

**Control of domain structures in lithium tantalate  
using interferometric optical patterning.**

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***Abstract***

We report a room temperature technique for periodically inverting the domain structure in a lithium tantalate crystal, via the simultaneous application of optical and electric fields. Ultraviolet light from an Ar ion laser was incident on a 200 $\mu$ m thick z-cut lithium tantalate crystal, illuminating the y face which had been polished to form a bi-prism. The resulting interferometric pattern, formed between planar liquid electrodes applied to the +z and -z crystal faces, had a period of 6.3  $\mu$ m. We show the results of optical control of the poling process, and discuss the theory behind light induced ferroelectric switching.

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## 1. Introduction.

The patterning of domain structures within ferroelectrics continues to attract great interest for a number of applications ranging from quasi-phase matched (QPM) nonlinear optical frequency conversion via second harmonic and parametric generation processes [1], to fabrication of novel electro-optic Bragg deflectors [2], and even two dimensional photonic band gap (PBG) devices [3]. The period of domain inversion required for QPM applications lies in the few  $\mu\text{m}$  to tens of  $\mu\text{m}$  region, whereas PBG devices require sub- $\mu\text{m}$  scale lengths for operation in the visible spectral region.

Electric field poling has become the established method for achieving high quality periodically poled structures in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . Using patterned electrodes, periods down to  $\sim 2 \mu\text{m}$  are routinely produced, by applying an electric field between the +z and -z faces which exceeds the coercive field  $E_c$  : ( $E_c = 22.5\text{kV mm}^{-1}$  for  $\text{LiTaO}$  at room temperature in the samples we have measured [4]). Although conceptually simple, this method requires access to photolithographic patterning facilities, and subsequent high voltage application. The quality of the resultant periodically poled material can depend on a number of factors, including the definition of the patterned photoresist and hence electrodes, the mark-to-space ratio used, the type of liquid or gel electrodes used, the exact procedure for high voltage application, displacement current monitoring and so forth. Periodicities below  $\sim 2 \mu\text{m}$  are difficult to produce however, particularly with simultaneously large aspect ratios , and hence other methods are currently being investigated that do not rely on applied electric fields alone.

An alternative method for the production of periodically patterned domain structures is optical periodic poling, a technique involving the simultaneous application of combined electrical and optical fields: the electric field is applied via *planar* electrodes, while light is used to define those regions where domain inversion should occur. The optical poling route therefore offers a potentially simpler method, effectively eliminating the photolithographic patterning steps, and associated clean room fabrication requirement. Using interferometric methods, the periodicity of optically induced domain structures is a function of laser wavelength, and intersection angle of the two interfering beams, and hence is easily changed. Submicron periodicities can readily be achieved, by generating interference patterns using UV light, and by adopting a counterpropagating standing wave geometry, periods of <100nm can be realised.

There have been several reports of this optical poling technique within the past few years, in materials such as  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  (SBN) [5-7] and  $\text{LiTaO}_3$  [4,8,9]. With specific reference to  $\text{LiTaO}_3$ , earlier work has shown that light can influence the internal field that is present within the crystal [8-10]. Photogenerated charge carriers within illuminated regions of the crystal can increase the local coercive field. By ramping the applied electric field up to, but not beyond the optically elevated value of coercive field, domain inversion can be locally controlled. Illuminated regions experience frustrated poling, where domain reversal will not occur, while the surrounding unilluminated regions experience normal domain inversion.

The presence of an internal field reveals itself in the observed asymmetry of the ferroelectric hysteresis loop. There is an inequivalence between the +z and -z crystal directions, which

manifests itself in a difference in the  $E_c$  required to achieve domain inversion when poling in the 'forward' and 'reverse' directions. This inequivalence in the value of  $E_c$  in the forward direction,  $E_f$ , and the reverse direction,  $E_r$ , is evidence of a frozen-in internal field, which is probably ionic in character, and is extremely long-lived at room temperature. Additionally, there is an internal electric field which is electronic in origin, and which relaxes at a much faster rate following repoling. It should be noted here that the underlying causes and temporal behaviour of these internal field components is somewhat involved. Existing literature is not consistent regarding the various field components, their origins and dynamic behaviour following a domain reversal. Fast and slow components have already been proposed within the internal field recovery process [11], but their role within the context of optical poling has not yet been adequately described. We have identified at least three separate recovery processes, with time constants spanning a few seconds to several months, which we discuss in more detail later.

A further complication arises when several *successive* forward and reverse polings are performed. The first forward poling has an  $E_c = E_{f1}$ , the second an  $E_{r2}$  and so on, with equivalent nomenclature applying to the reverse poling case,  $E_{r1}$ ,  $E_{f2}$  etc. The values of  $|E_{f1} - E_{r1}|$ , and also  $|E_{f1} - E_{r2}|$  are a function of the time elapsed between polings, due to relaxation of internal electric fields [8,9]: light incident on the crystal can assist this field relaxation, thereby enabling the light induced domain manipulation reported here.

Due to its large nonlinear optical coefficients, short wavelength transparency and commercial availability, recent reports concerning optical poling have predominantly addressed  $\text{LiTaO}_3$ .

LiNbO<sub>3</sub> is also a good candidate for optical poling, and has so far been the material most extensively researched in the context of quasi-phase matched nonlinear optical interactions. We have also investigated optical poling in LiNbO<sub>3</sub> but have observed, as has also been reported in [12], that the displacement current recorded during domain inversion is not well defined. For LiTaO<sub>3</sub>, with planar electrodes, the displacement current profile is smooth with an approximately triangular profile obtained under ramped voltage conditions. LiNbO<sub>3</sub> however, yields a displacement current that is spiky and ill-defined, with a FWHM width approximately twice that of LiTaO<sub>3</sub>.

Chao et al. were the first to report optical poling behaviour in LiTaO<sub>3</sub>, to our knowledge, using a tungsten lamp [8], and laser source [9] respectively. Subsequent reports by Ross et al [4] used shadowing of a 280µm binary grating to achieve patterned domain poling using UV illumination. In this paper we report what we believe to be the first example of optically controlled periodic domain patterning in LiTaO<sub>3</sub> using an interferometric technique, which has been suggested, but so far not reported to our knowledge.

