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Optical control of domain structures in strontium barium niobate (SBN)

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ABSTRACT

We investigate the use of combined optical and electrical techniques to control domain formation in ferroelectric SBN, and examine the periodic structures induced by spatially modulating the light intensity through the crystal during the electrical poling process. The role of photoexcited charges in compensating and stabilising the induced domain structures is summarised, and the importance of thermal effects established. The process of domain re-ordering is shown to be particularly sensitive to temperature changes close to a domain freezing point of SBN, which occurs near room temperature. The resulting light-induced domain re-ordering is assessed using current monitoring during the repoling process, and photorefractive two-beam coupling of the resulting structures.

Keywords : ferroelectric, domains, quasi-phase matching, phase transitions, relaxor, photorefractive

1. INTRODUCTION

With recent interest in the development of compact, coherent blue-green and near infrared sources, second harmonic generation (SHG) and optical parametric oscillation (OPO) continue to attract considerable attention. Both SHG and OPO are classed as second order nonlinear optical interactions and occur in materials, such as ferroelectric crystals, which lack inversion symmetry. An important consideration in efficient light generation using such nonlinear optical processes is the phase matching condition which, in the case of SHG (for frequency doubling infrared laser diode radiation to the visible), means matching the refractive indices of the fundamental and second harmonic frequencies, $n_\omega = n_{2\omega}$. This ensures the constructive addition of second harmonic light generated throughout the crystal. Figure 1, curve (a), illustrates the second harmonic intensity generated in such a phase matched process. If the induced second harmonic is polarised orthogonally to the fundamental then the crystal's natural birefringence (with appropriate angular or temperature tuning) may be used to ensure that the refractive index witnessed by each beam is equal, resulting in efficient conversion from fundamental to second harmonic. If, on the other hand, the phase matching requirement is not satisfied, then, rather than energy being transferred simply from fundamental to second harmonic, a small amount of energy is exchanged periodically between the beams as they propagate through the crystal as shown in figure 1, curve (c). Energy is coupled into, and then out of, the second harmonic over a distance 2 l_c where

$$l_c = \frac{\lambda}{4\,(n_{2\omega} - n_\omega)} \qquad (1)$$

is called the coherence length. λ is the free space wavelength of the fundamental beam. Essentially, conversion to the second harmonic occurs over one coherence length, which is typically only a few microns, resulting in a very poor conversion efficiency as shown in curve (c). The technique of quasi-phase matching (QPM) was proposed as early as 1962 as an alternative means of phase matching the nonlinear optical process and increasing the effective interaction length.[1] By periodically inverting the

crystal structure (and thus the sign of its nonlinear optical coefficients) the phase mismatch can be compensated and efficient conversion again achieved, as shown in figure 1, curve (b). Equation 2 describes the development of the second harmonic intensity, at intervals of l_c, through a crystal whose structure is inverted every coherence length. In deriving the equation, we assume negligible depletion of the fundamental beam power and no significant absorption in the material.

$$I_{2\omega} \propto E_{2\omega}^2 = \left(\frac{2AL}{m\pi} \right)^2 \tag{2}$$

where

$$A = E_{\omega}^2 \omega d \sqrt{\mu/\epsilon} \tag{3}$$

describes the dependence on incident light and material parameters. L is the length of the periodic structure and d the effective nonlinear optical coefficient which changes sign every ml_c. In other words, the phase matching structure has a period of $\Lambda = 2ml_c$. $m = 1,3,5,...$ is called the "order" of the QPM structure. Even values of m result in no net second harmonic output. Although proposed over 30 years ago, QPM has only recently received considerable attention as a viable technique for blue and infrared light generation. In fact, QPM offers many advantages over birefringent phase matching both in terms of the materials that can be used and the nonlinear coefficients that can be addressed. QPM can be achieved for any frequency in a material's transparency range and, as birefringent phase matching is unnecessary since both the fundamental and second harmonic may have the same polarisation, Brewster angled optics may be employed to reduce losses. Additionally, QPM has given rise to reports of reduced photorefractive damage in the material.[2]

