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Aging of the ferroelectric hysteresis in Ce-doped Strontium-Barium-Niobate observed by holographic phase gratings

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ABSTRACT The ferroelectric hysteresis of Strontium-Barium-Niobate single crystals doped with Ce (SBN:Ce) is measured by a holographic method. The hysteresis loop flattens out when measured repeatedly. The size of this aging effect strongly depends on the modulation depth m of the light intensity pattern: for $m = 1$ the aging is less pronounced than for smaller m. This behavior is explained in the context of the model of frozen internal charges for the ferroelectric relaxor SBN.

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1 Introduction

A specific property of ferroelectric Strontium-Barium-Niobate ($Sr_{0.61}Ba_{0.39}Nb_2O_6$, SBN) is its relaxor-kind phase transition, which is characteristically reflected in the temperature behavior of the order parameter, the spontaneous polarization P_S [1, 2]. The determination of P_S is central in the investigation of the basic principles of this phenomenon, which is still under deep discussion [3, 4]. Standard P_S-measurements rely on the collection of electric charges accumulated on the crystal surface. These charges result from various effects of the crystal bulk such as changes in the ferroelectric domain structure, electric currents through the crystal as well as from surface effects such as the build-up of an electric screening field near the electrodes. An unambiguous distinction between individual effects is doubtful. To overcome this problem a holographic method was introduced, which allows the undisturbed detection of the polarization in the crystal bulk and has been successfully applied to SBN [5, 6]. This method is based on the hysteresis-like behavior of the two-beam-coupling gain Γ (optical bistability) under varying external fields. This behavior is due to the dependence of Γ on the spontaneous polarization. As a result, the orientation of the polar c-axis governs the amplification in the beams involved.

In this paper, we present measurements of the diffraction efficiency η of an elementary holographic grating in Cerium-doped SBN (SBN:Ce) with varying external electric fields. We show that an aging of the ferroelectric hysteresis, which has been observed before by electrical measurements [7–9], also occurs in our measurements. The size of this aging effect depends on the modulation depth of the intensity distribution during the recording of the hologram: if the modulation depth is equal to unity, the aging is less pronounced than for smaller modulation depths. We discuss our observations in the framework of the model of internal random electric fields.

2 Experimental details

A single crystal of SBN doped with 0.66 mol % Ce was grown using the Czochralski technique and cut parallel to the crystallographic axes into a cuboid with dimensions of $5.4 \times 0.68 \times 3.10\,\text{mm}^3$ along the a-, b- and c-axis, respectively. Previous to the holographic measurements, the sample was electrically poled by heating it up to 140 °C, applying an external electric field of 350 V/mm along the crystallographic c-axis and then slowly cooling it down to room temperature before removing the field (field-cooling process). Therefore, the domains are aligned parallel to the applied external electric field. The crystal is then mounted on the holder of the holographic setup. The c-faces of the crystal are connected with silver paste to the electrodes of a high-voltage power supply. The polarity of the applied voltage with respect to the c-axis of the crystal at the beginning of a measurement of the ferroelectric hysteresis is shown in the upper left part of Fig. 1.

For the writing and the read-out of the holographic gratings, a polarized HeNe-laser with a wavelength of 632.8 nm is used. A beam expansion guarantees that the whole crystal between the electrodes is illuminated. The intensities and light polarizations of the signal and pump beam are adjusted independently by half-wave retarder plates ($\lambda/2$) and Glan–Thompson polarizers (P). An extraordinary light polarization is chosen for both beams. The signal and pump beam were adjusted for symmetric incidence under a Bragg-angle of $\theta_{\text{Bragg}} = 20°$ on the large a-face of the crystal, corresponding to an absolute value of the grating vector of $K_g = 6.79\,\mu\text{m}^{-1}$. The total writing intensity, i.e. the sum of the intensities of signal and pump beam I_S and I_P, was kept constant at $I_{\text{tot}} \approx 50\,\text{mW/cm}^2$, the modulation depth $m = 2 \cdot \sqrt{I_S \cdot I_P}/(I_S + I_P)$ was varied for different measurements between $m = 1$ and $m = 0.062$. The temperature was held constant at $T = 24$ °C. The beam overlap of the writing beams was controlled and

