PERIODICALLY POLED LITHIUM TANTALATE CRYSTALS CREATED BY INFLUENCE OF OPTICAL RADIATION

R. W. Eason, P. T. Brown and A. R. Pogosyan*

Optoelectronics Research Centre, University of Southampton, United Kingdom;
*Institute for Physical Research, Armenian National Academy of Sciences, Ashtarak, Armenia

Quasi-phase matching by periodical inversion of ferroelectric domains can achieve high conversion efficiency for second harmonic generation [1]. Intensive studies on fabrication, characterization and performance of second harmonic generation devices on periodically inverted ferroelectric domain $LiTaO_3$ crystals are taking place [2], but studies on basic material properties of $LiTaO_3$ in the domain inversion process are lacking. On the other hand all post-growth techniques for achieving periodic domain profiles require either specialist clean-room photolithographic fabrication of patterned electrodes, or lengthy thermal or electron-beam scanning processes. Recently the experiments demonstrating the advantages of direct optical control of ferroelectric domain profiles have been carried out [4]. Here we present our findings and detailed analysis on time dependence of the ferroelectric coercive field after domain inversion of the $LiTaO_3$ crystal and report a simple room temperature technique for patterning the domain profile by the simultaneous application of optical and electric fields without the need for photolithographic processing.

The $LiTaO_3$ crystals used in our experiments were 0.2 mm thick, z-cut optical grade wafers (x, y sides were 10 mm) of Czochralski grown material supplied by Mitsui Corporation, Japan. At room temperature $LiTaO_3$ is ferroelectric with crystal class *3m* (spontaneous polarization P_S = 50 $\mu C\ cm^{-2}$). The direction of P_S is reversed easily by applying an electric field along Z-axis in excess of the coercive field E_C . The external field was applied to the crystal plate through liquid electrodes ($\phi \sim 5$ mm) and was ramp up from 2 kV at fixed rate (see Fig. 1).

The displacement current was monitored during the poling processes (Fig. 2). The external field at which the maximum displacement current occurs is defined as the switching field of the crystal. It is known that the switching fields in forward direction E_f (from "virgin" state of crystal to domain reversed state) and in reverse direction E_r (from domain reversed state to "virgin" state) are different, i.e. the ferroelectric hysteresis loop of $LiTaO_3$ is asymmetrical [4]. Moreover

it was found that E_f and E_r depend also on time between two successive poling operation (we define it as time interval Δt) and light intensity [5]. In [6] it was shown that the asymmetry of switching electric fields depends on temperature and there is necessity of stabilization time after switching.
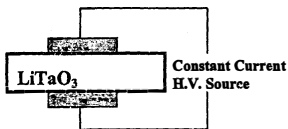

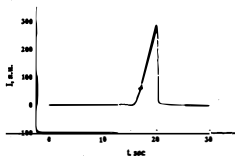Fig. 1. The experimental setup

Fig. 2. The displacement current during the poling process

In Fig. 3 the switching electric field vs time interval Δt in forward direction measured in our experiments is presented.

Now we consider in more detail physical processes occurring at the poling of ferroelectric crystals. In the single domain ferroelectric crystal spontaneous polarization P_S there is an electric field equal to $P_S/\varepsilon\varepsilon_0$ (it is the depolarization field E_d). It is clear from energetic reasons that this
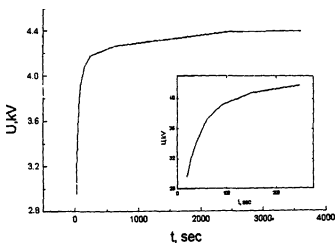

Fig. 3. Switching electric field vs time interval Δt in forward direction

field has to be screened. It is known also that even in wide band dielectric screening may be internal and have purely electronic nature. Add that the availability of surface electronic levels may also give the essential contribution to the screening. The screening, reducing the free energy of a single domain crystal, makes possible the existence of single domain crystals. At cooling of a crystal from phase transition temperature T_C up to room temperature there is a continued growth of polarization (and E_d) and correspondingly it is necessary the increasing of space charge field E_S which has to screen E_d. Note that in various temperature intervals the screening is executed by those carriers, which determine the conductivity of a crystal. In lithium tantalate, as it is known, the conductivity at $T > 150^oC$ has ionic character and at $T < 150^oC$ - electronic. Thus a space charge field E_S, screening the depolarization field E_d, consists of two components: electronic E_e and ionic E_i.