## **2. Experimental arrangement.**

Figure 1 illustrates the experimental arrangements used. UV light from an Ar<sup>+</sup> laser was used at a total power of ~150mW. The laser was operated without an intracavity wavelength selecting prism assembly, so all lines within the lasing spectral region between 351nm and 364 nm could in principle lase simultaneously. In practice, even without wavelength selection, the majority of the lasing output (~70%) was at the wavelength of 364nm. Figure

1(a) illustrates a y-face illumination experiment, which has been reported before in [4], and is the orientation adopted for the interferometric patterning experiments reported here. Figure 1(b) illustrates a z-face illumination experiment, which requires that the electrode material is transparent to the incident UV light. Although optically assisted domain frustration was observed in this configuration, the possibility that any periodic patterning observed could merely have been due to UV light induced chemical degradation of the transparent liquid electrodes added an undesirable experimental uncertainty.

The LiTaO<sub>3</sub> was 200 μm thick, optical grade, congruent composition, single domain, z-cut material (purchased from Roditi International). Several methods were investigated for producing interferometric patterning within the LiTaO<sub>3</sub> crystal as illustrated in figure 2. To optimise the fringe stability, and reduce Fresnel losses from additional optics, a biprism was polished directly onto the y-face. The apex thus formed bisected the incident UV laser beam, ensuring good spatial overlap beneath the electrode area. The polish angle,  $\theta$ , 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 polarising optical microscope. From figure 3, which is a more detailed version of the schematic in figure 2(c), we see that the fringe spacing is determined by the angle  $\theta$ , the incident free space wavelength  $\lambda$ , and the crystal refractive index,  $n_e$ , accessed by the incident vertically polarised laser beam. The periodicity,  $\Lambda$ , within the crystal is therefore given by:

$$\Lambda = \lambda / [2 n_e \sin\{\theta - \sin^{-1}(\sin\theta / n_e)\}] \quad (1)$$

Using a value of  $n_e = 2.335$  at  $\lambda = 0.364 \mu\text{m}$ , [13], yields a value of  $\Lambda = 5.2 \mu\text{m}$  for an angle  $\theta = 1.5^\circ$ . However, due to the 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 the optically frustrated poling reported here was  $\sim 6.3 \mu\text{m}$ .

As indicated in figure 1(a), an external electric field was applied across the crystallographic z-axis, over an electrode area,  $A$ , to produce domain inversion. This was achieved by ramping the voltage at a fixed rate, until the d.c. field exceeded the (time dependent) coercive field. The signature for domain inversion was a displacement current,  $i$ , corresponding to movement of charge  $q = 2P_s A$ , where  $P_s$  is the value of spontaneous polarisation for  $\text{LiTaO}_3$ , with a value of  $50 \mu\text{C cm}^{-2}$  [10]. The coercive field was recorded as the value corresponding to the peak in the displacement current traces obtained. The voltage start and end points, ramp rates and displacement current monitoring were all under computer control. It was of critical importance to maintain the applied field for the correct time, to ensure domain reversal in the unilluminated areas. During a careful study of electric field addressed domain inversion in  $\text{LiTaO}_3$ , Gopalan and Mitchell [11] have investigated domain inversion dynamics, as a function of the magnitude and duration of the applied electric field. They have established that a domain stabilization process occurs, whereby the applied electric field must be maintained for durations of  $\sim 2\text{s}$  for forward poling, and  $\sim 0.2 \text{s}$  for reverse poling. It is thus very important to use a voltage ramp rate that is both slow enough that the applied field does not exceed the value of coercive field in the illuminated areas during this domain

stabilisation time, and fast enough to maximise the difference between coercive fields in illuminated, and unilluminated regions, as this difference is itself time dependent. Further discussions of this aspect are dealt with in the following theoretical section.

All experiments were conducted on new 'virgin' crystals. Samples could be poled in either forward or reverse directions, with a time delay,  $t$ , between successive polings. The use of a computer controlled voltage ramp meant that the minimum delay between successive polings was  $\sim 20$ s however. This is somewhat faster than the minimum delay times reported in [8,9], and has allowed us to observe and measure the time constants for an assumed double exponential recovery behaviour. When optically frustrated poling was implemented, the UV laser beam illuminated the crystal from the start of a poling run, and was focussed down to fill the 200  $\mu\text{m}$  aperture of the  $\text{LiTaO}_3$  sample. Before we describe the results of periodic domain patterning, we discuss some relevant aspects concerning the coercive field measured under repetitive forward and reverse poling, and the implied presence of an internal electric field which can be manipulated to enable optical frustration of domain repoling.

### **3. Theoretical considerations.**

Earlier work has established that the coercive field required to pole a crystal of  $\text{LiTaO}_3$  is different in the forward and reverse poling directions:  $E_f \neq E_r$  [8-12]. Furthermore, there is also a difference between the value of coercive field for the first forward poling,  $E_{f1}$ , and subsequent forward polings,  $E_{f2}$ ,  $E_{f3}$ , etc. To this extent  $E_{f1}$  represents a unique value of coercive field, which is recorded for virgin crystals only. Shown in figure 4, is a schematic



of the results we have obtained for  $E_{fi}$  and  $E_{ri}$  ( $i= 1$  to  $n$ ) for a virgin  $\text{LiTaO}_3$  sample. It has also been pointed out in [8,9] that the value of both forward and reverse coercive fields is a function of elapsed time,  $t$ , following a previous poling, and that  $E_{fr}(t)$  is sensitive to external parameters such as the presence of an external light field. In the absence of any external influence,  $E_c(t)$  will gradually recover to its original value,  $E_c(\infty)$ . This internal field has been hypothesized as being composed of a depolarization field, and a time varying space-charge field, of opposite sign [8]. The action of an external influence such as light can speed up the recovery of this internal space-charge field, thereby increasing the rate at which  $E_c(t)$  returns to  $E_c(\infty)$ .

