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Study of ferroelectric switching by domain-wall induced light scattering

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Measurements of 90°-scattering of weak laser light are used to investigate pulsed domain switching in ferroelectrics. The studies were performed on Strontium-Barium Niobate (SBN) single crystals. A good agreement of the switching parameters estimated from the optical measurements with those obtained by means of conventional electrical methods proves the validity of the optical method for switching studies. Due to the limited scattering volume in all three spatial dimensions the method facilitates a local probing of the switching within the crystal bulk. Particularly, local specialities of the domain density can be detected. Furthermore, the excellent time resolution inherent to optical probing techniques allows for a comprehensive study of the dynamics.

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Studies in ferroelectric switching take at present on special significance in view of developing the optical frequency conversion in the quasi-phasematching (QPM) mode of operation on periodically-poled, i. e., regular domain structures (RDS) in ferroelectrics. The ferroelectric solid solution $\mathrm{Sr}_x\mathrm{Ba}_{1-x}\mathrm{Nb}_2\mathrm{O}_6$ (SBN-x) represents a material appropriate for these purposes due to relatively high nonlinear-optical susceptibilities [1] and rather low coercive fields $E_c \propto 10^3\,\mathrm{V/cm}$. Two successful attempts of optical frequency conversion on RDS in SBN crystals were reported [2, 3]. Manufacturing RDS requires studies of ferroelectric properties, particularly of ferroelectric switching. However, there are only a few publications devoted to direct studies of the polarization process in SBN [4, 5, 6, 7]. The results of [4, 5] were obtained under quasi-static (slowly varying) fields, switching under pulsed fields was observed by means of the conventional method of switching currents [6, 7].

In the present work we report for the first time to our knowledge, on investigations of the ferroelectric switching of SBN crystals performed by means of light scattering measurements at domain walls. This method provides certain advantages over electrical methods, because it permits to observe the switching process in good spatial resolution over the complete crystal and because it shows a better time resolution.

In SBN crystals a 90°-scattering of a laser beam propagating normally to the polar axis was formerly reported [8, 9]. The scattering intensity drastically decreased in poled (single-domain) crystals or at temperatures above the phase transition to the paraelectric phase [9] and could be modulated by applying a low-frequency sinusoidal field [8], so it was undoubtedly attributed to domain evolutions. This type of scattering is due to the domain walls which are the regions of an inhomogeneity in the dielectric permittivity ϵ and can be treated, for example, as sandwich-like optical local inhomogeneities in the refractive index n_i [10]. Following this assumption, an incident plane wave characterized by a momentum vector k_i is partially reflected by a domain wall into a direction $k_r = k_i + 2(k_i q_m) q_m$ where q_m is the normal unit vector describing the wall geometry. The reflected amplitude due to a differential inhomogeneity δn and wall area dA can be approximated as

$$dE_r = E_i |k_i| H \frac{\delta n}{2n} \cdot dA, \tag{1}$$

where H is the thickness of the wall corresponding to δn (approximation valid for $|k_i|H \ll 1$). The total scattered intensity is obtained by integrating dE_r for a typical coherence volume and then – incoherently – by integrating over the illuminated volume. Following eq. 1 the complete intensity of the 90°-light scattering is proportional to three parameters: 1) the average domain wall thickness, 2) the typical magnitude of the inhomogeneity in n in the vicinity of the wall, 3) the total wall area (i.e., number of domain walls within the illuminated volume). In its turn, δn depends on the applied field E via the linear electrooptic effect.

The crystals under study were SBN-0.75 and SBN-0.61 for which we recently published the measurement of

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switching currents under pulsed fields [6, 7]. The samples were optically polished cubes of $5 \times 5 \times 5$ mm in size. A focused beam from a He-Ne-laser propagated normally to the polar axis z along x-direction, and the 90°-scattered radiation was registered in the mutually orthogonal direction y. Both, incident laser beam and scattered light were polarized parallel to the z-axis (extraordinary polarization). We measured the scattering only within a small part of the illuminated area limited by a small diaphragm placed directly in front of the crystal. Electric field pulses with a rise time of less than 1 μsec were applied in z-direction. Due to a low intensity ($0.05\ \mathrm{W \cdot cm^{-2}}$) of the propagating laser beam any photorefractive effects under applying fields were avoided and a uniform voltage distribution within the crystal bulk could be assured.