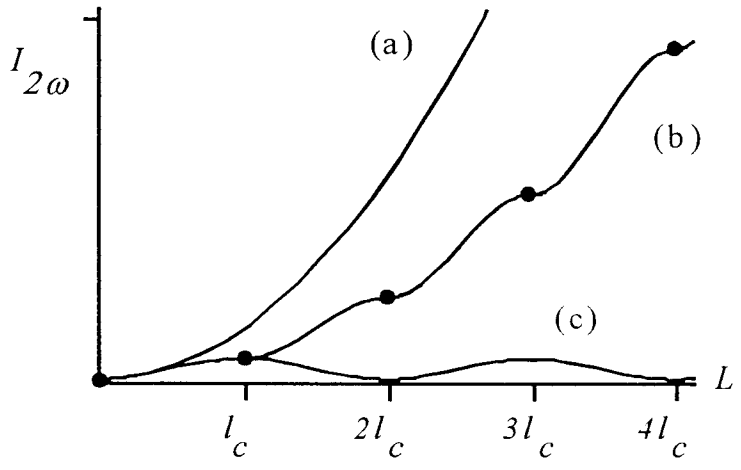

Figure 1 Second harmonic intensity as a function of propagation distance. (a) phase matched, (b) first order quasi-phase matching and (c) unmatched. The solid points are plotted according to equation 2.

2. PHOTOASSISTED DOMAIN SWITCHING

Fabrication of QPM grating structures has been demonstrated by the rather labourious method of cutting a crystal into thin slices, polishing them, and reassembling the pieces in alternating directions. Other techniques reported include electron beam irradiation[3] and diffusion based processes[4] which involve technically complex stages of sputtering, heat treatment, photolithography and etching. The resulting structures depend strongly upon the precise experimental conditions which, unfortunately, go largely unreported in the literature. There is still great interest in the development of a simple, reliable technique. Fortunately, easier ways of inverting the sign of the nonlinear coefficients exist because in ferroelectric crystals, reversing the sign of the spontaneous polarisation, P_S, is equivalent to inverting the structure. Such domain reversal can be carried out by applying a large electric field across the crystal, and, by using patterned electrodes, it is possible to periodically domain invert a thin sample of ferroelectric material.[2] Thus, periodic spatial modulation of the d coefficients is achieved by periodic modulation of P_S. The term "periodic poling" is sometimes used to describe this method of preparation of QPM structures. Examination of equation 2 reveals that efficient QPM results when the grating is of low order (ie. m = 1, first order, fine period) and long (ie. L large). Formation of fine period gratings (~3μm suitable for blue light generation) using electric fields and patterned electrodes alone becomes difficult in bulk samples due to fringing fields and electrical breakdown. In the case of photoassisted domain switching, an optical method of periodic domain reversal would provide a simple, elegant alternative to existing techniques. Generation of periodic optical patterns throughout the material using interference techniques has the advantage of being simple experimentally, compatible with both bulk and waveguide formats and flexible in that the period of the inverted domains can be easily varied by appropriate choice of angle between the interfering beams. Long gratings with periods on the order of 1μm, which are difficult to obtain photolithographically, are routinely achieved using the holographic approach where no complex photolithographic processing is necessary. It may even be possible to create curved structures throughout the material which would have very interesting properties. This work investigates possible mechanisms for photoassisted domain switching in a ferroelectric material by applying simultaneous optical and electrical fields.

