except exchanging roles of forward and reverse directions in the aforementioned descriptions, apply to the measurement of the coercive field in the reverse direction. The result is shown in Fig. 1(b). For every measurement of forward (or reverse) coercive field; the sample has to be inverted in the reverse (or forward) direction beforehand. We found that the curves in Figs. 1(a) and 1(b) were independent on when the reverse (or forward) inversion was carried out. It implies that a single domain inversion operation erases the memory of the domain from previous inversion. Therefore, Figs. 1(a) and 1(b) can be directly viewed as changes of coercive field versus time after a single domain inversion operation. The coercive field for the very first domain inversion in forward direction with the brand new sample was 10 900 V/0.5 mm.

In Figs. 1(a) and 1(b), O curves were measured in dark, triangular and square curves were measured under illumination by a fiber-guided tungsten lamp at 40 and 160 mW total optical power level measured at the output end of the fiber, respectively. The illumination was concentrated on a circular area of ~1 cm diam on the sample surface, and it was kept on constantly throughout the measurement process.

Figures 1(a) and 1(b) show that the coercive field dropped right after domain inversion, then recovered. The recovery was fast in the first few minutes after the domain was inverted, then gradually slowing down. We have ob-

[a)]Electronic mail: schao@ee.nthu.edu.tw
[a)]Present address: E-Tek Dynamics Incorporated, San Jose, CA 95131.

 0003-6951/95/67(8)/1066/3/$6.00

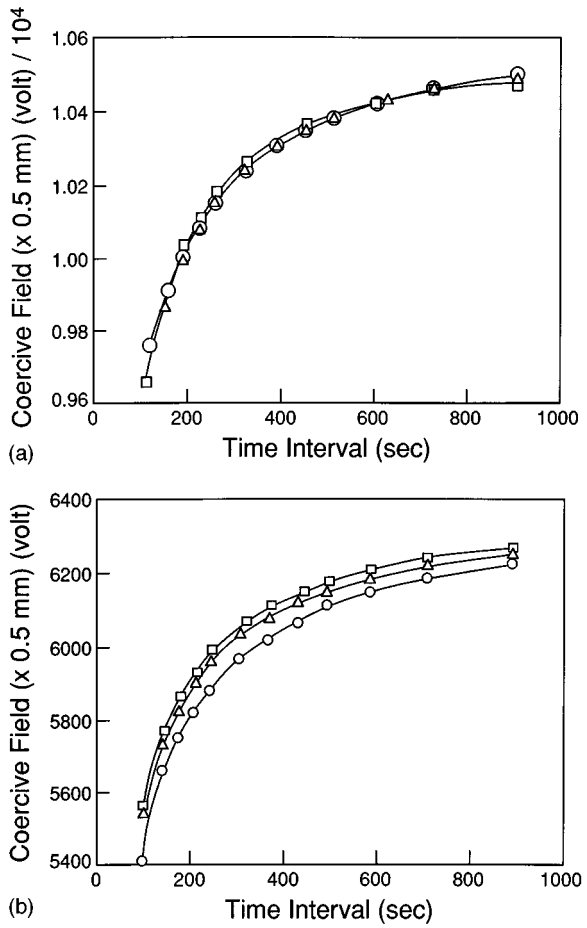

FIG. 1. (a) Coercive field of forward domain inversion versus time interval. (○) in dark, (△) 40 mW, (□) 160 mW. (b) Coercive field of reverse direction domain inversion versus time interval. (○) in dark, (△) 40 mW, (□) 160 mW.

served the recovery process in the time frame of months, the coercive field of forward direction slowly recovering toward its original value of 10 900 V/0.5 mm. These figures also show that the phenomenon is dependent on the intensity level of a relatively white-lighted illumination. The light intensity dependence is stronger for the reverse rather than the forward direction of domain inversion. We have also observed the light-sensitive behavior with SUV illumination for both directions, since the intensity level of the SUV source was not determined, the result for SUV illumination is only qualitative.

Since the coercive field drops after domain inversion, a smaller external field can invert the domain in the following inversion operation. It implies that an internal field might exist after previous inversion, such that the internal field would assist the external field in the following inversion operation. The internal field should be in the opposite direction to the spontaneous polarization, and it is time varying; it gradually decreases to zero, so that the coercive field gradually recovers.

Temperature of the sample surface during light illumination was monitored with a direct in-contact thermal couple. Only room-temperature fluctuation was detected. If there is any change in coercive field produced by room-temperature fluctuation, it should be appeared in curves, that were measured in dark, with the same magnitude as the changes produced by light illumination in other curves, that were measured under light illumination. Figure 1(b) clearly shows that the effect produced by light illumination is not temperature effect, but it is possible related to effects of photogenerated charge carriers.