There are several complicating factors here however. The first is that there is little direct evidence concerning the exact nature of the internal field present. The recovery process by which  $E_c(t)$  returns to  $E_c(\infty)$  must involve the internal rearrangement of electric fields associated perhaps with point defects,  $\text{OH}^-$  complexes, and local non-stoichiometry [10-12]. While the macroscopic parameters of this recovery process can be investigated and controlled, the microscopic explanation is still the subject of discussion. Recent results report the most conclusive evidence so far relating the origin of the internal field to the concentration of nonstoichiometric point defects in  $\text{LiNbO}_3$  [12] and  $\text{LiTaO}_3$  [14]. The second factor concerns the exact time dynamics of the recovery of the internal field. The ability to control the *differential* recovery rate between a sample that is exposed to light, and a sample kept unilluminated is the basis for light induced domain frustration. In [8,9], the authors present recovery curves that appear to follow a simple exponential:  $E_c(t)$  should therefore obey the following equation:

$$E_c(t) = E_c(\infty) - \{E_c(\infty) - E_c(0)\} \exp(-t/\tau) \quad (2)$$

where  $E_c(0)$  is the value of the coercive field at time  $t=0$ , and  $\tau$  is the relevant time constant.

The problems here are two-fold. Firstly, as the minimum time required in our experiments to change the polarity of the applied field, and hence repole the sample, is  $\sim 20$ s, we have no method of directly measuring  $E_c(0)$ . Secondly, our experimental data reveals that the recovery process is not governed by the expected single exponential suggested by equation (2). There appears to be at least three time constants involved in the recovery process, one corresponding to ionic conductivity, which is not influencable by an external light field, and two due to electronic conductivities, as discussed further below.

Figure 5(a) shows the results obtained for  $E_c(t)$ , for time delays spanning values of 20s to 3600s. A virgin sample, cut from the same  $\text{LiTaO}_3$  wafer was used for each data point. Following equation (2) above, a plot of  $\ln[E_c(\infty) - E_c(t)]$  versus  $t$  should yield a straight line graph, with gradient  $-1/\tau$ , and intercept  $\ln[E_c(\infty) - E_c(0)]$ . Clearly the data we obtain does not fit to this single exponential equation, as seen in figure 5(b). We have performed a least squares fit to the data in figure 5(a), assuming an equation of the form:

$$E_c(t) = E_1 [2\exp(-t/\tau_1) - 1] + E_2 [2\exp(-t/\tau_2) - 1] \quad (3)$$

as suggested in [11], where  $E_{1,2}$  represent values of internal field components, with respective time constants  $\tau_{1,2}$ . Examination of equation 3 shows that at time  $t=0$ ,  $E_c(0) =$

$E_1 + E_2$ , while for long delay times  $E_c$  approximates to  $-(E_1 + E_2)$ . From the results of figure 5(a) in which  $E_c(t)$  is positive for long delay times, we expect the value of  $E_c(0)$  to be negative. The fit results show that a double exponential of this form can provide good agreement to the data, yielding two time constants of values  $\tau_1 = 8.3 \pm 0.8\text{s}$ , and  $\tau_2 = 132 \pm 49\text{s}$ . The error bars for this second component are large due to the accuracy required to measure values of coercive field that are very close to their fully recovered values. Ideally, more results are required in the time spans covering 1,000s to >10,000 s. The values of internal field components are  $E_1 = -3.89 \pm 0.1\text{ kV}$ , and  $E_2 = -0.465 \pm 0.1\text{ kV}$  for the 200  $\mu\text{m}$  thick sample.

Shown in figure 6 is the best fit curve for this calculated internal field recovery, with our experimental data superposed. Of interest is the time at which this internal field changes sign. The mechanism by which new domains are stabilised relies on a sign change of the internal electronic field components. The time at which this field reverses sign can be deduced from the fitted results to be  $\sim 6.5\text{s}$ . This value is interesting, as it is of similar order to the values of domain stabilisation measured experimentally for  $\text{LiTaO}_3$  [11]. We can also confirm these results, obtained during our optical poling experiments. Unless the applied d.c. field is maintained for several seconds following a domain inversion, back flipping can occur, leaving no net observable domain patterning. This has been a serious problem in our work so far, and this fast component within the internal field recovery process may well be the cause of such domain stabilisation behaviour.

Following the results in [9], we chose a standard time delay of 90s between one poling cycle

and the subsequent repoling. This was not the shortest time delay that had been achieved in performing repoling experiments, as shown in the data in figure 5(a), but an intermediate realignment check was always necessary under interferometric patterning experiments. Ideally, the shortest delay time possible would be most desirable, to maximise the difference between the time-dependent values of coercive field  $E_c'(t)$  and  $E_c(t)$ , in the presence, and absence, of external illumination respectively. We also ensured that the applied field was maintained for at least two seconds after domain inversion so that self back-switching did not occur, as discussed earlier [11]. Successful optically frustrated domain inversion simultaneously requires therefore a sufficiently large value of  $E_c'(t) - E_c(t)$ , and a voltage ramp rate which is slow enough so that the applied field does not exceed  $E_c'(t+t')$ , where  $t'$  represents the several seconds required for domain stabilisation. As can be seen, using an arbitrarily slow ramp rate is not sufficient, due to the natural time dependence of both  $E_c$  and  $E_c'$ .

#### **4. Experimental demonstration of periodic patterning**

A series of experiments was performed using the arrangement shown in figure 3. The  $\text{LiTaO}_3$  wafers were not pre-exposed to any UV light, to avoid the possibility of any latent patterning effects. Following optical periodic poling, the exposed wafers were etched in a 1:2 mixture of HF and  $\text{HNO}_3$  acids for 5 hours, to allow differential etching of domains, to reveal the presence of any periodic patterning. Microscopic examination of the crystal through crossed polarisers reveals a periodic structure which was largely confined to the front section of the electrode area, where the UV intensity was greatest. Figure 7 shows a

portion of this pattern, which illustrates several typical regions of interest. Region (a) illustrates the periodic patterning, that was present in the central region of the interference pattern. Uniform domain frustration has not been achieved so far however, as seen in region (b), where the  $\text{LiTaO}_3$  crystal has started to invert in the characteristic triangular shapes seen during normal electric field poling. Region (c) illustrates areas that did not achieve uniform contact between electrode and the crystal surface, due to the nature of the gel electrode material. The important region (a) however, shows the clear influence of optical frustration leading to periodic patterning.

