Light-induced removal of 180° ferroelectric domains in Rh:$BaTiO_3$

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Abstract: We show that optically-induced photorefractive space-charge fields can remove 180° ferroelectric domains in rhodium-doped barium titanate. The cross section of the domains must be small (less than 100 microns) for this process to occur.
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Photorefractive gratings are produced when an inhomogeneous light pattern, such as the interference pattern produced by two overlapping light beams, redistributes charges among trap sites of the crystal, creating a non-uniform distribution of electric charge. This charge distribution induces an electric field, known as the space-charge field, which in turn alters the index of refraction of the medium through the linear electro-optic (Pockels) effect [1]. The

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resulting photorefractive gratings can couple the same beams that produced them. A well-known case is that of two-beam coupling in which two interfering beams exchange energy in such a way that the intensity of one beam increases as it propagates through the photorefractive medium at the expense of a decrease of the intensity of the other beam. Which beam gains and which one loses energy is determined, among other things, by the sign of the effective electro-optic coefficient.

Ferroelectric crystals, which are crystals that posses a spontaneous polarization that can be flipped by applying an electric field, have been used extensively as photorefractive media, mainly due to their large electro-optic coefficients. To a first approximation, the origin of these large electro-optic coefficients -in fact, of all the second-order nonlinearities in ferroelectric crystals- is the spontaneous polarization of the medium acting as a biasing field on third-order nonlinearities [2,3]. Consequently, if the magnitude or direction of the spontaneous polarization is changed, so will the electro-optic tensor. In the case of two-beam coupling, the direction of the spontaneous polarization determines the sign of the effective electro-optic coefficient and therefore which of the interacting light beams gains and which loses energy.

Can the optically-induced space-charge field invert the direction of the spontaneous polarization? This question has been addressed before, the answer being different for different crystals. In $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN:75), which is a relaxor or glassy ferroelectric (ferroelectric crystals in which the Curie temperature is not well defined) there is some evidence that the space-charge field can significantly alter the spontaneous polarization, or possibly even induce the formation of small (sub-micron) 180° ferroelectric domains [4]. In "hard" ferroelectrics, such as $BaTiO_3$ and $LiNbO_3$, there is evidence that light can alter the domain structure. Lemeshko and Obukhovskii [5] observed that needle-shaped 180° domains are formed in iron-doped $LiNbO_3$ when it is illuminated by 441 nm light. Their interpretation of this phenomenon, however, does not involve a space-charge field created by an interference pattern; instead, it is explained in terms of the formation of a uniform electric field created by photogalvanic currents. Similar observations in $LiNbO_3$ were reported by Kovalevich et al.[6] In nominally undoped $BaTiO_3$, it has been observed that the space-charge field can modify the shape of ferroelectric domain walls [7], leading to interesting effects such as photorefractive domain fixing [8,9]. However, to the best of our knowledge, there is no evidence that a space-charge field can entirely remove 180° domains in $BaTiO_3$. The coercive field, which is the magnitude of the field required to invert the spontaneous polarization, is between 0.3 and 1 kV/cm for undoped $BaTiO_3$. By an appropriate selection of the grating spacing, the amplitude of the space-charge field can exceed 2 kV/cm in $BaTiO_3$, so that, at least in principle, the space-charge field may create or destroy 180° domains.

In this paper we present what we believe to be the first evidence that photorefractive space-charge fields can repole rhodium-doped barium titanate crystals; in other words, optically induced space-charge fields can remove 180° domains from the bulk of the crystal. These domains must be narrow in order to be removed, of less than 100 microns by side.

The experimental technique to remove 180° domains as well as to detect them are one and the same and is shown in Fig. 1. It is exactly the same method used by Grubsky et al. to detect 180° domains using photorefractive two-beam coupling, known colloquially as the "Swiss cheese technique" [10]. A photorefractive grating is recorded by interfering two beams inside the photorefractive crystal, a probe beam which is collimated and which propagates parallel to the crystal's c-axis, and a reference beam, which can either enter the crystal through the c-face, as shown in Fig. 1 a), or through an a-face, as shown in Fig. 1b). In both cases, the photorefractive grating will change the intensity of the probe beam, increasing or decreasing it depending on the orientation of the c-axis. If 180° domains are present, the image of the probe beam exiting the c-face will not be uniform, bright spot; it will consist of a bright background with dark spots (like Swiss cheese) indicating where domains are located, or a dark background with bright spots, depending on the orientation of the crystal. The contrast of these spots will depend on the length of the domains along the c-axis, being maximum when they extend from one c-face to the other. Most domains do [10,11], since this

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configuration is energetically more favorable; head-to-head domains require free charge to electrically compensate the discontinuity of the spontaneous polarization at the domain wall. However, wedge-shaped domains that end inside the bulk can occur in barium titanate [12,13], and can be detected by using the set-up shown in Fig. 1b). By focusing the reference beam with a cylindrical lens the domain structure of a slice of the crystal can be analyzed, and by simply translating the reference beam a tomographic image of the domain structure can be obtained [10].

