Patricia, Submitted to Appl Phys Lett. 1330

Temperature sensitivity of repoling in strontium barium niobate near to the glassy transition.

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Abstract

We report the observation of an enhanced temperature sensitivity for transient repoling near to the domain freezing temperature in ferroelectric strontium barium niobate (SBN). This is the first report to our knowledge of domain freezing in SBN. This work has important consequences for the use of optical fields to control domain patterns in such materials. We model the repoling characteristics of the material using a Vogel-Fulcher type response and present results showing the degree of repoling as a function of field and temperature, for short duration repoling times.

Controlled manipulation of domain structures, at the few micron length scale, is proving to be very important for generating quasi-phase matched structures in ferrolectric materials. These materials have a number of applications in nonlinear optics including efficient harmonic generation and phase matching for parametric oscillators. A number of fabrication techniques have proved very successful, see for example the review article by Houé and Townsend[1], but difficulties remain in obtaining the very fine periodicities needed for certain applications and in poling bulk samples, particularly in materials such as $LiNbO_3$ which have large coercive fields. An interesting approach to controlling domain patterns is through the combined use of light and electric field during the repoling process. There are several approaches to this problem [2][3][4], depending on the number of repolings carried out and on the type of domain structures formed. In this paper we consider the simplest of the schemes using light and applied field, as demonstrated by Kahmann et al.[2] and report on our findings for the mechanisms of light controlled poling in SBN at, or near, the domain freezing temperature near room temperature.

Strontium Barium Niobate is a solid solution, and because of the consequent breakdown in translational symmetry is one of the family of so-called "relaxor" or "glassy" ferroelectrics characterised by a diffuse Curie temperature and dispersion in the temperature of the maximum of the dielectric susceptibility[5]. Controversy exists as to the precise nature of these materials, but they are known to exhibit several types of interesting behaviour including a change in the refractive index due to a transition from a glassy polarization (or super-paraelectric) phase to a conventional paraelectric phase at a temperature far in excess of the Curie temperature. In the glassy polarization phase there is no net spontaneous polarization, however the average value of the r.m.s. polarization is not zero. They also exhibit a diffuse Curie temperature which in the case of SBN is at around 75°C. It is thought that this corresponds to a change from the super-paraelectric phase into an effective ferroelectric phase.

Kahmann et al [2] have used cerium doped SBN:61 to demonstrate optical control of domain structures. They illuminated a crystal with a 100 micron periodicity binary intensity pattern, using an argon ion laser at 514nm. During illumination an electrical pulse was applied to the sample, (of between 1.4 and 3.5 kV/cm). The switching time (t_s) was strongly field dependent and found to be proportional to:

$$t_s \propto \exp(a/E) \tag{1}$$

Where E is applied field and a is an activation field found to be 15.9kV/cm[2].

The resulting domain patterns were examined by using two-beam coupling topography[6], which showed clear evidence of light controlled domain formation, although they were not able to provide a definitive explanation for the mechanism by which this occured.

The most obvious explanation for such light controlled domain formation is differential heating of the crystal between light and dark stripes, but, as pointed out by Kahmann, this can be ruled out because the maximum temperature difference that can exist in such a periodically illuminated crystal is:

$$\Delta T_{LD} < \frac{8\alpha I_0}{\pi K_D^2 \lambda_{th}} \tag{2}$$

where α is the absorption coefficient, I_0 the intensity, $K_D = 2\pi/\Lambda_d$, where Λ_d is the period of the illumination and λ_{th} is the thermal conductivity. Using standard data for SBN this gives a maximum temperature difference of less than 0.4mK for a 100 micron grating. Comparing this small value to the relatively large difference between room temperature and the Curie temperature (approximately 25 and 50 degrees centigrade respectively) they concluded the mechanism for domain control was not heating of the crystal.

We have attempted to repeat Kahmann's results at finer periods to provide a way of producing periodically poled material for nonlinear optical applications. For this work we used a cerium doped SBN:61 crystal supplied by Deltronics crystal industries. We found that we could partially control domain formation during repoling with light from an argon ion laser, but we were unable to scale the effect to the finer periodicities required for nonlinear optical processes. Consequently we have investigated the repoling characteristics of illuminated SBN to further elucidate the mechanism of optical domain control. As it is hard to monitor domain formation directly in ferroelectric crystals during repoling, we elected to measure the displacement current during switching as a function of applied voltage ramp. The current was detected using a sensitive trans-impedance amplifier in series with the crystal.