Fig.1 shows a typical scattering response (lower curve) upon an electric-field pulse (upper curve) in a

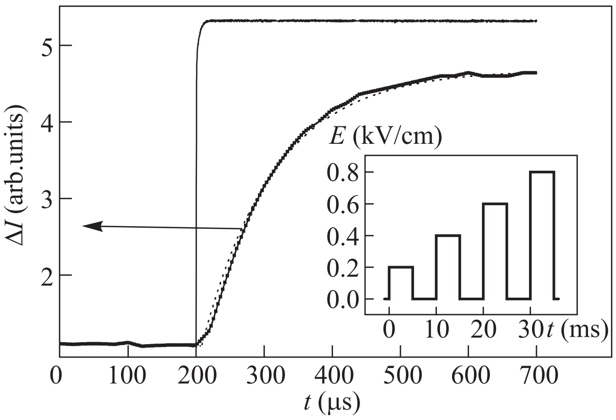

Fig.1. An example of the scattering kinetics (the lower curve) for applying a rectangular field pulse (the upper curve). The dashed curve in the lower represents a fit of experimental data to the exponential function. The inset shows the field pulse trains

poly-domain SBN-0.75 sample. At $E = 0$, both in poly-domain and poled SBN crystals a non-zero scattered intensity I_b exists which may be related to a variety of reasons – additionally to a contribution from domains. Below in terms of domain evolutions, we discuss a change of the scattered intensity $\Delta I = I_s - I_b$ (a "flash") under an applied field pulse. According to [9] we can assume that in first approximation a variation in the scattered intensity under applied fields may be attributed to variations in the domain wall density. Field-induced changes in H (see Eq. (1)) should only contribute as a second order effect. Field-induced changes of the refractive indices are to be neglected as they should follow the field immediately and not in a retarded way as we find it in the $\Delta I(t)$ response (Fig.1). Therefore, temporal characteristics of $\Delta I(t)$ depend on domain evolutions under a field pulse.

The kinetics of pulsed switching in ferroelectrics is characterized by switching times τ_s and velocities $v_s \propto \tau_s^{-1}$ depending on the field amplitude (e.g. [11]). Using our technique we deduce τ_s directly from the kinetics of $\Delta I(t)$ (Fig.1), which may be fitted by an exponential function $\Delta I = \Delta I_{\mathrm{sat}}[1 - \exp(-t/\tau_s)]$ (the dashed lower curve in Fig.1). From a set of $\Delta I(t)$ curves obtained under a pulse train (presented in the inset in Fig.1) we can derive the dependencies $\tau_s(E)$ and $\tau_s^{-1}(E)$. Fig.2 presents the plot $\tau_s(E)$ in an initially poly-domain sample SBN-0.75.

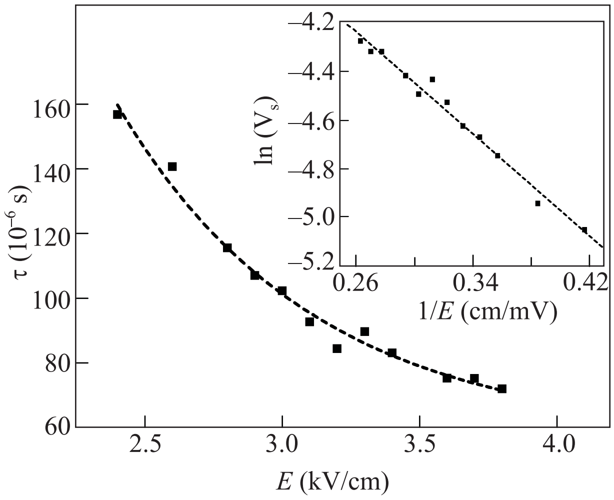

Fig.2. Switching times as a function of the field amplitude in a poly-domain SBN-0.75. The inset shows the switching velocity τ_s^{-1}, the dashed curve represents its fit by the exponential function (see text)

The values of τ_s range in tens of microseconds and are in a good agreement with switching times obtained under pulse fields in the same crystal by the switching current method [6, 7]. The field dependence of the switching velocity $\tau_s^{-1}(E)$ in ferroelectrics at moderate fields often obeys an exponential law $\tau_s^{-1} = A \exp(-E_a/E)$ [11]. A fit to the measured values of τ_s^{-1} – shown as a dashed line in the inset in Fig.2 – yields $A = 5.42 \cdot 10^4\,\mathrm{s^{-1}}$ and $E_a = 5.1\,\mathrm{kV/cm}$. The latter amount characterizing an "activation field" of the switching is reasonable and close to the values of E_a found in other ferroelectrics, such as $BaTiO_3$ and TGS [11].

