A stochastical model for periodic domain structuring in ferroelectric crystals

Felix Kalkum, Helge A. Eggert, Tobias Jungk, and Karsten Buse
Institute of Physics, University of Bonn, Wegelerstr. 8, 53115 Bonn, Germany.
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A stochastical description is applied in order to understand how ferroelectric structures can be formed. The predictions are compared with experimental data of the so-called electrical fixing: Domains are patterned in photorefractive lithium niobate crystals by the combination of light-induced space-charge fields with externally applied electrical fields. In terms of our stochastical model the probability for domain nucleation is modulated according to the sum of external and internal fields. The model describes the shape of the domain pattern as well as the effective degree of modulation.

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The importance of ferroelectric optical materials is still contrasted by a lack of theoretical understanding. Comparing textbook knowledge with real experimental results yields many discrepancies. Some examples for the prominent ferroelectric materials lithium niobate and lithium tantalate: Domain walls can be pinned and can bow [1], the coercive field can be reduced by an order of magnitude by small changes in the lithium content [2], and the materials exhibit a memory effect for recent domain inversions [3]. The reason that it is so hard to predict and to model ferroelectric domain inversion and patterning results from the influence of defects (vacancies, impurities, ions on wrong lattice sites, etc.). The systems are too large to make first-principle calculations that consider these effects, although first attempts already yield impressive fundamental predictions [4].

The simplest periodic structure, that is ideally suited to compare theoretical and experimental data, is an elementary grating. Such periodically poled crystals are also of relevance for a variety of applications: Frequency conversion [5], parametric oscillation [6], the generation of terahertz radiation [7] as well as high-speed electro-optical switching [8]. Conventional periodic poling is achieved by applying high electrical fields with structured electrodes [9]. However, quality and size of domain structures fabricated by this method seem to be limited. The reasons are not clear because of insufficient theoretical modelling.

One possibility to describe ferroelectric domain reversal is the theory of Avrami, Kolmogorov, Johnson, and Mehl on first-order phase transitions adapted by Sekimoto to a form usable for our purposes [10, 11]. This theory relies on a purely stochastical description. According to it, domains nucleate and grow independently from each other, and within its framework the probability for domain inversion can be calculated. Usually the domain switching is studied by obtaining the time dependence of the inverted volume fraction during the poling process. It is an open and demanding question whether this theory can be applied to domain patterning as well.

In the present work electrical fixing [12, 13, 14, 15] is used to compare stochastical modelling of domain patterning to experimental data: Space-charge fields are created in a crystal via the photorefractive effect [16], and additionally an external electrical field is applied. According to the stochastical model a spatially modulated electrical field leads to a modulated probability for domain inversion. The dependence of the domain grating quality on the underlying probability density can be calculated by adapting the theory of Avrami, Kolmogorov, Johnson, and Mehl to the case of a spatially sinusoidally modulated probability for domain nucleation. Sekimoto [11] gives the following general formula for the probability $w$ that a point $\vec{r}$ has an inverted spontaneous polarization:

$$w(\vec{r}, t) = 1 - \exp \left( - \int_0^t dt' \int_{V} d^3r' I(\vec{r}, t') \left[ 1 - D(\vec{r}; t; \vec{r}', t') \right] \right).$$

Here $I(\vec{r}, t')$ denotes the probability density for domain nucleation at position $\vec{r}$ and time $t'$ and $V$ denotes the whole crystal volume. The function $D(\vec{r}; t; \vec{r}', t')$ is zero if such a domain contains $\vec{r}$ at time $t$ and is one otherwise. The time dependence in $D$ and $I$ is introduced to model the temporal evolution as domain nucleation probability and domain sizes may vary with time. As we are not interested in the temporal evolution here, we replace the time dependence by the dependence on domain length $l$.

Thus it follows:

$$w(\vec{r}) = 1 - \exp \left( - \int_0^\infty dl' \int_{V} d^3r' I(\vec{r}, l') \left[ 1 - D(\vec{r}, \vec{r}', l') \right] \right).$$

Here $I(\vec{r}, l')$ is the probability that a domain located at $\vec{r'}$ with length $l'$ can be found.