3. MATERIAL

The ferroelectric material selected for analysis was SBN. SBN is a solid solution of strontium and barium niobates described by the formula $Sr_xBa_{1-x}Nb_2O_6$ (often abbreviated to SBN:A where A=100x describes the percentage of strontium). Values of $50 < A < 75$ are typically reported in the literature as having stable configurations with good optical quality. In the ferroelectric phase of crystalline SBN all the metal ions in the structure are displaced from the nearest oxygen plane in the same sense. In other words, the centres of positive and negative charge no longer coincide giving rise to a spontaneous dipole moment, P_S=28μCcm^{-2}.[5] The symmetry of this unique polar axis is such that P_S occurs either parallel or antiparallel to the polar axis thereby defining the orientation of the c-axis. Thus, only 180° domains can occur in SBN - making it suitable for QPM studies where just such reversal of P_S is required. The non-centrosymmetric structure permits second order nonlinear optical effects with coefficients d_{33}= 12.8 and d_{31} = 5 in units which are relative to d_{36} of KDP.[6] Being ferroelectric, SBN also possesses piezoelectric and pyroelectric properties, and its well known photoconductive and photorefractive features make it an interesting candidate for the investigation of light-induced changes.

SBN undergoes a phase transition at the Curie temperature, T_C, which is indicated by a peak in the permittivity-temperature curve. At temperatures below T_C it is ferroelectric (tetragonal 4mm) and transfers to a paraelectric, nonpolar modification (4/mmm) above this.[7] A crystal may be poled initially into a single domain state for device studies by heating it above T_C (to its paraelectric phase) and then cooling slowly back to room temperature with an applied electric field. Of interest in the following experiments, however, is the possibility of influencing the domain state by applying large electric fields close to room temperature. The electric field required to reverse the polarisation state of a crystal is called the coercive field, E_C, and, for SBN near room temperature, $E_C \sim 3$kVcm^{-1}. This is significantly lower than the coercive field of other common ferroelectric materials

(such as $LiNbO_3$ which has a coercive field of 240kVcm^{-1} near room temperature). The lower fields required to pole even thick (a few mm) samples of SBN, once again make SBN a suitable choice for experiment. Unlike $LiNbO_3$, however, the coercive field of SBN is a fairly poorly defined quantity - critically dependent upon crystal composition, temperature and impurity inclusion, and tends to be diffuse. Similarly, the phase transition temperature, T_C, is also ill-defined. These complications arise because SBN belongs to a class of materials known as relaxor materials. Relaxor behaviour is typically observed in solid solution systems and complex perovskite oxides and is characterised by diffuse phase transitions.[8] In such materials, P_s is observed to persist several degrees above T_C, the Curie-Weiss law $\epsilon \propto (T - T_C)^{-1}$ is not strictly obeyed and a large frequency dependence of dielectric properties is measured.[8] This dependence on dielectric relaxation lends the name "relaxor" to this group of materials. The consequences of these complex temperature effects on the rate of domain switching and periodic poling are considered further in the following section.

4. TEMPERATURE EFFECTS

Clearly with such a complex material there is a huge parameter space with which to work when considering photoassisted electrical poling near room temperature. These parameters include the duration, magnitude, polarity and sequence of applied voltages, the wavelength and intensity of light applied, the composition and dopants of the crystal and finally the temperature at which the experiment is carried out. Fortunately, we are guided by methods used by Kahmann[9] and Horowitz[6] towards conditions suitable for the analysis of optically-induced effects. We begin with light-induced temperature effects. For this work we used a 5mm^3 SBN:61 crystal (doped with 0.05wt% CeO_2 in the melt) supplied by Deltronics Crystal Industries. (Cerium doping is often introduced with the intention of enhancing the photorefractive properties of SBN.[7]) Silver paste electrodes were applied to the crystal c-faces to allow application of an electric field along the polar axis.