The limitations experienced so far include the high absorption constant of  $\alpha = 4 \text{ cm}^{-1}$  experienced by the UV light, on traversing the crystal in this y-face orientation. An alternative, which needs to be explored further, involves illumination of the crystal z-face, as illustrated in figure 1(b), and we shall be returning to this orientation, which has the capacity for producing larger area, more uniform periodic domain patterning.

Further work is also in progress in two related areas. Photonic band gap devices in  $\text{LiTaO}_3$  and  $\text{LiNbO}_3$  are envisaged through the use of either standing wave optical poling, followed by etching, or the use of phase masks, operated in the near-field illumination regime, where complex 2-d and even 3-d optical patterns can be generated [15]. We are currently investigating precision micro-engineering of domain structures, on a submicron scale, using the above techniques. Secondly, work is in progress which relates the presence of this noncompensated internal field, which leads to the observed hysteretic behaviour, to ionic and electronic conductivities following forward and reverse poling. These results will be

published elsewhere.

## **5. Conclusion**

In conclusion we have demonstrated that the domain structure of lithium tantalate may be periodically inverted using optical interference patterning techniques. The chief benefit to such a technique is the ability to fabricate small, submicron period gratings, which will open up possibilities for applications involving backward wave parametric generation. Chirped gratings, and other non-standard spatial profiles are also a possibility using such optical addressing. Two components have been identified in the internal electronic field recovery process, the faster having a time constant of the same order as previously reported domain stabilisation times.

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## Figure captions

Fig 1. Illumination geometries adopted for optical poling experiments.

(a) y-face illumination in which light propagates along the crystal y direction. This arrangement has already been reported in ref [4].

(b) z-face illumination, in which light is transmitted through transparent liquid electrodes. Light propagates along the crystal z direction.

Fig 2. Schematics of optical poling through interferometric patterning: (a) illustrates normal two beam interference. (b) illustrates the use of an external Fresnel biprism. (c) shows the arrangement adopted here, in which the biprism is directly polished onto the front crystal surface.

Fig 3. Detailed version of figure 2(c), showing nomenclature used for the polish angles.

Fig 4. Coercive field values,  $E_c$ , determined for repeated forward and reverse poling cycles. Note the large difference of  $\sim 9$  kV/mm between typical forward and reverse poling coercive field values.

Fig 5. (a). Measured values of  $E_c(t)$ , for delay times ranging from 20s to 3600s, for a 200 $\mu$ m thick sample.

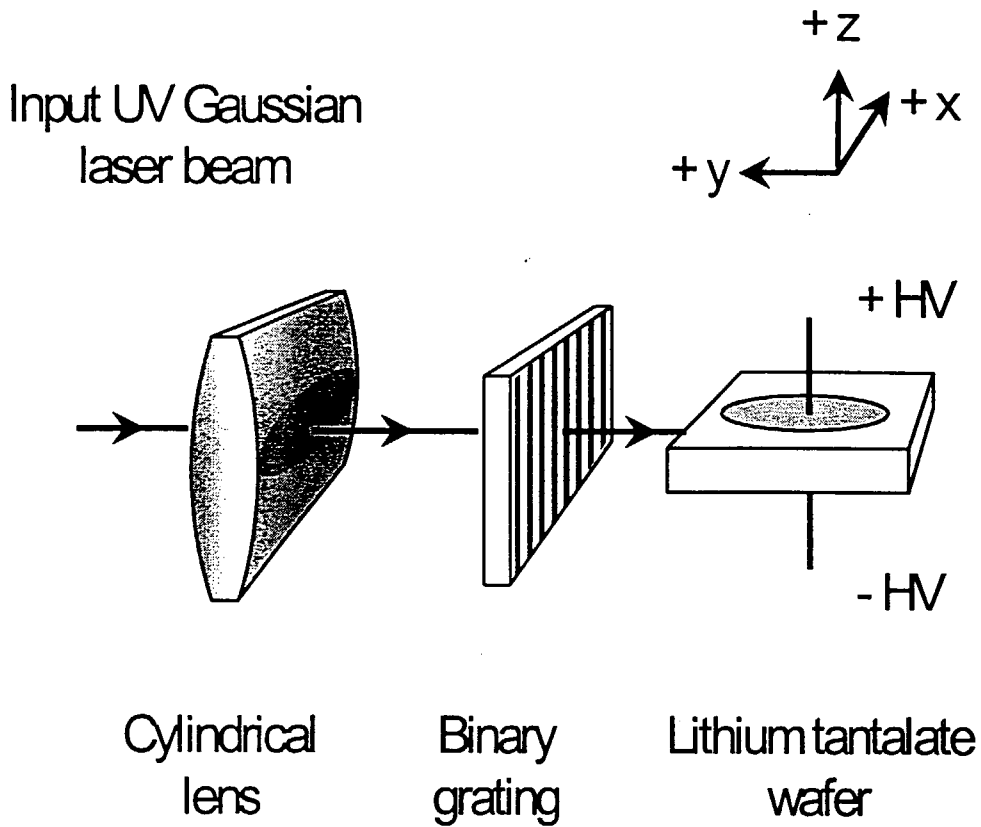
(b). Ln plot of  $[E_c(\infty) - E_c(t)]$  versus delay time. Note the lack of a linear gradient, indicating a non-single exponential recovery process.

Fig 6. Experimental data for measured  $E_c$  versus delay time, with calculated field values as deduced via equation 3. Note the sign change of internal field at time  $t \approx 6.5$  s

Fig 7. Micrograph of interferometrically patterned area of LiTaO<sub>3</sub> crystal sample, illustrating typical results from optical patterning. (The diagonal line in the top left

corner, is a scratch that has become enlarged during chemical etching).