We now assume that due to a periodic space-charge grating the probability for domain nucleation is periodically modulated. Thus we write:

$$I(\vec{r}, l') = [\alpha + \beta \sin(Kr'_z)] n_l(l').$$

Here $n_l(l')$ describes the size distribution of domains. So $\beta/\alpha$ is a measure for the strength of the influence.
of the space-charge grating on domain nucleation. Here $K = 2\pi/\Lambda$ is the spatial frequency of the space-charge grating. The domain shape is assumed to be cylindrical with length $2l$ and area $A(l)$ and to be centered around $r^2$ which is described by the function $D$. Instead of a modulated probability for domain nucleation, a modulated domain-wall growth can be assumed by adapting $I(r^2, l')$. However, within the framework of our methods both assumptions lead to very similar predictions, hence the latter is not investigated within this article. Inserting equation (2) into equation (11) and using the specific domain form, we get:

$$w(r) = 1 - \exp \left( -2\alpha \int_0^\infty dl n_l(l)A(l)l \right) \times \exp \left( -2\sin(Kr_2)\frac{\beta}{K} \int_0^\infty dl n_l(l)A(l) \sin(Kl) \right)$$

We define $\gamma = 2\alpha \int_0^\infty dl n_l(l)A(l)l$ and $\eta = 2(\beta/K) \int_0^\infty dl n_l(l)A(l) \sin(Kl)$. The former is a measure for the volume of inverted spontaneous polarization whereas $\kappa = \eta/\gamma$ measures the modulation degree of the domain grating ($0 \leq \kappa \leq 1$). Expanding the second exponential function in the last expression for $w$ up to the first order we get as an approximate expression for $w$:

$$w(r) = 1 - \left[ 1 - \gamma \kappa \sin(Kr_2) \right] \exp (-\gamma).$$

The area fraction $q$ with inverted spontaneous polarization (degree of poling) can be found by taking the spatial average of $w(r)$:

$$q = \frac{1}{\Lambda} \int_0^\Lambda dz q(z) = 1 - \exp (-\gamma).$$

The degree of modulation of the domain grating $\Delta q$ can be calculated as the first Fourier coefficient for $K$:

$$\Delta q = \gamma \kappa \exp (-\gamma) = -\kappa (1 - q) \ln(1 - q).$$

Equation (3) expresses the domain grating modulation solely as a function of the degree of poling. For no or complete reversal of the spontaneous polarization no grating at all can be found. A maximum is found in between. Numerically evaluating equation (3) for several assumptions yields that for the height of the curve $\max \Delta q \approx 0.4\kappa$ roughly holds.

To test these predictions experimentally, electrical fixing experiments are performed. Lithium niobate crystals doped with 0.05 mol% iron from Deltronic Crystal Industries are used. To reduce the coercive field a vapor transport equilibration treatment is applied [17]. The crystals are put into a special mount which is placed in a glass bin filled with silicon oil to prevent electrical breakdowns.

The optical setup consists of a detuned Mach-Zehnder interferometer, which allows to illuminate the crystal with a periodic interference pattern with grating periods of 5 to 100 $\mu$m. Light of the wavelength 488 nm from an Argon-ion laser is used. The illumination creates a space-charge field which induces an index-of-refraction grating via the electro-optic effect. This photorefractive volume grating is detected by Bragg-diffraction with light of the wavelength 633 nm from a HeNe-laser. From the amount of diffracted light the amplitude of the modulation of the index-of-refraction and hence of the space-charge field can be calculated [18]. A detailed description of the setup can be found in reference [19].

The experiments are performed as follows: A space-charge field is written by illuminating the crystal with an interference grating. Either during or after the recording a voltage is applied to the crystal along the $z$-axis. The polarity of the voltage is chosen such that the electrical field supports domain inversion. The strength of the space-charge field is monitored during the whole experiment. When the space-charge field reaches steady state, the illumination is stopped and the external electrical field is shut off. After homogeneous illumination of the crystal no diffracted light is detected. Next the crystal is repoled to its single-domain state by applying an electrical field without any illumination. The degree of poling is determined by integrating the current during the poling process. This value is normalized by twice the spontaneous polarization $P_s$.

The revealed index-of-refraction grating provides information about the achieved degree of modulation of the domain walls. It is studied for different strengths and application times of the external field during the recording process. In Fig. 1 the revealed space-charge grating strength is plotted against the degree of poling. In Fig. 1(a) a space-charge field is written in the crystal before the external field is applied. The experimental parameter, which is varied, is the time this field is applied. In Fig. 1(b) the space charging is written in the presence of an externally applied field. Here the recording time is fixed but in order to change the degree of poling the external field is varied.

As can be seen, the strength of the revealed field becomes zero for $q \to 0$ as well as for $q \to 1$ and reaches a maximum in between. In Fig. 1(a) the dependence of the strength of the reappearing space-charge field is shifted to higher $q$-values compared to the results obtained with varying fields in Fig. 1(b).

Comparing theoretical predictions with experimental data for the strength of the revealed field under different fixing conditions, qualitative agreement can be found. The dependence on the degree of poling $q$ with different writing times as in Fig. 1(a) is very close to a $-(1-x)\ln(1-x)$ dependence as predicted by Eq. (3). The shift to lower $q$-values, when the field is varied, is understandable: Different external fields do not only influence $q$ but also change the relative influence of the space-charge field and thus $\beta/\alpha$.