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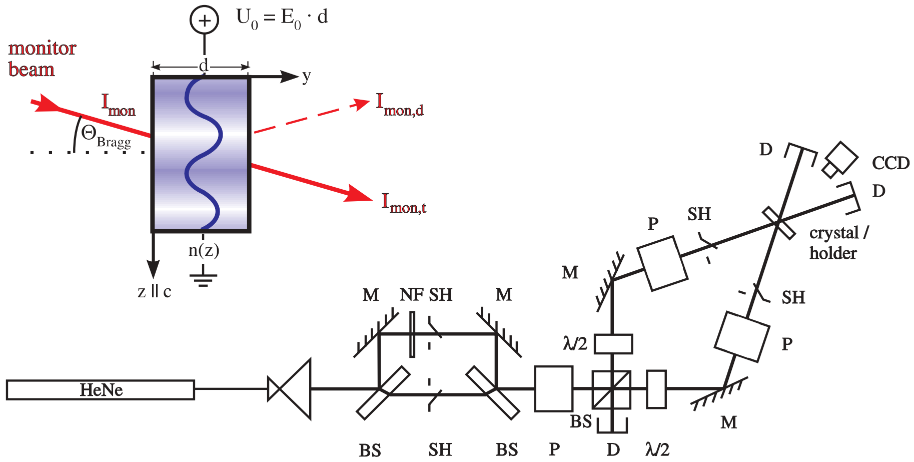

FIGURE 1 Experimental setup for the holographic measurement of the ferroelectric hysteresis. For details see text

optimized by a CCD camera. A hysteresis measurement was performed as follows:

1. recording of a hologram without an applied external electric field until a saturation state is reached
2. blocking of the writing beams and reading out the written hologram only with a weak monitor beam
3. step-by-step-application of an electric field during the read-out process and measurement of a certain number of sequent hysteresis loops

Details of this procedure are: Prior to each measurement sequence, the *c*-faces of the sample were short-circuited to ensure that the writing of the hologram is not influenced by any external electric field. The hologram was then written with a fixed modulation depth m until a saturation state was reached. Afterwards, both writing beams were blocked by means of shutters (SH), and the short-circuit was removed from the *c*-faces of the sample. An external electric field E_0 was applied stepwise, with an increase of $\Delta E_0 = -20\,\mathrm{V/mm}$ per step and a duration of $\Delta t = 5\,\mathrm{s}$ per step from $0\,\mathrm{V/mm}$ to $-460\,\mathrm{V/mm}$, back to $0\,\mathrm{V/mm}$ using the same step-width and duration, then from $0\,\mathrm{V/mm}$ to $+460\,\mathrm{V/mm}$, and again back to $0\,\mathrm{V/mm}$. After each step the diffraction efficiency η was determined using a weak monitor beam with an intensity of $I_{\mathrm{mon}} \approx 0.1\,\mathrm{mW/cm^2}$ (see upper part of Fig. 1). The transmitted and diffracted intensities, $I_{\mathrm{mon,\,t}}$ and $I_{\mathrm{mon,\,d}}$ as well as the laser intensity were detected by silicon photodiodes (D). For small modulation depths, the weak signal beam was used as the monitor beam, as it automatically fulfills the Bragg condition.

For $m = 1$, the monitor beam originated from an additional read-out branch of the holographic setup. It was coupled out from and back into the writing branch by two beam splitters (BS). The intensity of the monitor beam is adjusted by a neutral density filter (NF). A Glan–Thompson polarizer (P) is placed in front of the third beam splitter (BS) to guarantee the same light polarization in the writing and the read-out branch.

The measurement technique described above corresponds to a holographic measurement of the ferroelectric hysteresis. Each measurement consists of about ten consecutively recorded hysteresis loops. From the measured values of $\eta(E_0)$ the amplitude of the refractive index modulation $\Delta n(E_0)$ is determined according to the well known Kogelnik formula [10]. The graph of $\eta(E_0)$ has the shape of a typical butterfly curve, i.e. it contains information only about $|\Delta n(E_0)|$. To obtain the sign of Δn, we have to consider that the passing of η through zero is equivalent to a change of the sign of Δn. To check this, the value of the two-beam-coupling gain Γ of the hologram was read out in the vicinity of the coercive field. Since $\Gamma \sim \Delta n$, the sign of Γ gives us the sign of Δn.