(a) Y face illumination



(b) Z face illumination

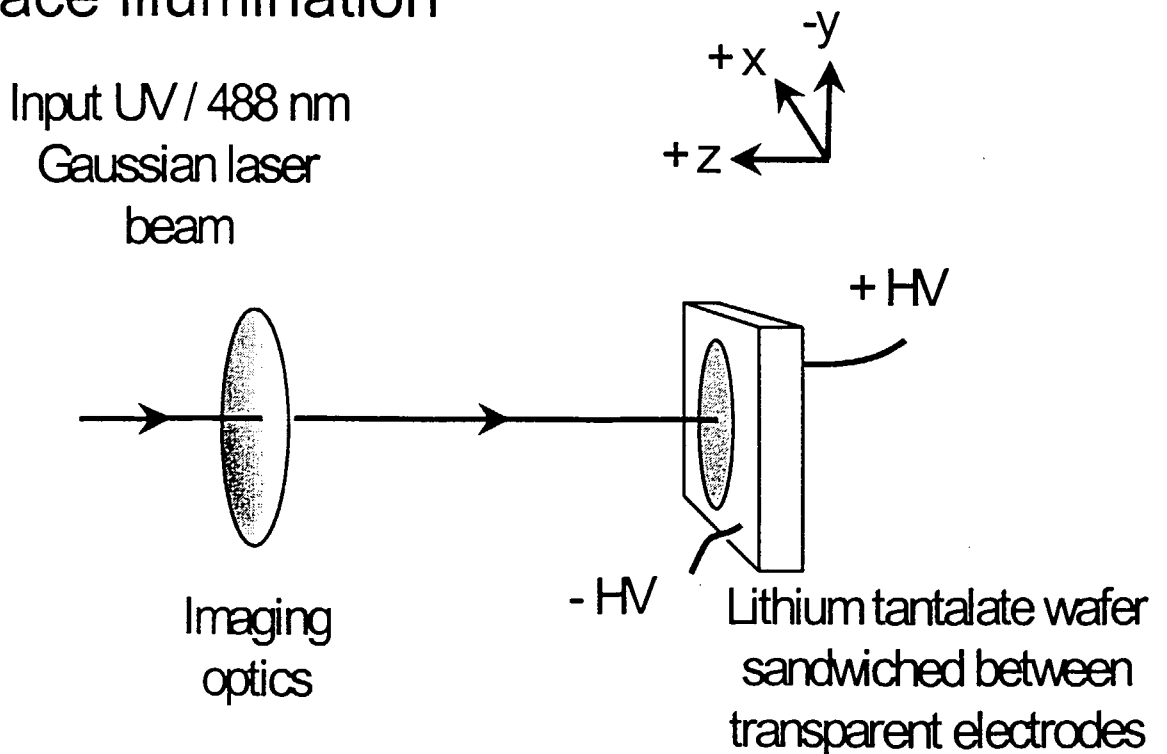


Fig 1.

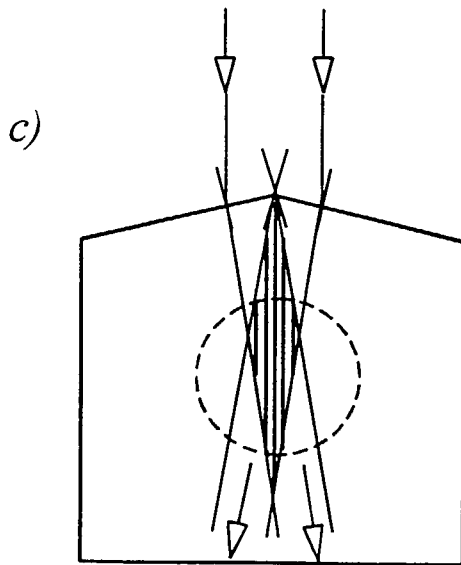
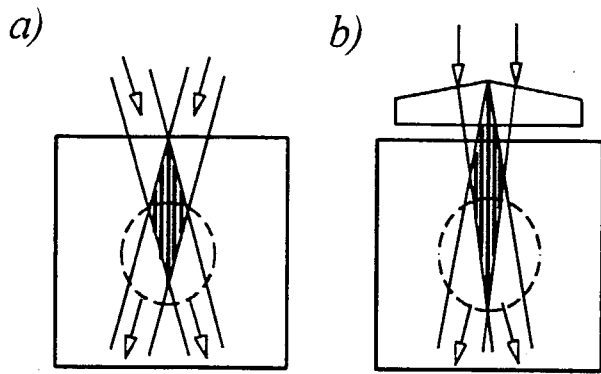