Experimental data for different grating periods is shown in Fig. 2. For period lengths smaller than 15 $\mu$m the strength of the reappearing space-charge field quickly drops to zero. However, for large period lengths exceed-
FIG. 1: The index-of-refraction modulation $\Delta n$ is plotted versus the degree of poling $q$. The period $\Lambda$ of the fixed grating is $\Lambda = 15.7 \, \mu m$. In Fig. 1(a) the degree of poling is varied by applying an external electrical field for different times. The solid line is a plot of Eq. (3) where $\kappa$ is a fit parameter. In Fig. 1(b) different external fields are applied for a constant time. The dashed line is a guide to the eye.

Fig. 2 not only shows the measured strengths of the revealed index-of-refraction grating for different period lengths $\Lambda$, but also a calculation of the degree of modulation. Here assumptions on the domain size distribution have to be made: A Gaussian distribution centered at 0 with a width of 5 $\mu m$ is assumed. The height of the plotted curve is used as a fit parameter. The basic message is that if a broad domain size distribution is assumed, as it is found in real crystals by the PFM measurements, the model predicts that no revealed grating should be found for period lengths smaller than the length of most of the domains. For higher period lengths the grating quality increases. These predictions are in agreement with measured data.

To check whether a space-charge grating is revealed all over the crystal or only in some parts of it, the index grating induced by the space-charge field is imaged with differential interference contrast microscopy (DIC) after repoling the crystal. This method allows to detect very small gradients of the index-of-refraction in the crystals.

We use this as a method to observe restored space-charge fields and to determine qualitatively the shape of fixed domain gratings. This is possible because after repoling of the crystal uncompensated charges appear at the former domain walls. These charges cause electro-optic index changes which are a replica of the original domain pattern [13]. Figure 3 shows the result. As it can be seen, the grating reappears all over the crystal.

Piezoelectric force microscopy (PFM) is used to directly image the ferroelectric domain structure after electrically fixing a space-charge grating. The PFM is a
scanning force microscope operated in contact mode with an additional alternating voltage applied to the tip [20]. In piezoelectric samples this voltage causes thickness changes and therefore vibrations of the surface which lead to oscillations of the cantilever that can be read out with a lock-in amplifier. In the present work we imaged the non-polar faces of LiNbO$_3$.

The faces of the crystal are polished down stepwise by some hundred micrometers to ensure that volume domains are visualized. Figure 4 shows that ferroelectric volume domains can be found after electrical fixing of holograms in lithium niobate crystals. However, a periodic structure is not immediately evident. In fact, the length of some areas with inverted spontaneous polarization are bigger than one period of the fixed grating.

However, from the PFM images we conclude that electrical fixing indeed leads to ferroelectric volume domains with inverted spontaneous polarization in head-to-tail configuration, but the periodicity is not evident locally. The DIC images suggest that averaged over the whole crystal thickness a well defined grating is present. Both observations are consistent with the predictions of the model. The degree of modulation is too small to be obvious from direct domain visualization, but an average periodicity is visible which can be detected by the help of light diffraction at the revealed space charge grating.

After revealing, local fields are created according to the former domain structure. Typical values of such fields $E_{\text{loc}}$ presumably are determined by material parameters, as the spontaneous polarization and field-limiting effects like the electric-breakdown field. The $E_{\text{loc}}$ form a corresponding index-of-refraction grating via the electro-optic effect which is detected by diffraction of a light beam. The effective, averaged field $E_{\text{eff}}$, which is measured by this method, is given by the modulation degree multiplied by the local electric field $E_{\text{loc}}$. Thus theoretical predictions for $\Delta q$ link a material dependent factor $E_{\text{loc}}$ with the experimental value $E_{\text{eff}}$, i.e., these values are proportional to each other.

Alltogether it is found that the predictions of the model are in agreement with all available experimental data, indicating strong support for the model presented herein. None of the assumptions of the theory is specific to the material lithium niobate. So the stochastic description offers a general way to analyze and discuss experimental dependencies in all electrical fixing experiments which have been performed in a large variety of ferroelectric materials. For Example in Ref. [21] the same dependence of revealed grating strengths on the degree of poling and the same dependence on the grating period $\Lambda$ is found for electrical fixing in barium titanate crystals.

Furthermore, the stochastic description enables quantitative predictions. Provided better knowledge of local fields after revealing is gained, the factor $\beta/\alpha$, i.e., the influence of local fields on the poling dynamics, can be analyzed. This is a point which is hard to access by alternative means. As the influence of defects presumably can be described by local fields, deeper understanding of ferroelectric domain switching becomes possible.

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