3 Experimental results

As an example, Fig. 2 shows the typical dependence of the two-beam-coupling gain Γ on the illumination Q during the writing process for $m = 0.089$, corresponding to a ratio of $I_{\mathrm{P}}/I_{\mathrm{S}} \approx 500$. In the saturation state, a value of $40\,\mathrm{cm^{-1}}$ is reached. Once more, it has to be emphasized that the hologram was written without an applied external electric field and under symmetric incidence of the writing beams ($\theta_{\mathrm{Bragg}} = 20°$). After the writing process was finished, i.e., at about $Q = 850\,\mathrm{W\,s/cm^2}$ in the case of the measurement shown in Fig. 2, $\Delta n(E_0)$ was measured as described above.

Figure 3 shows $\Delta n(E_0)$ for two different modulation depths m. Part (a) belongs to $m = 1$, meaning equal I_{S} and I_{P}, while part (b) corresponds to $m = 0.089$. In both cases,

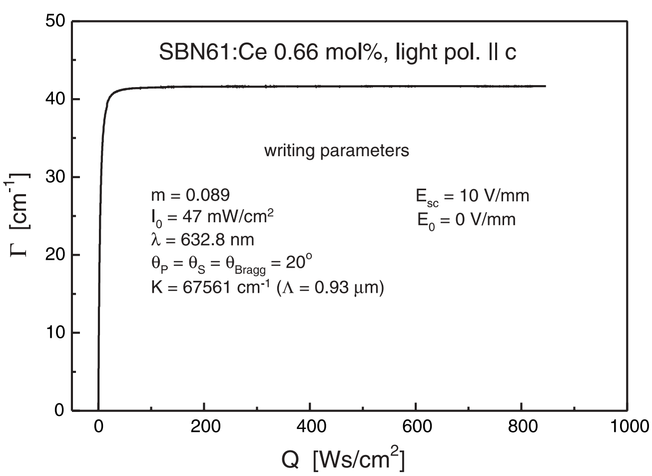

FIGURE 2 Typical dependence of the two beam coupling gain Γ on the illumination Q during the writing of a hologram. Note that no external electric field was applied during the writing process

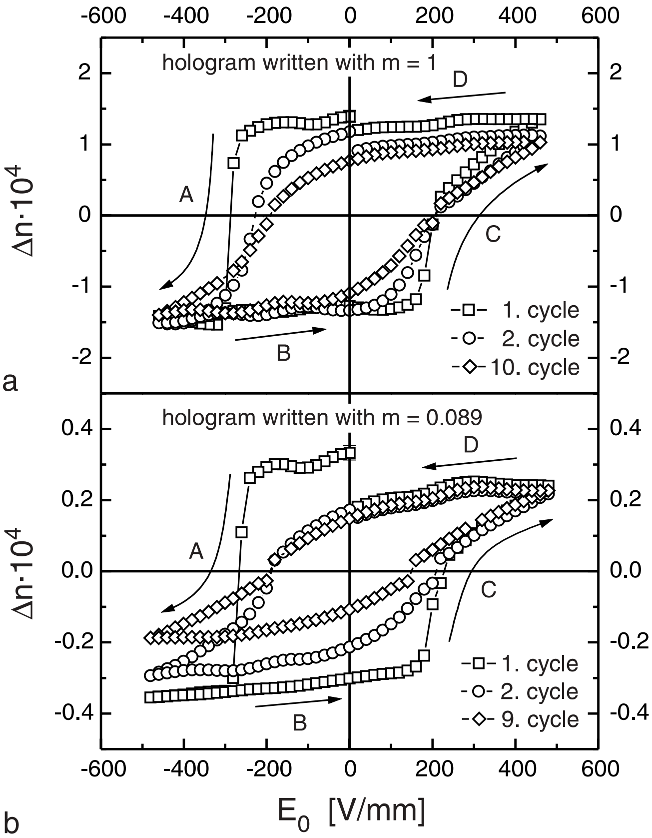

FIGURE 3 Holographically measured cycles of hysteresis loops in SBN:Ce 0.66 mol%. The first hologram was written with a modulation depth of $m = 1$ **a** and $m = 0.089$ **b**, respectively