Fig 2

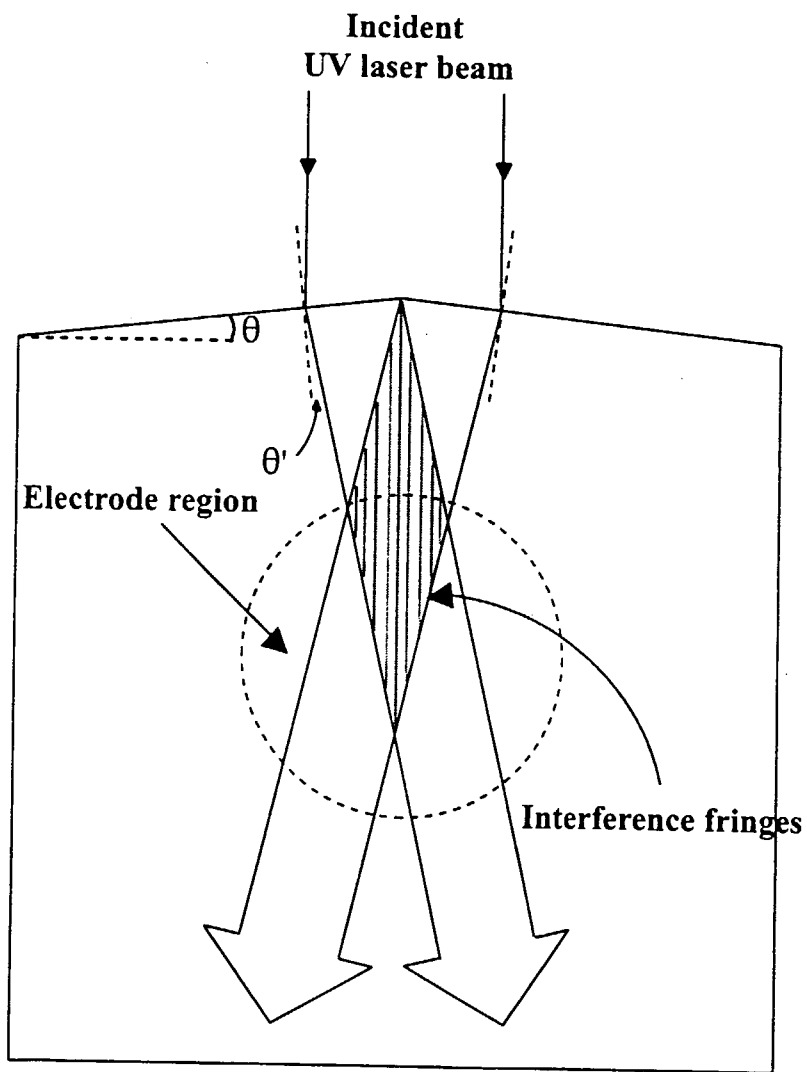
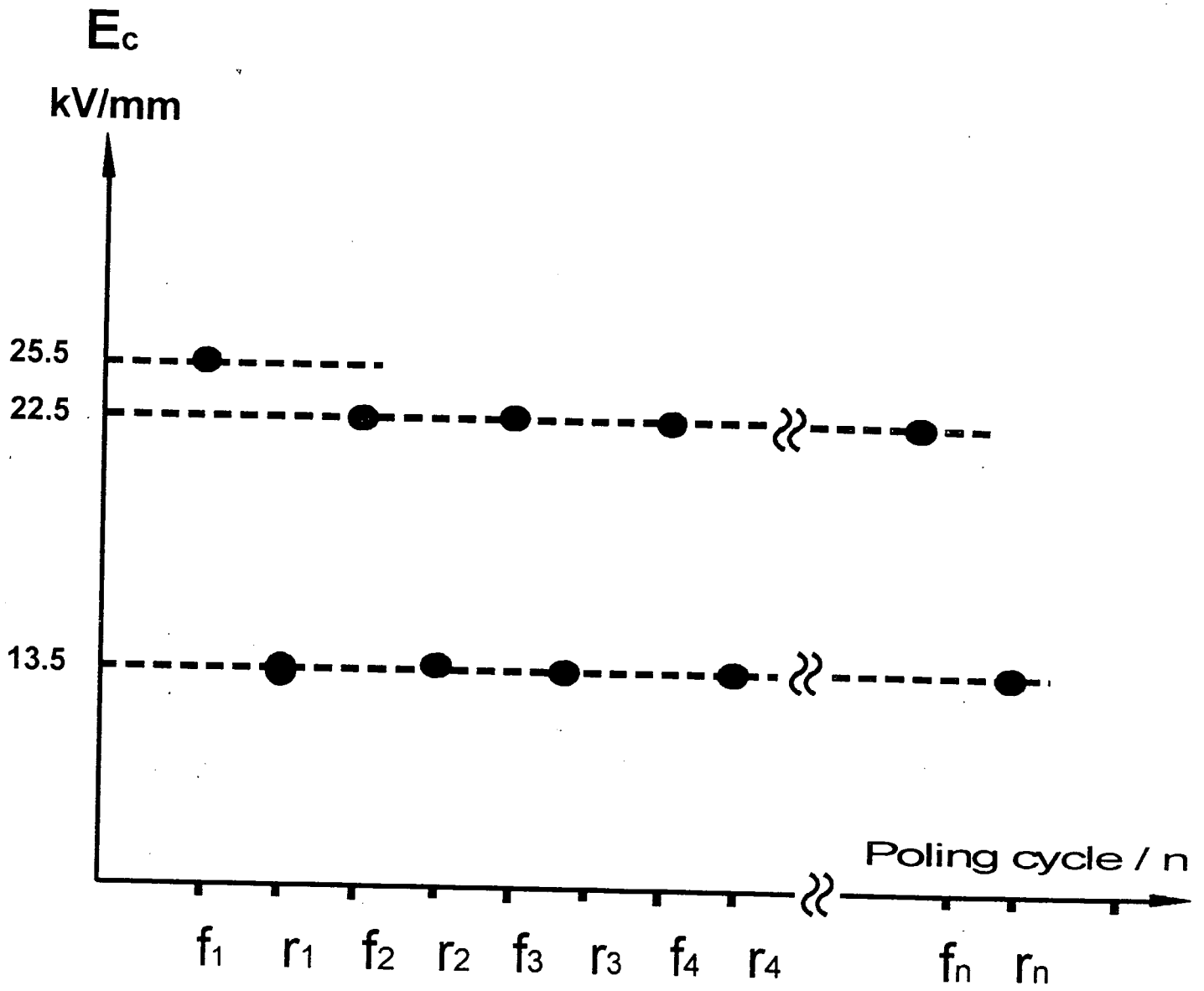