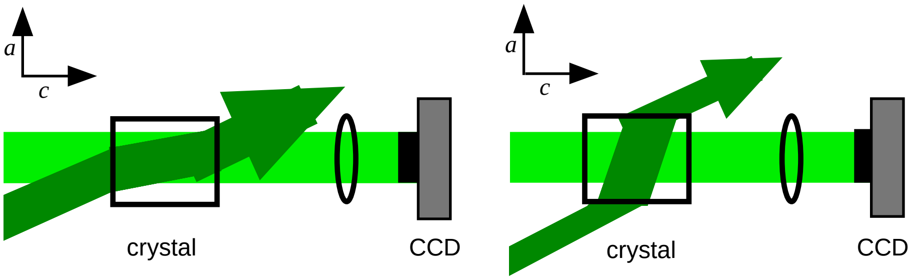

Fig. 1. Experimental set-up. a) The reference beam enters through the "c" face. b) The reference beam enters through the "a" face.

In order to check the quality of rhodium-doped barium titanate crystals, in preparation for another experiment (not relevant to this paper), we set up the "Swiss cheese experiment." Using the configuration shown in Fig. 1 a), we observed many small dots of light against a dark background, perhaps more than one hundred, all of them with an estimated maximum diameter of 100 microns, possibly much smaller. The reason why we use vague terms to describe the number and size of these dots is that we did not have a chance to measure them: after approximately ten minutes the dots disappeared completely and did not reappear. We tried varying the angle of incidence of the reference beam in order to rule out beam fanning as a cause of the disappearance of the dots, but it was not possible to observe them again. By leaving the crystal in the dark for a week only some of the dots, not more than ten, reappeared, and when they did they decayed in less than a minute when observed by the same technique. The interpretation of these observations is that the crystal originally had many needle-like 180° domains which were removed by the same photorefractive space-charge field that allowed us to detect them, and that, if given enough time, some of these domains would spring back.

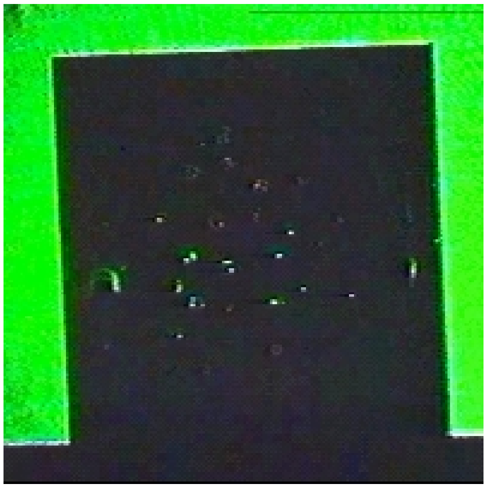

Fig. 2. (2.2MB) Movie of the the decay of domain structure. The domains are visualized using the configuration shown in Fig. 1a. $\lambda = 515$ nm ; intensity per beam ~ 20 mW/cm^2. Exterior angle between beams: 60°.

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To see if this effect was reproducible, we repeated this experiment on another crystal which had been stored for over 6 months. This crystal is a dark blue, 3200 ppm rhodium doped barium titanate crystal that measures 3.47 X 3.55 X 3.84 mm. Fig. 2 shows the first frame of a movie of the time evolution of the probe beam. The tempo of this video has been increased by a factor of ~75; in real time the movie lasts eight and a half minutes. We observed essentially the same effect: thin, needle-like domains, of no more than 60 microns by side, were initially present and vanished within less than 10 minutes of observation, without reappearing again. As before, the angle of incidence of the reference beam was changed in order to rule out beam fanning as the cause of the disappearance of the domains.

However, if we made the reference beam enter through an a-face instead of the c-face, some domain structure could be observed, although not with the same contrast. In addition, instead of being dots of light, the domains appeared to be squares centered where the dots were located previously. We checked the distribution of the domains throughout the bulk of the crystal by scanning a tightly focused (100-200 micron thin stripe) reference beam, as described in Ref. [10]. The angle of incidence of the reference beam was kept constant (exterior angle of 65° with respect to the c-axis) as the focused beam was scanned along the a-face in 100 micron increments. The first frame of a movie of this scan is shown in Fig. 3.

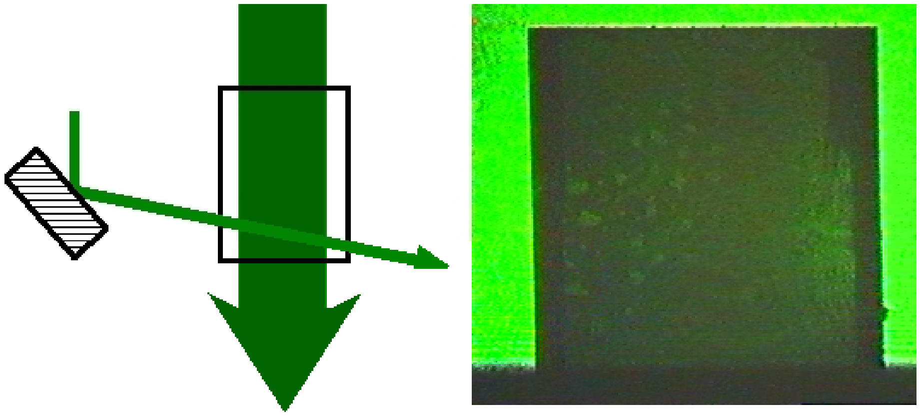

Fig. 3. (2MB) Tomography of the domain structure after optical poling. The figure on the left shows the position at which the reference beam enters the a-face of the crystal. The figure on the right shows the domain structure of the region sampled by the reference beam.