the value of Δn decreases only very weakly with respect to the initial value when the external field is changed from 0 V/mm to -250 V/mm. When the external field exceeds -270 V/mm, Δn changes its sign and quickly reaches an absolute value comparable to that at the cycle start. This value decreases only weakly when E_0 is lowered to 0 V/mm, but starts to decrease at $E_0 > 0$ V/mm. Note that the coercive field E_c is asymmetric. The negative coercive field is $E_c^- = (-290 \pm 10)$ V/mm for $m = 1$ and $E_c^- = (-270 \pm 10)$ V/mm for $m = 0.089$, while the positive coercive field values are $E_c^+ = (+210 \pm 10)$ V/mm for $m = 1$ and $E_c^+ = (+230 \pm 10)$ V/mm for $m = 0.089$. When E_c^+ is exceeded, the sign of Δn changes once again, but $|\Delta n|$ is clearly lower than before. This attenuation of $|\Delta n|$ continues in the subsequent loops, until a steady state closed loop is obtained after about ten cycles. In the following, this attenuation process of $|\Delta n|$ will be referred to as aging. During the cycles, $|E_c^-|$ decreases, while $|E_c^+|$ does not change, making the hysteresis curve more symmetric.

The two measurements shown in Fig. 3 do not only differ in the amplitude of Δn at the beginning of each measurement, but the relative decrease of $|\Delta n|$ is also significantly smaller for the grating written with a modulation depth of $m = 1$. For this measurement, Δn decreases from 1.33×10^{-4} to 0.93×10^{-4}, or about 30%. For smaller m, the aging becomes more pronounced. For $m = 0.089$, Δn decreases from 0.32×10^{-4} in the first cycle to 0.13×10^{-4} for the tenth, a decrease of about 60%. This relative decrease of $|\Delta n|$ proved to be independent of the total writing intensity: When I_{tot} was increased from 50 mW/cm^2 to 250 mW/cm^2, the aging behavior did not change, neither for high nor low modulation depths m.

For a description of the attenuation of $|\Delta n|$ the positive quantity $\delta n = (\Delta n^+ - \Delta n^-)/2$ is calculated for each cycle. The determination of a mean value is necessary, because $|\Delta n^+| \neq |\Delta n^-|$. This approach refers to the electric measurements, where the same phenomenon of an asymmetry has been observed [9]. To allow a comparison of measurements for different values of m, δn was normalized with respect to the starting value. The result is shown in Fig. 4. Obviously, the decrease of δn of about 60% is comparable for the small modulation depths $m = 0.49$, 0.089 and 0.062. For $m = 1$ a decrease of only 30% was found, making this case of maximum contrast of the light intensity pattern an exceptional one.

Changes of the shape of the curves due to flattening and rounding are described by taking the derivatives at E_c^- and E_c^+ for each cycle, see Fig. 5. For a comparison the curves are again normalized with respect to their starting values. Note that the value at $E_0 = E_c^-$ corresponds to 1/4 of a full cycle, and the value at $E_0 = E_c^+$ corresponds to 3/4 of a full cycle. In contrast to the behavior of Δn, the derivatives are not affected by m. There is a clear decrease within the first two cycles and a stable state afterwards.

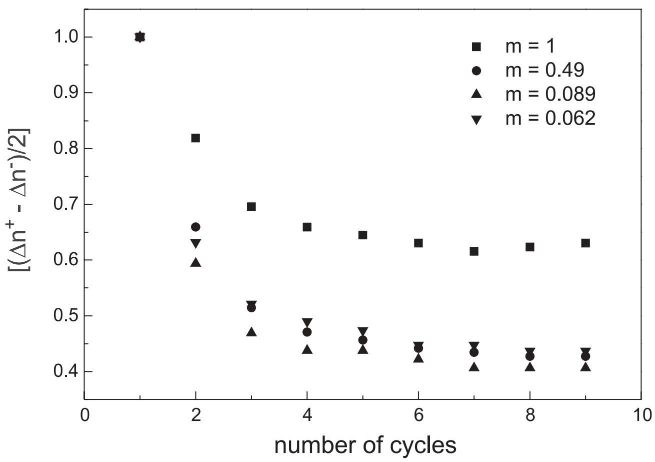

FIGURE 4 Amplitudes of the hysteresis loops for different values of m as a function of the number of cycles. Note that all values are normalized with respect to the starting value