The following experiment was then performed. The crystal was first thermally poled as described in the previous section. To avoid electrical ageing[10] it was vital to ensure that the crystal was reset to a reproducible configuration between each run of the experiment. By heating the crystal to 120°C in an oven and then cooling with an applied field of 4kVcm^{-1} we were able to obtain consistent results. After this thermal poling step, the electric field was then reversed to repole the crystal in the opposite direction. We monitored the displacement current during this repoling step as a function of applied voltage ramp in order to assess domain reversal. Current was detected using a sensitive current to voltage amplifier. The effect of uniform illumination during this repoling step was examined. Illumination was provided by the 514nm line from an argon ion laser. The voltage across the crystal sample was ramped up to 2kV over 300s. The rationale for this was that it allowed us to make a quasi-static measurement of the coercive field. By ramping the voltage 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 (shown in figure 2) allow us to determine the distribution of coercive fields within the crystal. The distribution of poling current with field is fairly broad in SBN so the coercive field is fairly poorly defined, in the region of 3kVcm^{-1} (defined by the maximum of current curve (a)). The effect of uniform illumination using 1Wcm^{-2} is shown in curve (b). A shift in the position of the peak is clearly resolved and is seen to be about 1kVcm^{-1}. There is also an increase in the current flowing due to photoconductivity and this gives a slope to curve (b) which can be easily corrected for by subtraction of a reference curve. The shift in peak position, we believe, is due to laser-induced heating of the crystal : the argon laser light is fairly intense and is easily able to heat the crystal by many tens of degrees. We measured this with a thermocouple placed next to the crystal and found that the temperature rose to approximately 50°C. By placing the crystal in a thermal enclosure we were able to take an unilluminated current at the same temperature. It too showed a reduced coercive field, and so we attribute the reduction in the coercive field in figure 2 to heating of the crystal.

Although we found that we could partially control domain formation with light from the argon laser during repoling, scaling the effect to fine period gratings required for nonlinear optical processes proved to be more troublesome. Instead of uniform illumination during the repoling step, a binary grating was imaged on the crystal to form a pattern of light and dark fringes with

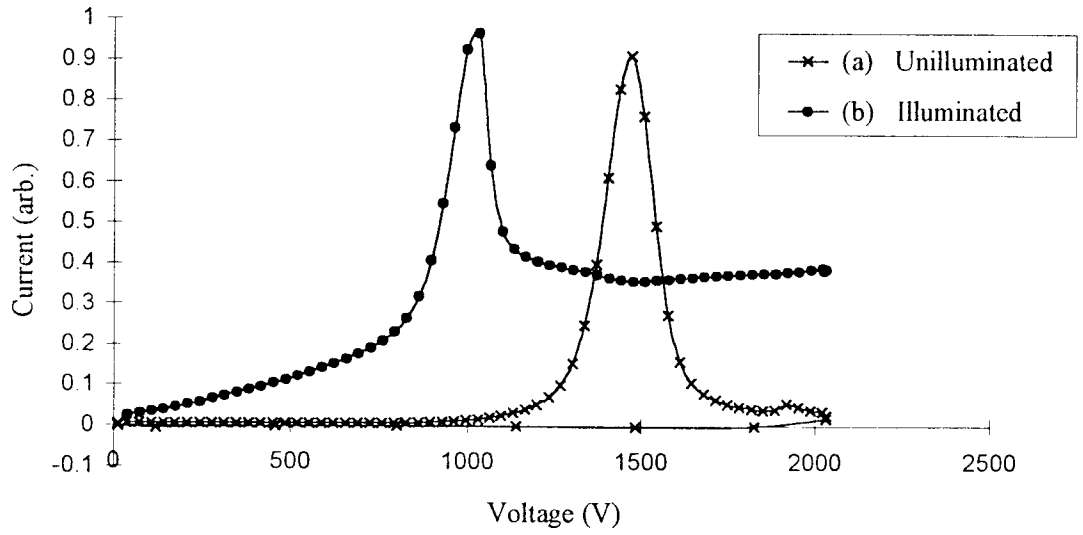

Figure 2 Repoling current as a function of applied voltage (ramped up to 2kV over 300s) showing optically-induced temperature effects. (a) no illumination (~25°C), (b) illuminated with 1Wcm^{-2} at 514nm (~50°C).

the grating wavevector, k_g, perpendicular to the c-axis. The technique of two-beam coupling was then used to assess the quality of grating formation. This assessment technique is based on the well-known phenomenon of energy transfer between two interfering beams within a photorefractive medium. Since the direction of energy transfer depends upon the direction of the c-axis, the transmitted beams are modulated according to the domain pattern in the crystal thereby allowing direct visualisation of any domain structure. Even at large grating periods (~300μm) to permit easier visualisation, we found the gratings formed using this technique to be of poor quality. On this scale, the maximum temperature difference that can exist between light and dark fringes[9] is less than 0.05°C and is therefore unlikely that laser-induced heating close to T_C can account for any finely-resolved structure. Use of lower intensities (to avoid appreciable heating) appeared to result in no structural formation whatsoever.