We continue with a discussion of the field dependence of the scattering intensity, i.e. of the domain density. Fig.3 presents the plots $\Delta I(E)$ for initially poly-domain SBN-0.61 and SBN-0.75 crystals. The right and left branches of the curves correspond to "+" and "-" field

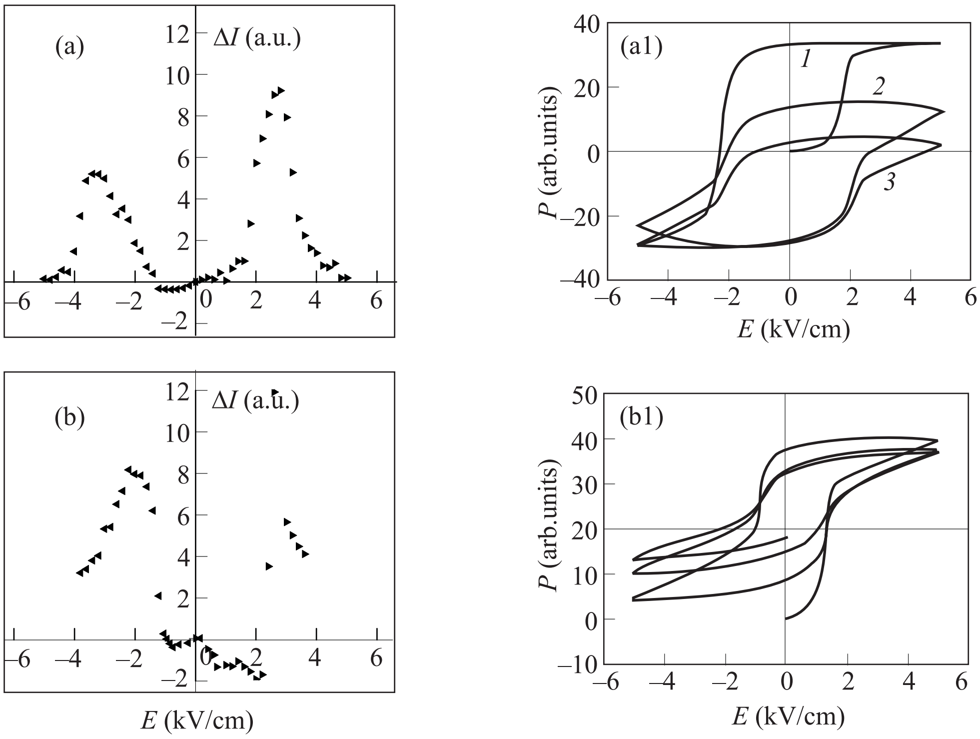

Fig.3. Light scattering intensities as a function of the field amplitude in poly-domain crystals SBN-0.61 (a, a1) and SBN-0.75 (b, b1). Panels (a1) and (b1) show $P-E$ loops obtained under quasistatic fields in the same crystals, labels *1*, *2*, *3* denote successive field cycling