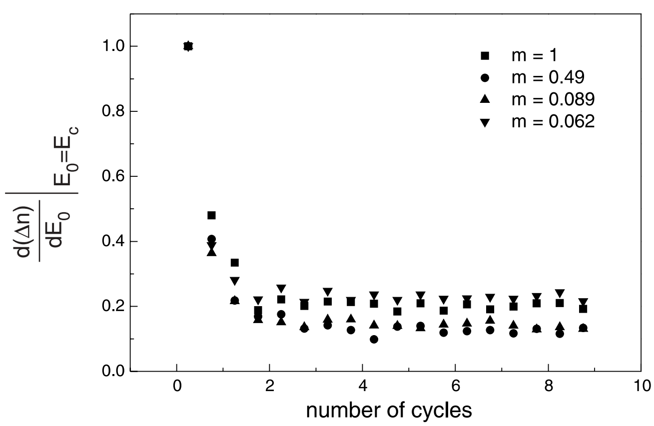

FIGURE 5 Slopes of $\Delta n(E_0)$ for different values of m as a function of the number of cycles. All values are normalized with respect to the starting value

A problem that has to be addressed here is the fact that the maximum value of $|\Delta n|$ before the start of the hysteresis measurement is not proportional to m, although it should be according to (1) (see below). While m differs by a factor of 11 in the two measurements shown in Fig. 3, the corresponding values of Δn differ only by a factor of 4. To explain this seeming contradiction, one has to keep in mind that the value of m has been determined by measuring I_S and I_P before the beams enter the crystal. Once the beams are in the crystal, they write holographic gratings, and the energy transfer between the two beams starts. The intensity ratio of the beams changes as they travel through the crystal, I_S increases while I_P decreases. Thus, the effective m will not be the same as that outside the crystal. However, because of using a thin crystal ($d = 0.68$ mm), one can be sure that a larger m outside the crystal will lead to a larger m inside the crystal. This makes a quantitative analysis of the relation between m and the relative loss of P_S due to aging difficult, while the qualitative argument still holds.

4 Discussion

Measuring the diffraction efficiency $\eta(E_0)$ clearly allows one to determine the ferroelectric hysteresis $P_S(E_0)$ of SBN:Ce. The results are complementary to our previous investigations [6], where the ferroelectric hysteresis of SBN doped with Ce and Tm was measured by means of holographic two-beam-coupling using intense probing beams. In comparison with all-electrical measurements [7–9], the holographic method clearly offers advantages: standard electrical methods measure P_S by accumulating charges on crystal surfaces. Therefore, surface effects like leakage currents or the influence of contact materials may influence the ferroelectric hysteresis. In contrast, the holographic method is bulk sensitive. Therefore, the optically measured ferroelectric hysteresis unambiguously mirrors the genuine bulk behavior of the spontaneous polarization. Repeated hysteresis measurements result in a decrease of P_S, the so-called aging, which has already been observed with all-electrical measurements. The observation of this phenomenon in the measurement presented here bridges the gap between the apparently contradicting results reported in [6, 9].

In order to discuss our results, we will recall some theoretical aspects connected with the recording of holograms in SBN:Ce. SBN:Ce is photorefractive via the electro–optic effect, whereby diffusion is the dominating charge transport mechanism. Illumination with a sinusoidal light intensity pattern of spatial frequency Λ results in an internal electric space charge field with amplitude:

$$E_{sc} = m\,\frac{k_B T}{e}\,\frac{K_g}{1+\left(\frac{K_g}{K_d}\right)^2}. \qquad (1)$$

Here, m is the modulation depth of the light interference pattern, k_B is Boltzmann's constant, T the temperature, e the unit charge, $K_d = \sqrt{\frac{e^2 N_{eff}}{\varepsilon_{33}\varepsilon_0 k_B T}}$ is the inverse Debye screening length with the static dielectric constant ε_{33}, and $K_g = 2\pi/\Lambda$ denotes the absolute value of the grating vector. The effective density of photorefractive centers N_{eff} must not be confused with the density of free electrons in the conduction band N_e. Due to the linear electrooptic effect, E_{sc} causes a modulation of the refractive index n with the amplitude $\Delta n = -(1/2)\cdot n_{eff}^3 \cdot r_{eff} \cdot E_{sc}$. It is noteworthy to recall that Δn is proportional to P_S via the linear electrooptic tensor [11]: $r_{ijk} = 2\cdot\varepsilon_0\cdot\varepsilon_{ll}\cdot g_{ijkl}\cdot P_S$. Therefore, the sign of Δn changes if the orientation of the ferroelectric polarization is reversed by an external electric field.