Fig 3



$n \sim 4$

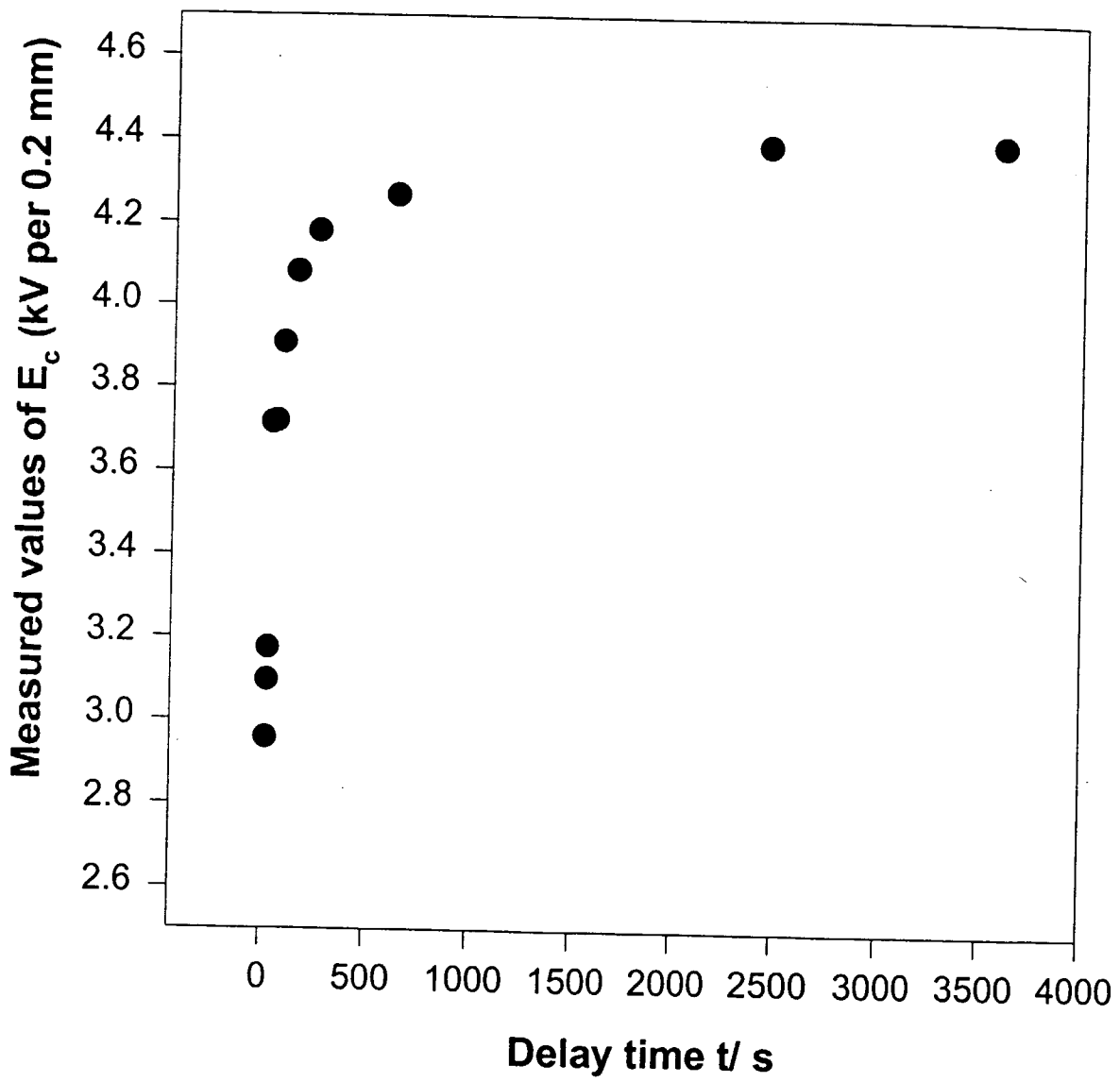


fig 5(a)