signs, respectively, uniquely settled with respect to the crystal geometry. Every time before applying a pulse train of a given polarity, the crystal was brought into a poly-domain equilibrium by annealing it in the paraelectric phase. This means that $+E$ and $-E$ branches of $\Delta I(E)$ were measured under identical conditions. The following common features may be recognized in the curves $\Delta I(E)$ for two crystals under study. In the range of relatively low fields of the both signs, ΔI only very slightly varies with E; at certain $E_{\max}$ depending on the composition, ΔI passes a maximum; the curves are asymmetrical, namely, in a given crystal the values of the $E_{\max}$ and peaks ΔI are different for two field polarities. To discuss these curves in the language of ferroelectricity, recall that according to the classical model [11], the polarization (or switching) process proceeds only very slightly under low external fields, and is strongly enhanced when approaching the coercive field E_c. At E close to E_c, the domain structure is reconstructed, namely, new domains are being nucleated and growing through the crystal bulk either frontally, or by means of the side domain-wall movement [11]; the domain density is drastically increasing when approaching E_c. Provided that the pulse duration exceeds the switching time, the crystal is totally polarized (or repolarized) during a single pulse $E \propto E_c$, so on further enhancing the field amplitude the domain density tends to zero. Therefore, the dependence of the domain density on the pulse train amplitudes would schematically look as $D \neq 0$ for $E < E_c$; $D = D_{\max}$ for $E = E_c$ and as $D = 0$ for $E > E_c$. In the light of this simplified presentation, the values of $E_{\max}$ in the curves of Fig.3 should correlate with the coercive field E_c. Different absolute values of $E^+_{\max}$ and $E^-_{\max}$ and different peak intensities for $+E$ and $-E$ branches in a given crystal should characterize the so-called unipolarity, i.e. a preferable direction of P_s or, what is the same, an initial non-equality of the domain densities of "+" and "-" domains, in a crystal on a whole or at a given crystal position.

To justify this interpretation we show in the insets in Fig.3 dielectric hysteresis loops obtained in the same samples in a quasistatic regime with a cycling loop of about 2 hours. The observed specific of $P-E$ hysteresis, namely, "open-shaped" loops and a non-coincidence of their trajectories on several first cycling is characteristic for all SBN crystals [4, 5] and is accounted for by a relaxor origin of this material [12]. Averaged values of E_c estimated from several first $P-E$ cycles for SBN-0.75 and SBN-0.61 are 1.5 and 2.5 kV/cm, respectively which is in good agreement with the average values of $E_{\max}$ for the same crystals (2 and 3 kV/cm). The $P-E$ loops are unipolar, that is shifted along the E axis. The unipolarity is usually characterized by a bias field $E_b = (|E_1 - E_2|)/2$, where E_1 and E_2 are coercive fields corresponding to the left and right halves of a $P-E$ loop [11]. Averaged values of E_b estimated from first $P-E$ cycles are 0.15 and 0.3 kV/cm in SBN-0.75 and SBN-0.61, respectively. For the optical curves $\Delta I(E)$ we define a bias field in a similar manner $E_b = (|E^+_{\max} - E^-_{\max}|)/2$, yielding $E_b = 0.3$ kV/cm and 0.4 kV/cm for SBN-0.75 and SBN-0.61, respectively. These amounts are in reasonable agreement with the dielectric results. The values of E_b in $P-E$ loops slightly differ from that obtained from $\Delta I(E)$ curves because of different measurement conditions and rather conventional estimates of $E_{1,2}$ from "open-shaped" $P-E$ loops.

The results presented in Figs.1–3 demonstrated the validity of the optical method for ferroelectric switching studies, because all parameters deduced from the optical measurements (coercive and bias fields, unipolarity, switching times and velocities) agree with those obtained by traditional electrical methods.

We now emphasize a fundamental divergence of the switching process in SBN as reported in [4–7] from the usual model scenario [11]. In SBN crystals, unlike in ideal ferroelectrics, no uniquely determined coercive field exists and a switched charge Q_s is controlled not only by field amplitudes, but the pulse duration as well. The total polarization (or polarization reversal) requires applying fields during tens of seconds [6, 7], so under short pulses $Q_s \ll P_s$ even at $E \gg E_c$. Under our experimental conditions we deal with a partial switching. For this reason the background intensity I_b in a poly-domain crystal is practically unchanged after applying a pulse train, and the peak $\Delta I_{\max}$ is smeared over a rather wide field range. The times shown in Fig.2 describe the switching of a small part of the crystal volume. Note again that despite the fact that the crystals were preliminary annealed in the paraelecric phase to bring them to a poly-domain state, they retain an unipolarity. That is why the initial domain density after annealing $D_0 < D_{\max}$ (the initial light scattering $I_0 < I_{\max}$). This unipolarity in an annealed crystal seems to be a specific of a relaxor ferroelectric.