So the total internal field in the crystal is: $E_{int} = (E_d - E_s)$. In steady state this field is equal to a zero and switching field is equal to coercive field E_C. The screening space charge is concentrated in a surface layer of the crystal, the thickness of which is equal to a Debye length of a screening $L_D = (\varepsilon \varepsilon_0 kT / e^2 n)^{-1/2}$, where n is a concentration of carriers.

Let now consider the processes of poling and repoling in a crystal (Fig. 4).

a) State I: virgin, t = ∞   b) State II: domain reversed, t = 0

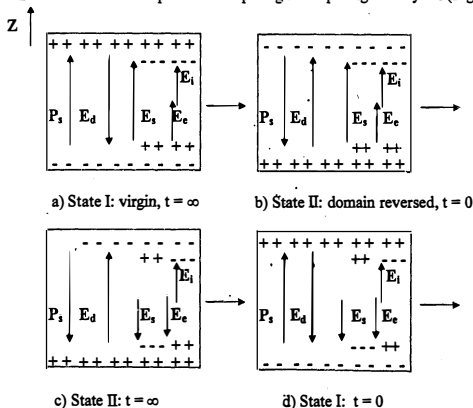c) State II: t = ∞   d) State I: t = 0

Fig. 4

Fig. 4 (a) corresponds to virgin state of crystal when we can write for switching electric field in forward direction:

$$E_f(\infty) = E_c - E_{int} = E_c - (E_d - E_s) = E_c - E_d + E_e + E_i = E_c' + E_e + E_i = E_c^{ef}. \quad (1)$$

Here E_c^{ef} is the effective coercive electric field of the crystal and $E_c^{ef} \approx E_c$. After switching in forward direction P_S and E_d change their direction but E_S at t=0 doesn't change and becomes antiparallel to the new polarization direction (and parallel to the new depolarization field direction). So we can write for switching electric field in reverse direction at t=0 (Fig. 4b):

$$E_r(t=0) = E_c - E_{int} = E_c - (E_d + E_s) = E_c - E_d - E_e - E_i = E_c' - E_e - E_i = (E_c^{ef} - 2E_e - 2E_i). \quad (2)$$

This state is not stable because there is a large internal field $E_i = E_d + E_s$ in the crystal. So the space charge field E_S in this domain reversed state tends to realign antiparallel to the new depolarization field direction with time (note, if $E_c^{ef} - 2E_e - 2E_i < 0$ then we need a time for stabilization of state II; we can define this time as time when $E_r(t) = 0$). But this realignment is incomplete even after long time at room temperature because only electronic component of space charge field E_e may realign due to electronic conductivity while ionic component stays stable (at room temperatures the ionic conductivity is "frozen"). So the internal field in this state is not equal to zero (below we more detailed consider why the electronic component can not completely screen the ionic field; but briefly we can say that the situation is very similar with the temperature fixing of holographic recording) and we have (see Fig. 4c):

$$E_r(\infty) = E_c - E_{int} = E_c - (E_d - E_s) = E_c - E_d + E_e - E_i = E_c' + E_e - E_i = (E_c^{ef} - 2E_i). \quad (3)$$

We can see that there is a large asymmetry for forward (1) and reverse (3) switching fields and it is equal to $2E_i$. It means we have large internal field in State II (there are some experimental evidences of the existence of a strong internal electric field after domain inversion [6]). After poling crystal from domain reverse state II back to the virgin state I we have (Fig. 4d):

$$E_f(t=0) = E_c - E_{int} = E_c - (E_d + E_s) = E_c - E_d - E_e + E_i = E'_c - E_e + E_i = (E^{ef}_c - 2E_e). \quad (4)$$

The situation in the state I at t=0 is like the situation in the state II at t=0. In this state also there is stabilization time (if $E^{ef}_c - 2E_e < 0$), but in this case it have to be smaller. Then after screening of depolarization field we again obtain the crystal in virgin state (Fig. 4a and eq. (1)).