It would seem that temperature does indeed play an important role in transient repoling. We have found evidence, however, that the relevant temperature is not T_C, but instead a domain "freezing" temperature. As our results below demonstrate, there is a very significant temperature sensitivity in repoling at around room temperature when short voltage pulses are used. To investigate this effect we elected to use a 2s ramp to 2kV which corresponds to the shortest ramp times used in reference 9, but is still long enough to give appreciable domain switching. We constructed a temperature controlled thermal enclosure to allow accurate control of the experimental conditions. All temperatures were measured using thermocouples. Figure 3 shows the total charge switched during the current pulse as a function of temperature. This corresponds to the variation of switched polarisation. It is clear that there is a significant variation in the degree of poling at a temperature around room temperature. At 20°C poling is incomplete whereas at 30°C the process of domain switching appears significantly more efficient. It should be stressed that no such variation is seen when long ramp times are used, thus this is solely due to the transient applied field. Because each run of the experiment (including resetting the crystal as described above), 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 diffusion of the electrodes 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.

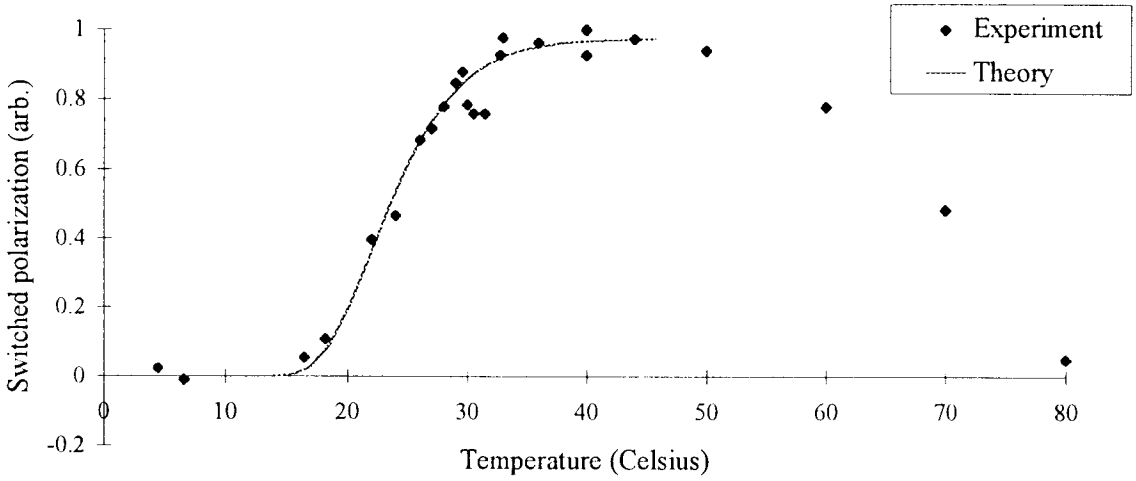

Figure 3 Temperature dependence of switched polarisation using a ramped voltage to 2kV over 2s. Theoretical curve fitted by a Vogel-Fulcher model.

It is possible to analyse this apparent "inertia" of crystal repoling as a function of temperature using a Vogel-Fulcher model.[8,11] The model is an empirical one and proposes that the rate of repoling slows asymptotically to zero on cooling to a "glassy freezing" temperature, T_F. This phenomenological approach is based on an Arrhenius response shifted to the glassy temperature with the time dependent applied electric field included through the term E_0 in the numerator of the exponential in equation 4. The rate of repoling, Γ, is given by

$$\Gamma \propto \exp\left(-\frac{E_a - \alpha E_0}{k_B(T - T_F)} \right) \tag{4}$$

where E_a is an activation energy for the switching process, k_B the Boltzmann constant and T ($> T_F$) the temperature of the sample. Modelling the results of figure 3 using the Vogel-Fulcher model yields a good qualitative fit to our experimental data which clearly describe an extremely complex effect. We obtain a freezing temperature of 13°C. At temperatures below this, domains become "frozen in". At temperatures above this, near room temperature, it becomes easier to influence the domain state of the crystal with an applied electric field. Figure 3 also clearly shows a decrease in the switched polarisation at temperatures far in excess of T_F. This corresponds to the decrease in P_S as the crystal approaches its non-polar paraelectric phase.