Now we show an example of a local speciality of ferroelectric switching in SBN, which was observed by scanning the bulk, and hence not found by integrating electrical methods. The field dependencies $\Delta I(E)$ presented in Fig.3 with a small scatter in the values of $E^{\pm}_{\max}$ are qualitatively similar in any region of a given crystal apart from the electrodes. However, when approaching them, these dependencies become qualitatively different. Fig.4 presents curves $\Delta I(E)$ obtained in SBN-0.75 (the same, as in Fig.3b) in spots adjacent

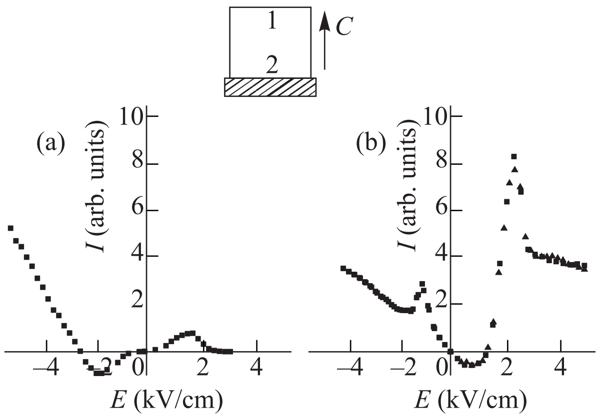

Fig.4. Light scattering intensities as a function of the field amplitude in the vicinity of the upper (*1*) and lower (*2*) electrode in a poly-domain SBN-0.75 crystal. The inset represents schematically the layout of the sample

to electrodes, approximately 0.1 mm apart from the upper and lower ones, respectively (the inset in Fig.4). Both branches of these curves were obtained in the poly-domain state, again after a preliminary annealing in the paraelectric phase. These edge-related dependencies of $\Delta I(\pm E)$ show a pronounced asymmetry. When a positive potential is applied to an electrode, the dependence $\Delta I(+E)$ is similar to $\Delta I(\pm E)$ apart from the electrodes, it shows a maximum at $E^+_{\max}$ coinciding with the average $E_{\max}$ in the bulk and comes to a low saturation level at $E > E^+_{\max}$. In contrast, if a negative potential is applied to the same electrode (left branches of the curves Fig.4a,b), then ΔI) after passing over a slight maximum, gradually increases with E without tending to saturate. It should be emphasized that these dependencies unambiguously correlate to the polarity of the electrode: a gradual increase of $\Delta I(E)$ is observed always close to the negative one. This means that with increasing field amplitude, the domain density is growing at the negative electrode only and becomes non-uniformly distributed along the polar axis. The only explanation of this asymmetry in the domain density is a preferable domain nucleation at the negative electrode and their subsequent evolution in the region adjacent to it, whereas the positive electrode is "silent". This asymmetry in the domain density under short field pulses corroborates the fact that a total polarization (or polarization reversal) in SBN requires applied fields for tens of seconds [6, 7], so domains nucleated at the negative electrode cannot germinate through the crystal bulk during applying short pulses even at $E \gg E_c$. Such a non-equiprobability of the domain nucleation is not unique, for example, a preferable domain nucleation at the negative electrode was observed in $LiNbO_3$ as well [13] by means of a successive etching the crystal in the course of a long-term field application. An in situ observation of a non-uniformity of the domain density distribution in SBN crystals presented here, would be useful for elaborating techniques for creation of RDS.

The domain-wall induced light scattering is obviously common for a wide group of ferroelectric crystals. For example, it was also observed in Gd_2MoO_4 [14] and $Sn_2P_2S_6$ [15]. In SBN crystals this effect is very pronounced, perhaps because of a relatively large thickness of a domain wall, or, to be more precise, of a perturbed layer adjacent to it. A possible reason may be either an elastic strain or a space-charge field in the vicinity of the domain wall, which would lead to a large inhomogeneity in the refractive indices via the elasto- or electrooptic effects, respectively. A large elastic strain at a moving domain wall may be specific for ferroelectric crystals with a high piezoelectric effect. A space-charge field arises, if domain walls are inclined with regard to P_s which is actually realized in SBN, e. g. [16].

In summary, we could demonstrate that 90°-light scattering is an excellent tool to investigate ferroelectric switching. The scattered light intensity is due to contributions from domain walls. The results can complement and extend those obtained by conventional electrical measurements. In addition to a good time resolution, the method facilitates spatially resolved measurements of switching processes. For example, we detected a preferred polarity of the electrode for the domain nucleation. Potential application of the technique includes a wide group of crystals, particularly those possessing extended domain walls.

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