From this phenomenological consideration of the poling processes we can write the joint expression for necessary switching electric fields in forward and reverse directions:

$$E_{f,r}(t) = E'_c + E_e(1-2\exp(-t/\tau_e)) + E_i(1-2\exp(-t/\tau_i)) = E^{ef}_c - 2E_e \exp(-t/\tau_e) - 2E_i \exp(-t/\tau_i), \quad (5)$$

where τ_e, τ_i - relaxation times for electronic and ionic components of space charge electric field.

In (5) there is no difference between virgin and domain reversed states or between forward and reverse poling processes. This equation is correct if τ_i is not very large. But because $\tau_i = \varepsilon\varepsilon_o/\sigma_i$ (σ_i - ionic conductivity of the crystal) we can use eq. (5) only when the crystal temperature T>150 °C. At lower temperatures due to "frozen" ionic conductivity we obtain different expressions for forward and reverse poling:

$$E_f(t) = E'_c + E_e(1 - 2\exp(-t/\tau_e)) + E_i = E^{ef}_c - 2E_e \exp(-t/\tau_e), \quad (6)$$

$$E_r(t) = E'_c + E_e(1 - 2\exp(-t/\tau_e)) - E_i = E^{ef}_c - 2E_e \exp(-t/\tau_e) - 2E_i. \quad (7)$$

Note that virgin and domain reversed states are distinguished only by their "history". If we heat the crystal in domain reversed state up to 150 C and activate the ionic conductivity then the domain reversed state is become the virgin state and contrary.

Now we will try to calculate the parameters of the eq. (6) and (7) using experimental data. From Fig.3 and [4,5] we can obtain: $E_f = 210$ kV/cm, $E_r = 130$ kV/cm, $E_i = 40$ kV/cm.

The approximation of an experimental dependence $E_f(t)$ in Fig. 3 with the help of equation (6) shows, that the experimental curve is described by the equation which is similar (6), but have two exponents (we consider yet not the weak dependence of E_f on t at t > 300 sec; this fact we'll consider below):

$$E_f(t) = E_c' + E_e^f (1 - 2exp(-t/\tau_f)) \ + \ E_e^s (1 - 2exp(-t/\tau_s) + E_i \ , \qquad (8)$$

where $E_e^f + E_e^s = E_e$. The parameters' values obtained from Fig. 3 are equal to: $E_c' = 50$ kV/cm, $E_e = 120$ kV/cm, $E_e^f = 90$ kV/cm, $E_e^s = 30$ kV/cm, $\tau_f = 6$ sec, $\tau_s = 130$ sec.

On Fig.5 the dependencies of $E_f(t)$ and $E_r(t)$ calculated from eq. (8) are shown. You can see, that the equation (8) describes both the asymmetry of switching fields and asymmetry of stabilization times.
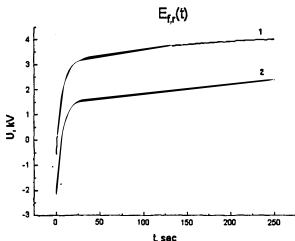

Fig. 5. The calculated dependencies of switching electric fields in forward (1) and reverse (2) directions on time interval between poling processes.