On the basis of this reasoning, we hypothesize the origin of the phenomenon as follows: There exists a time-varying internal electric field in the crystal after domain inversion. The internal field is composed of the depolarization field caused by the spontaneous dipole moments and a time-varying space-charge field that is in the opposite direction to the depolarization field. After domain inversion, the space-charge field gradually builds until it becomes equal to the depolarization field in magnitude. The space-charge field is due to redistribution and possibly trapping by impurities of free carriers, which consist of the dark carriers and photogenerated carriers. The carriers transport in the crystal under the influence of the depolarization field. The space charges recombine when the spontaneous polarization is inverted, then regenerate and redistribute after the inversion. For low electric conductivity dielectric crystal, the regeneration and redistribution processes of the charge carriers would be slow, these processes would also be dependent on the concentration of the photogenerated charge carrier, therefore, on the intensity level of the illumination.

We have observed that charged toner particles attached strongly to the newly domain-inverted area on the crystal plate. This observation provided a direct qualitative evidence for the existence of an internal field after domain inversion.

An electro-optical effect should be observed if an internal field exists. We have designed a simple *in situ* optical monitoring technique to optically monitor the domain inversion process and time evolution of the internal field. The setup is a simple, low finesse Fabry–Perot interferometer. We used a low power He–Ne laser beam incident with the crystal plate at normal angle along the c axis through the transparent liquid electrode. The reflected light from the top and bottom surface of the crystal plate interfere because of the path difference β

$$\beta = 2\pi n d/\lambda, \tag{1}$$

where n is the ordinary refractive index of the crystal, λ is the wavelength of the He–Ne laser, and d is the thickness of the crystal plate. The change in the ordinary refractive index Δn, caused by the electro-optical effect follows the relationship[14]

$$\Delta n = -\frac{1}{2}\gamma_{13} n^3 E_t - \frac{1}{2} S_{13} n^3 E_t^2, \tag{2}$$

where γ_{13} is the linear electro-optical coefficient, S_{13} is the quadratic electro-optical coefficient, and $E_t = E_{ex} + E_{in}$. The total field E_t is composed of the external field E_{ex} and the internal field E_{in}. All fields are in either $+$ or $-$ c-axis direction. Without knowing the strength of the total field, the quadratic electro-optical effect should not be ignored.

The reflectance R of the system is given as[15]

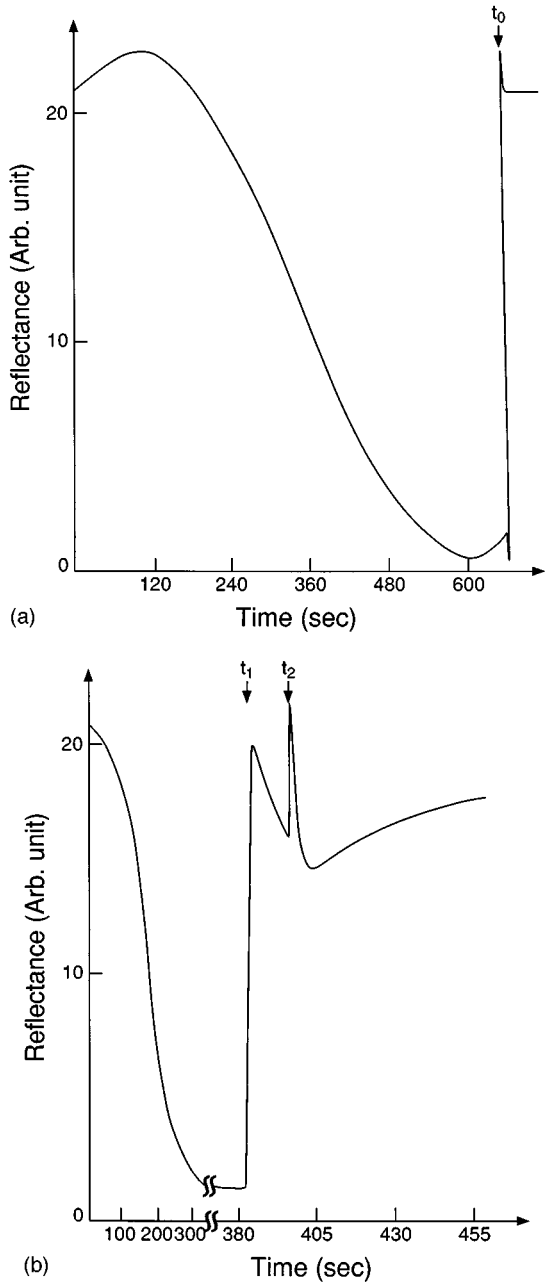

FIG. 2. (a) Reflectance vs time. The external field started from zero at time zero, ramped up at 16 V/s in the direction of spontaneous polarization. (b) Reflectance vs time. The external field started from zero at time zero, ramped up at 16 V/s in the direction opposite to the spontaneous direction.