It is evident from (1) that E_{sc} depends on the modulation depth m. For this reason, the absolute values of Δn are much smaller for smaller values of m (Fig. 3). The influence of E_0 on E_{sc} is negligible due to the extremely low dark conductivity, i.e., the testing hologram remains stable during the hysteresis measurement. Hence, the observed aging effect can only be attributed to a pure loss of P_S, which was explained in the case of all-electrical measurements by the pinning of domain walls at random electric fields inherent in the crystal bulk [7, 12]. Our findings are a further result supporting this model: the optical method allows the measurement of the ferroelectric hysteresis with various modulation depths of the probing hologram. Using modulation depths in the range of $0 < m < 1$, Δn always saturates at nearly the same value (Fig. 4). In our optical measurements, a special case was observed for $m = 1$, where both the light intensity modulation and the diffusion current density is maximal, because the local density of free electrons N_e is approximately proportional to the local light intensity [13]. In this case the saturation value of the aging remains at a value which is 34% larger compared to the other measurements. We have already shown with ferroelectric measurements that the aging process can be reduced by homogeneous light illumination ($m = 0$) [14]. In a first attempt, we assumed that photo-ionized charge carriers compensate internal random fields, so that aging can not take place. It is well known that intense illumination has a strong influence on the switching behavior of ferroelectric domains [15, 16]. However, most theories primarily consider the screening of electric fields at domain tips by photoexcited charge carriers, facilitating a reversal of the domain orientation. In our case, the sample is practically monodomain at the beginning. Any internal fields at domain tips will be compensated by free charge carriers during the field-cooling process [17], since the dark conductivity at $T > 130\,°C$ is several orders of magnitude higher than that at room temperature. Thus, the illumination during hologram writing will not change the field distribution at domain walls. The hysteresis measurements themselves are performed at room temperature without significant illumination, so both dark and photoconductivity are too small to allow an effective screening of fields at domain walls. We, therefore, believe that the process of hologram recording changes the structure of the internal field configuration existing in the crystal bulk. The internal fields are at first independent from the domain wall distribution, but lead to the aging of $P_S(E_0)$ by pinning of the domain walls during hysteresis measurements. Our present results prove the interplay between free-charge carriers and the random fields: For $m = 1$, i.e., at large ∇N_e, internal charge carriers responsible for domain wall pinning are compensated, greatly reducing the aging of the ferroelectric hysteresis. A lower m corresponds to a lower ∇N_e, thus the compensation is not sufficient, and aging is observed. In contrast to the modulation depth, an increase of the total writing intensity I_{tot} does not influence the aging behavior at a given m. An increase of I_{tot} increases N_e, but ∇N_e depends only on the contrast and thus on m. This shows that a compensation requires both a transition to the conduction band and a subsequent diffusion induced movement of the charge to the pinning center. It is important to note that screening fields or the space charge field induced by the written hologram apparently play no role in the aging process or its reduction: If they did, one might expect that for the special case $m = 1$, the case with the most pronounced contrast between bright and dark areas and the largest space charge field, areas would exist in the crystal that are impassable to moving domain walls due to screening fields. The screening model, thus, predicts a more pronounced aging for higher values of m, which is clearly contrary to our observations. Our results indicate that the randomly distributed internal charge carriers acting as pinning centers have only a very limited effective range: If the effective range of a pinning center exceeded Λ, i.e., $\approx 1\ \mu$m, the induced field would attract electrons for compensating the pinning center. We can, thus, conclude that the effective range of an internal random field is much smaller than 1 μm.

The current dependence of the compensation of pinning centers also explains why the aging effect was not observed in hysteresis measurements by holographic two-beam coupling [6]. In those measurements, the crystal was illuminated all the time during the hysteresis measurement. In these conditions, we have a strong contribution of drift current to the formation of E_{sc}. The total current, the sum of drift and diffusion current, is high enough to compensate more or less all internal charges acting as pinning centers, thus aging is not observable.

5 Conclusions

Our measurements show that the aging of the ferroelectric hysteresis can be detected with a holographic method. Therefore, in contrast to pure electric measurements, it can be guaranteed that the aging actually originates from the crystal bulk. A characteristic dependence of the strength of the aging on the modulation depth was found, and an explanation based on the compensation of random fields by diffusion currents of photo-ionized charge carriers is given.

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