In our initial experiments we used long ramp times of approximately 300 seconds. The rationale for this was that it allowed us to make a quasi-static measurement of the coercive field. By ramping the field slowly enough, we ensure that all of the domains which can switch at a given field get a chance to do so. The resulting current curves allow us to determine the distribution of coercive fields within the crystal. To avoid electrical ageing [7] it was vital to ensure that the crystal was reset to a reproducible starting condition before each experimental run. By heating the crystal to 120°C in an oven and then cooling with a field of 4kv/cm we were able to obtain consistent current curves.

We investigated the effect of uniform illumination on the repoling current curves, Fig 1. The distribution of poling current with field is fairly broad in SBN so the coercive field is poorly defined, it lies roughly in the region of 3 kV/cm (defined by the maximum of the current curve) Fig 1. (a). The effect of light during repoling is shown in Fig. 1 (b) where the crystal was illuminated with 1.6Wcm^{-2} of 514nm light from an argon ion laser. The shift is clearly resolved and is seen to be about 1 kV/cm. There is also an increase in the current flowing due to photoconductivity, which gives a background slope to the curve which can be easily corrected by subtraction of a reference curve. This shift, while clearly quite significant can be attributed to direct heating of the crystals by the laser light. At the laser power used in the experiments the crystal can heat by many tens of degrees. We have measured this with a thermocouple placed next to the crystal and found that the steady state temperature was approximately 50°C, with equilibrium being reached within 1 minute. By placing the crystal in a thermal enclosure we were able to carry out an unilluminated repoling at the same temperature as a means of comparison. It too showed a similar reduction in coercive field, and so we attribute the reduction in the coercive field in Fig. 1 to heating of the crystal with a concommitant reduction in the coercive field.

This reduction in coercive field due to increased temperature cannot explain either our results or Kahmann's results that light can control the domain pattern in coarsely patterned crystals. Furthermore, we agree with Kahmann's analysis for the temperature difference in a periodic structure, which means that simple heating to close to the Curie temperature cannot be the explanation for light controlled domain structures.

Despite the apparent failure of a thermal model to explain the results, we have found evidence that temperature can play a *very significant* role in determining the repoling behaviour of SBN, although it does not provide an explanation for the mechanism for optical poling. As our later results will show, the repoling rate is extremely temperature sensitive around room temperature when short voltage pulses are used.

To investigate the effect of a short applied voltage pulse we elected to use a 2 second ramp from 0 to 2kV. This choice corresponds to the shortest times used by Kahmann, but is still long enough to give almost total domain switching under the right conditions (of temperature). We constructed a thermal enclosure with a PID controller to allow accurate control of the temperature during experiments. The enclosure allowed optical access to investigate the influence of light. During illuminated experiments we reduced the amount of resistive heating to allow for the heating effect of the laser light, which meant that experiments could be carried out a predefined temperature regardless of laser power. All temperatures were measured with thermocouples.

Fig. 2 shows the poling fraction switched during the current pulse as a function of temperature, corresponding to the degree of switched polarization. Where poling fraction is the switched polariztion normalised to the switched polarization at 39°C. It is clear that there is a significant variation in the degree of poling at a temperature around room temperature. It should be stressed that no such variation is seen when long ramp times are used (ie 300s), thus this effect is solely due to the transient applied field.

We further investigated whether light had any influence on the degree of repoling with 2 second ramps. We allowed the temperature to stabilise with the laser beam present, and then repoled the crystal. We specifically investigated the temperature region around 25°C where maximum variation occurs, but we were unable to find any effect which was not simply due to heating.

These results were fairly unexpected for SBN, as there is little evidence, to our knowledge, of such a dramatic change in the repoling characteristics near to room temperature. Although, Kewitsch et al. [8] have noticed a substantial increase in polarization viscosity leading to an enormous increase in the lifetime of holograms stored by optically induced domain reversal. They modeled this using a domain freezing model similar to that adopted in this work.

Similar glassy effects have been seen in the ferroelectric phase of the KDP family [9], where dispersion is seen in the electric susceptiblities in a mixed crystal of $Rb_{1-x}(NH_4)_xH_2PO_4$. This was attributed to finite freezing temperature, where the distribution of relaxation times results from a Vogel-Fulcher law. However, these results effectively correspond to "small-signal behaviour", because the applied fields were insufficient to repole the material, and only the linear part of the permittivity is being considered. In our experiments, however we are clearly in the large signal regime, and as such the effects may well be more complex.

The switching dynamics of SBN have been investigated by Bezhanova et al.[10], who measured the switching time as a function of applied field at two different temperatures and found a substantial variation in the repoling rate between 41 and 48°C, although they did not directly investigate this temperature dependence.