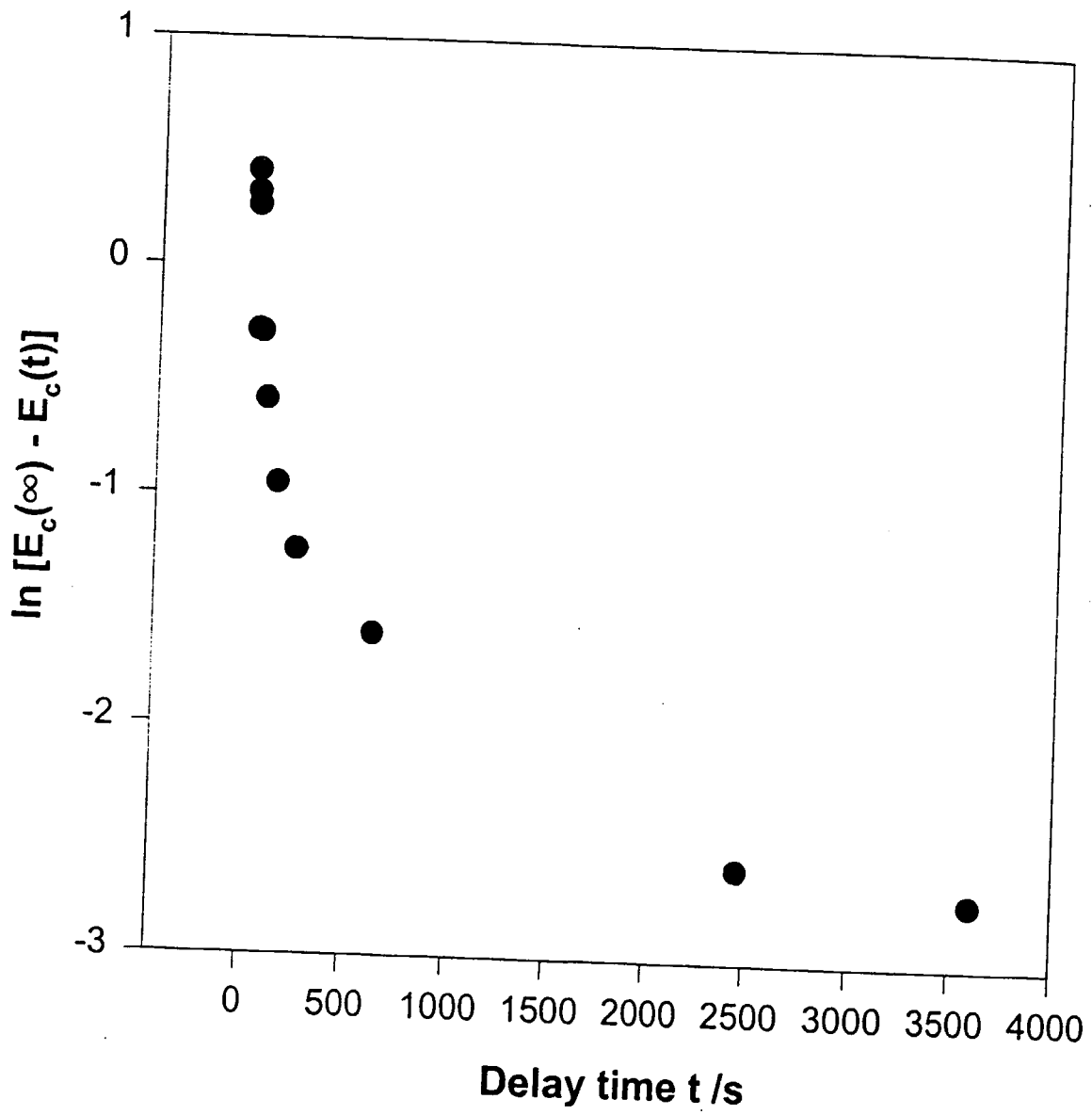


Fig 5(b)



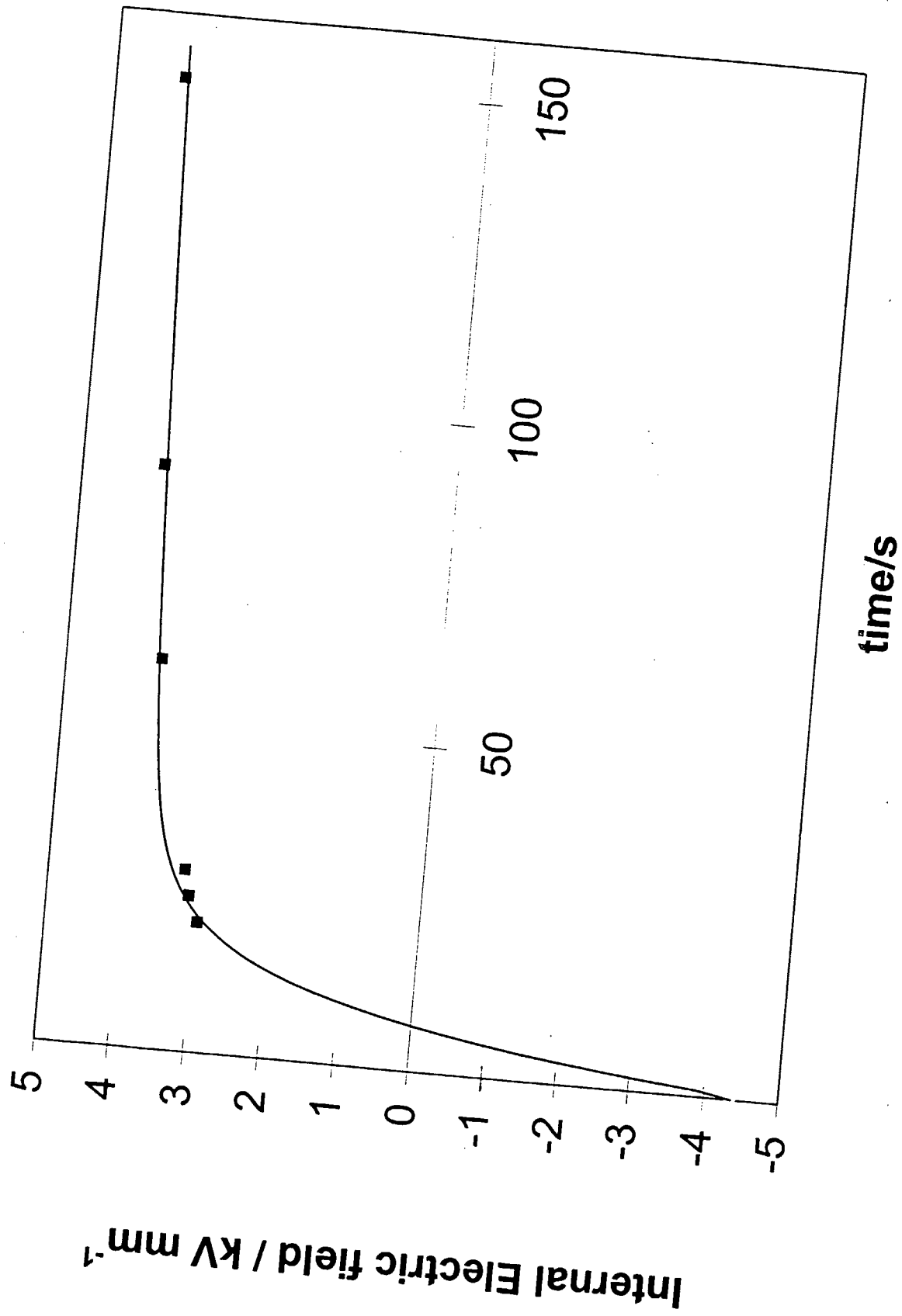


Fig 6

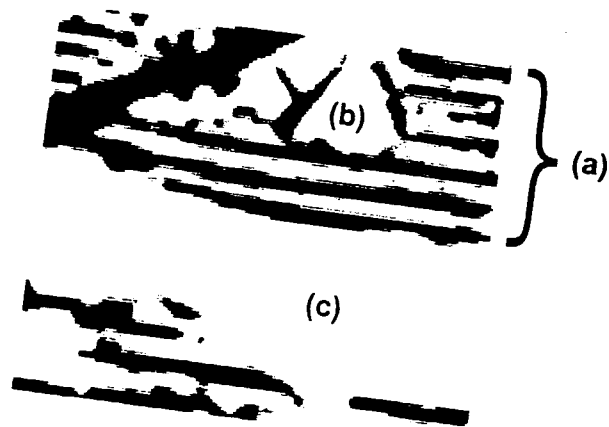


Fig 7.