Further work is currently being undertaken to establish whether the presence of laser illumination at 488nm or 514nm can influence the degree of repoling near the sensitive room temperature range (around 26°C where the maximum variation occurs). Clearly, from the above results, care should be taken with such an experiment to allow for any heating effect the illumination might have so that the desired temperature can be attained and stabilised during the repoling stage.

5. OPTICAL EFFECTS

As described in the previous section, a thermal mechanism alone is unable to induce the micron-scale structures required for QPM devices. Attention was therefore focused on optical, rather than thermal, effects. The procedure was similar to that used for the thermal investigations (described in the previous section) with one important additional step. As before, the crystal is poled by cooling through T_c with an applied field. This time, however, two voltage steps were used for repoling : the first in the direction opposite to that used for the initial thermal poling (a step referred to as "primary repoling"), and the second in the same direction as thermal poling (called "secondary repoling").[12] The effect of uniform low intensity (60mWcm^{-2}) 514nm illumination, which was incident only during the primary repoling step, was examined. During the primary repoling, the voltage was ramped up to 2kV over 20s. Secondary repoling current curves were obtained by ramping the voltage more slowly (up to 2kV over 300s) in order to obtain a quasi-static measurement. As laser-induced heating was negligible at these low intensities, effects which can be attributed to optical, rather than thermal, mechanisms were observed. It appears that domains in the illuminated regions of the crystal do not flip back to the original (thermally poled) direction during the second stage of repoling, whereas in the unilluminated regions some do. This is borne out by the current curves for the secondary repoling process (figure 4), which show a much smaller current at low voltage when illumination has been used during the primary repoling. It seems that illumination during the first stage stabilises the polarisation in its new state, preventing it from flipping back so easily.

In analysing this response to optical stimulus, we begin by noting that it is well known that SBN contains a rich structure of micro-domains.[11] This microscopic variation in the domain structure implies that charges must exist in the bulk of the material to compensate the variation in the polarisation. These charges (shown schematically in figure 5) stabilise the domain configuration of the crystal, and will oppose any repoling. In the unilluminated regions of the crystal, the primary repoling will cause micro-domains to flip through 180° (if the applied field exceeds the coercive field). The bulk charges (which are unable to move) now act to destabilise the new domain structure, so that during the secondary repoling stage the domains will flip back to the original direction at very low voltages. The situation in the illuminated regions is rather different because, during primary repoling, photo-carriers will be excited which can neutralise the effects of the bulk charges, so that the domains will not flip back