Let's consider a physical sense of equation (8). Earlier we noted that E_i is the uncompensated part of an ionic component of a space charge electric field screening a depolarization electric field. We have named two other parameters E_f and E_s as fast and slow components of an electrical field screening the spontaneous polarization. The physical nature of a fast component is not so clear. As it was mentioned in [6] it may be a reorientation of dipole moments of point defects or it may be high conductivity in very high electric fields. In any case for clearing up of a nature of this component the additional investigations are necessary. As to a slow component this component has an only electronic nature and is conditioned by redistribution of electrons' space charge due to electronic conductivity. This supposition is confirmed by the fact that the

relaxation time τ_s rather well coincides with a Maxwell relaxation time τ_m (direct measurement has shown, that dark conductivity for our samples is equal $3*10^{-13}\ \Omega^{-1} cm^{-1}$ and corresponds $\tau_m = 120$ sec). It means, that the relaxation time (and $E_{f,r}$) depends also on light intensity because $\tau_m = \varepsilon\varepsilon_o/(\sigma_d + \sigma_{ph})$, where σ_{ph} is a photoconductivity. Such dependence was observed in experiments [5] and also in our experiments. One practical conclusion also ensues from this. As it is seen from (8) the magnitude of a switching field in case of illumination of crystal in a defined time frame is higher than without illumination. Thereby for partial illumination of crystal the illuminated sites are poled at the higher values of an applied field than not illuminated. So there is a possibility of control of the domain structure with the help of light. Naturally for this it is necessary $\sigma_{ph} > \sigma_d$.

We shall return to a question why after poling the complete compensation of depolarization fields does not occur and there is an asymmetry of switching fields in forward and reverse directions. As we already marked, in Fig. 3 there is a weak dependence of E_f from t at $t > 300$ sec., i.e. the curve E(t) is not actually described completely by the exponent. In this area τ_m begins to increase and the screening of depolarization field goes slower and slower, and in domain reversed state the complete compensation is not reached.

One of reasons of τ_m increase may be a reduction of a charge carriers concentration in the crystal volume owing to a very large concentration of the carriers in a surface layer (the concentration of carriers in the L_D area should reach $10^{18}\ cm^{-3}$). And the concentration of carriers necessary for complete screening, naturally, depends on value of electric field, which should be screened (in state II: (Ed + Ei), in state I: (Ed - Ei)). Thus, at identical concentration of carriers, the value of a noncompensated electric field in domain reversed state is higher than in virgin state, as results in asymmetry of switching fields.

Other possible reason may be diffusion current owing to a same large concentration of carriers in the L_D layer (similarly to a temperature fixing of the holograms). This process is essential in domain reversed state, where it is necessary to compensate much more large fields. As this effect works on the L_D length, it results to the increase of L_D, i.e. to the increasing of noncompensated internal field in a crystal.

However, unfortunately, at the present time the experimental data are not enough for an unequivocal conclusion about the mechanisms of this process.

As we have mentioned above our experiments have shown the possibility of direct optical control of domain patterning in LiTaO$_3$ crystals. We used special z-cut crystals for obtaining a light interference pattern in the crystal volume (see Fig. 6). To optimize the fringe stability, and reduce Fresnel losses from additional optics, a biprism was polished directly onto Y-face. The apex thus formed bisected the incident UV laser beam, ensuring good spatial overlap beneath the electrode area. The polish angle was chosen so that the interference pattern formed had a periodicity that was both small enough to demonstrate the utility of the technique, but large enough to be easily visible under a polarizing optical microscope. The calculated periodicity within the crystal was 5.2 μm for an angle 1.5°. However, due to polishing tolerances available, the inherent divergence of the incident laser beam, and the use of a weakly convergent cylindrical lens to help increase the incident UV irradiance, the measured periodicity obtained from optically frustrated poling here was ~ 6.3 μm.

Fig. 6
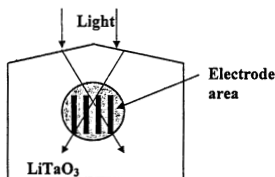
Optical illumination was provided by UV lines (predominantly 364 and 351 nm) of an Ar ion laser. Using cylindrical optics the beam was launched into the wafer through the +Y face. In order to assess the effect of the UV illumination during poling process the resulting structure was examined under an electronic microscope after etching of Z-face of the crystal. After simultaneous applying of UV light and switching electric field for poling in the forward direction we have obtained periodically domain-inverted structure under the electrode area with ~ 6.3 μm period.

References

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