Because each run of the experiment, which takes 4 hours, results in only a single data point, it is very difficult to investigate the effect more completely. An additional complication is the gradual physical deterioration of the crystal due to mechanical stress and the possible diffusion of the metal electrode material into the crystal. We were careful to choose a suitable random order for our temperature points so that systematic ageing would not bias our results.

We have attempted to model our results using the simple ansatz of a Vogel-Fulcher type response for the temperature dependence for the rate of repoling. (The Vogel-Fulcher model is used to model the dispersion of the susceptibilty maximum in relaxor ferroelectrics, for example see Viehland et al.[11]) In particular we have used a two level model closely akin to that of a transition state model for a chemical reaction with the absolute temperature in the usual Arrhenius response replaced by (T-T_g) with T_g representing a glassy temperature. We include the time dependence of the field through the term $E_{applied}(t)$ in the numerator of the exponential. The time dependent switching rate $\alpha(t)$ between the two ferroelectric states is therefore given by:

$$\alpha(t) = \alpha_0 \exp\left(\frac{-E_a \pm \beta E_{applied}(t)}{k_B (T - T_g)}\right) \tag{3}$$

with α_0 and β constants and T_g a parameter to be fitted.

We used a fourth order Runge Kutta method with adaptive step-size control [12] to solve the resulting coupled differential equations. With this model and by choosing suitable values for the various parameters we are able to achieve a good qualitative fit to our experimental data shown by the solid line in Fig. (2). We obtain a glassy temperature of 13°C. The fit is fairly impressive given the crudeness of the model.

This model is based on a large temperature sensitivity for the rate of repoling near to a glassy temperature, but it does not give any microscopic explanation for the effect. We intend to carry out further work to discriminate between genuine glassy behaviour, where the tail of relaxation times would lead to a frequency dependent glassy temperature, and a high temperature sensitivity for one or more of the parameters which control the repoling process. By investigating the temperature dependence of the high field permittivity for thin samples we hope to gain more information about this process than we were able to obtain from measuring the low field permittivity, where neither the real nor imaginary parts showed a divergence near the glassy temperature.

In conlusion, in the course of attempting to repeat Kahmann's work on optical control of domain structures we have discovered a high temperature sensitivity for transient repoling in the region of room temperature. This result is of importance to applications in hologram fixing and data storage in ferroelectric materials, as well as in terms of domain dynamics. Furthermore, we have provided a model for the process which leads to qualitatively correct results for the temperature dependence of transient repoling in SBN.

We would like to acknowledge the help of Dr. Malgosia Kaczmarek and Roger Garment of Southampton University. This work was supported by EPSRC through grant GR/K28251.

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Figure Titles

Fig 1. Repoling current curves for 300 second ramp showing effect of illumination.

Fig 2. Poling fraction for a 2 second ramp as a function of temperature. Solid lines shows theory and the points experimental data.

Fig. 1

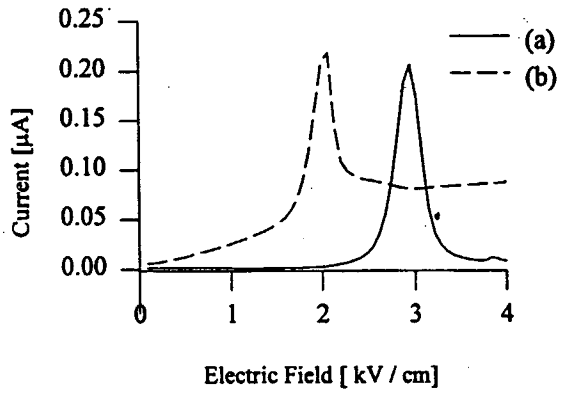

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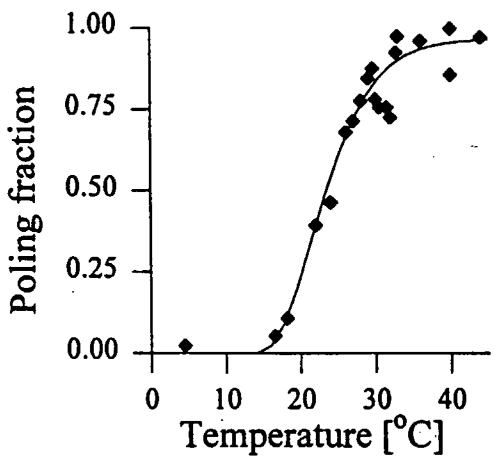
Fig2



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