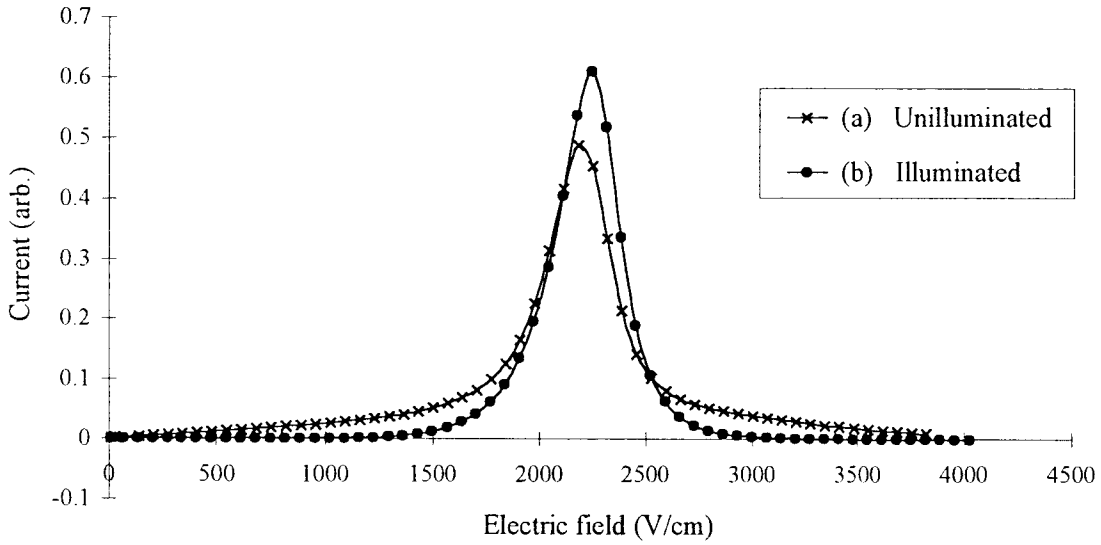

Figure 4 Secondary repoling current as a function of applied electric field. (a) No illumination during primary repoling step, (b) with illumination during primary repoling step. Note that the current at lower fields is lower when the crystal has been illuminated.

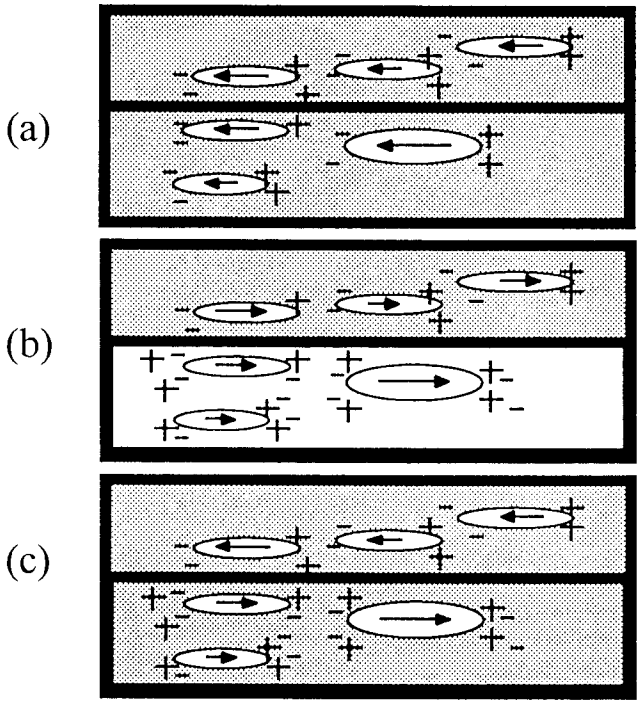

Figure 5 Micro-domain structure of SBN. (a) Thermally poled crystal. (b) Primary repoling at 4kVcm^{-1}: unilluminated (top), illuminated (bottom). (c) Secondary repoling at 2kVcm^{-1} : no illumination.

so easily at low voltages. Thus we may explain the current curves illustrated in figure 4, and, if the secondary repoling field is chosen carefully, we can arrange for very few of the illuminated micro-domains to flip back whilst many of the unilluminated regions will. Thus, after thermal poling, the procedure for structure formation would involve a primary repoling stage with a field greater than E_C and simultaneous patterned optical illumination, followed by secondary repoling using a lower field.

Spatially modulating the optical pattern by imaging a binary grating on the crystal appears to be able to produce partially-repoled domain structures of fairly high quality, although the degree of repoling (analysed, as before, by two-beam coupling) tends not to be very high. Domain gratings of period ~300μm have been successfully induced using this technique.

6. CONCLUSIONS

We have investigated domain control in ferroelectric SBN:61 using combined optical and electrical techniques. Photoassised domain switching has been demonstrated and the importance of thermal effects established. The process of domain re-ordering using short high-voltage pulses is shown to be particularly sensitive to temperature changes near room temperature. Further work currently includes closer examination of this temperature dependence and analysis of undoped samples of SBN.

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