As can be seen from the movie, the crystal is virtually free of domains in the region extending from the entrance c-face to about 0.5 mm from the exit c-face. The reason why these domains could not be detected using the configuration shown in Fig. 1 a) is that the effective electro-optic coefficient depends strongly on the orientation of the photorefractive grating's wavevector, and in this case is much larger when the reference beam enters through the a-face; the beam coupling produced by this last layer of the crystal is too small to be detected using the configuration shown in Fig 1.a. Also, the widths of these domains are larger than those shown in Fig. 2. The explanation for this is that the domains are wedge-shaped, with their base located on the exit c-face. In Fig. 2, the coupling is integrated along the entire c-axis, making the central portion of the wedge to appear brighter than the rest of it.

Finally, the domains of this last layer can also be removed by simply recording a grating in it. Figure 4 shows the first frame of a movie of the decay of these domains. In this movie the reference beam was also tightly focused onto the last layer of the crystal. As before, the tempo of the movie has been increased by a factor of ~100. The actual movie lasts 14.5 minutes.

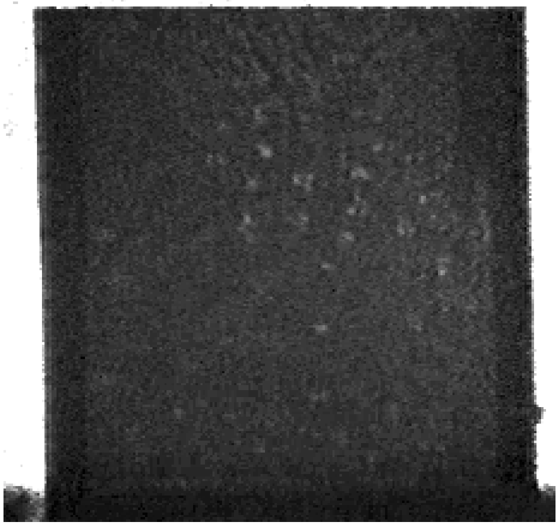

Fig. 4. (1.4MB) Movie of the decay of the domain structure at the exit face of the crystal.

There are different ways in which the removal of the domains can be explained. First, it can be argued that the space-charge field does not have a significant influence on the repoling, and that all that is happening is that the light removes free charges which pin the domains in place, allowing the domains to shrink. Second, photogalvanic currents can produce an electric field which would tend to repole the crystal. In both cases only the light intensity is important so that in the presence of only one beam (no interference pattern) the domains should go away. However, we believe that these effects are not the main reason why domains are removed, since continuous monitoring (over an hour) of the domain pattern using the configuration shown in Fig. 1 a) did not get rid of the remnant domain pattern shown in Fig. 3. This pattern was finally removed (Fig. 4) when the grating was recorded near the exit face of the crystal. There still remains the question whether the component of the space-charge field along the c-axis is large enough to induce polarization reversal. If we assume that the trap density of the crystal is large enough such that the space-charge field is diffusion-limited, then a simple calculation shows that for the configuration shown in Fig. 1 a) the amplitude of the component of the space-charge field along the c-axis is approximately 400 V/cm, and for the configuration shown in Fig. 1 b) it is approximately 1000 V/cm. In these calculations we have taken into account the polarization of the beams, which influence the modulation of the interference pattern and consequently the magnitude of the space-charge field, and have assumed that the amplitudes of the beams are equal. For both cases the field is equal to or larger than the coercive field, assuming that the coercive field is approximately 300 V/cm.

We have repeated these experiments in other Rh:BaTiO$_3$ crystals, obtained from different suppliers, obtaining essentially the same results: thin domains disappear in the presence of a photorefractive grating. These observations agree with anecdotal evidence that beam coupling in rhodium-doped barium titanate crystals increases the more they are used. Some of these crystals also had wider domains, of the order of half a millimeter or more. These domains were not removed by the photorefractive gratings, at least over the period of observation (hours). Also, we looked for this effect in nominally undoped barium titanate and saw no evidence of repoling, regardless of the size of the domains. The reason for difference of behavior between rhodium doped and undoped crystals is uncertain and is the subject of further investigation.

In conclusion, we have shown that photorefractive gratings can remove thin 180° domains from Rh:BaTiO3 crystals at room temperature without requiring an externally applied field.

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