$$R=|r-re^{-j2\beta}|^2/|1-r^2e^{-j2\beta}|^2, \tag{3}$$

where r is the Fresnel reflection coefficient of the liquid electrode-crystal plate interface.

Because of the large difference between d (0.5 mm) and λ (6328 Å), a change of 6.3×10^{-4} in n would produce a change of π in β, according to Eq. (1). Therefore, according to Eqs. (1)–(3), a small change in n would produce a large variation in reflectance as the total field is varying.

Figure 2(a) shows a typical measured reflectance versus time curve for which the external field was in the direction of spontaneous polarization, such that there is no domain inversion throughout the ramping-up of the external field. The reflectance followed a sinusoidal according to Eqs. (1)–(3) as the external field was ramping up. The external field was turned off at time t_0. The reflectance traced backward rapidly as the external field abruptly decreased to zero in about 5 s. Figure 2(b) shows a typical measured reflectance versus time curve for which the external field was opposite to the spontaneous polarization at the beginning of the ramping-up. The reflectance was changing as the external field was increasing. Around time t_1, displacement current occurred and maximum displacement current occurred at the time when the reflectance underwent an abrupt change, indicating a fast sign change of E_t relative to the inversion of the spontaneous polarization, and the direction of the c axis such that the reflectance traced backward abruptly according to Eqs. (1)–(3). At time t_2, the external field was turned off and it dropped back to zero in about 5 s. The reflectance kept on changing after the external field was turned off. According to Eqs. (1)–(3), the changing reflectance after turning-off of the external field indicated the existence of a time-varying internal field.

We have also observed that with oblique incidence, the reflectance and transmittance of both polarization of the incident He–Ne laser beam undergoes large changes after domain inversion and removal of the external field. This observation indicated that both ordinary and extraordinary refractive index are changed by the internal field through the electro-optical effect.

One can obtain the magnitude of the internal field and its time evolution directly from Figs. 1(a) and 1(b) for time interval greater than ~100 s, which is about the shortest time interval during which we can reset our instruments for the next domain inversion operation. In principle, it is also possible to calculate the magnitude of the internal field and its evolution by using data in Fig. 2(b) and Eqs. (1)–(3), providing that the quadratic electro-optical coefficient is known. It would also be important to further explore the wavelength dependence of this phenomenon. We expect that the wavelength dependence would rely on the band structure and the impurity levels' distribution in the band gap of $LiTaO_3$.

In conclusion, we have found that the coercive field of $LiTaO_3$ crystal drops right after domain inversion and recovers gradually. This phenomenon is light sensitive. We postulated the existence of an internal field to account for this phenomenon. We have observed the electro-optical effect caused by the internal field by means of an *in situ* optical monitoring technique for the domain inversion process.

[1] J. A. Armstrong, N. Bloembergen, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).
[2] S. Somekh and A. Yariv, Opt. Commun. **6**, 301 (1972).
[3] D. Feng, N.-B. Ming, J.-F. Hong, Y.-S. Yang, J.-S. Zhu, Z. Yang, and Y.-N. Wang, Appl. Phys. Lett. **37**, 607 (1980).
[4] E. J. Lim, M. M. Fejer, and R. L. Byer, Electron. Lett. **25**, 174 (1989).
[5] M. M. Fejer, G. A. Magel, and E. J. Lim, SPIE Proc. **1148**, 213 (1989).
[6] G. L. Tangonan, M. K. Barnoski, J. F. Lotspeich, and A. Lee, Appl. Phys. Lett. **30**, 238 (1977).
[7] K. Mizuuchi and K. Yamamoto, Appl. Phys. Lett. **60**, 1283 (1992).
[8] K. Mizuuchi and K. Yamamoto, J. Appl. Phys. **75**, 1311 (1994).
[9] A. Yariv and P. Yeh, *Optical Waves in Crystal*, 1st ed. (Wiley, New York, 1983).
[10] R. M. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, 1st ed. (North Holland, Amsterdam, 1977), p. 285.