1. INTRODUCTION

Ferroelectric crystals of the solid solution of strontium barium niobate \( \text{Sr}_{x}\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \) (SBN) represent uniaxial polar compounds with a structure of tetragonal tungsten bronzes of the general formula \( \text{AB}_2\text{O}_6 \) [1, 2] exhibiting the relaxor behavior [3]. The symmetry of SBN crystals in the ferroelectric phase corresponds to point group \( \text{C}_{4v} \) [2, 3]. The domain structure in SBN as in any uniaxial ferroelectric consists of domains separated by 180° domain walls [1].

The SBN single crystals exhibit high values of electro-optic, nonlinear-optic, piezoelectric, and pyroelectric coefficients [4, 5], which makes it promising for application in optoelectronics, piezotechnics, nonlinear optics, and holography [3, 6].

The SBN single crystals exhibit high values of electro-optic, nonlinear-optic, piezoelectric, and pyroelectric coefficients [4, 5], which makes it promising for application in optoelectronics, piezotechnics, nonlinear optics, and holography [3, 6]. The possibility of using SBN single crystals with a regular domain structure for laser wavelength conversion in the quasi-phase matching regime is discussed [7]. The laser wavelength conversion with a high efficiency requires the creation of a precise regular domain structure. However, the process of domain structure creation in SBN single crystals under the action of an electric field is still under investigation.

The ineffective attempts to visualize domains in SBN single crystals by optical microscopy after selective chemical etching or decoration were undertaken in the 1970s [3]. The static domain structure has been visualized for the first time using a polarizing microscope in plates cut at 45° to the crystal polar axis [8]. It was shown that application of the electric field exceeding the threshold value results in the formation of striped domain-like structures with a micron period in thermally depolarized samples [8].

Application of various modes of scanning probe microscopy allowed one to improve considerably the spatial resolution for investigation of static micro- and nanodomain structures in SBN single crystals [9–11]. Piezoresponse force microscopy (PFM) allowed one to reveal that the domain structure of SBN61 single crystals formed after thermal depolarization corresponds to island structures with characteristic sizes of the order of several hundred nanometers [10]. The coexistence of polar nanoregions (nanodomains) with the opposite polarization direction and nonpolar inclusions was revealed in SBN61 : Ce (0.80–1.13 at %) in the given temperature range [11]. A decrease in the temperature led to enlargement of polar nanoregions and to a decrease of nonpolar inclusions.

There are only a few publications devoted to investigation of the domain structure kinetics in SBN single crystals where the evolution of the domain structure was studied by methods with relatively low spatial resolution, such as optical microscopy [12–14] and decoration by nematic liquid crystals [15, 16].

In this paper, the maze initial domain structure formed after thermal depolarization and the domain structure obtained by switching from single-domain state were studied in SBN61 : Ce single crystals. PFM was used for domains visualization with a high spatial resolution. Fractal and correlation analysis of images of the original maze-type domain structure was carried out. The single-domain state was created in the surface layer using the application of the series of alternating electric field pulses.
electric field pulses. Images of the static domain structures formed after partial switching have been used for studying the structure and shape of isolated nanodomain ensembles, as well as the process of “merging” of neighboring ensembles.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

The studied plates were cut normally to the polar axis from the doped 0.004 wt % CeO₂ bulk-profiled Sr₀.₆₁Ba₀.₃₉Nb₂O₆ (SBN61 : Ce) single crystals grown from the melt by the modified Stepanov technique at the Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russia) [17]. The SBN61 composition was chosen because such single crystals demonstrate the best optical quality [3]. Polar faces of the studied 0.5-mm-thick plates were polished thoroughly.

Static domain structure investigations with high spatial resolution were implemented by PFM method using scanning probe microscope NTEGRA Aura (NT-MDT, Russia). The cantilevers DCP20 (NT-MDT, Russia) with a conductive diamond-like coating were used. Visualization of the domain structure was carried out by applying the modulating voltage with amplitude 5–15 V and frequency 12.5–17.4 kHz. The electric field was applied between the top mobile electrode which served as conductive probe contacting the sample surface and bottom electrode produced by silver paste. The fixation of the sample on a metal disk was done by silver paste also. Mechanical oscillations of the surface of ferroelectric induced by application of ac electric field caused by reverse piezoelectric effect were measured using a selective amplifier LockIn SR-830 (Stanford Research Systems, United States) [18].

Selective chemical etching by concentrated hydrofluoric acid HF for about 10 min at room temperature was used for revealing of the static domain structure. The formed surface relief was measured by contact atomic force microscopy.

The electric field for the polarization reversal was applied using a cell with liquid electrolyte electrodes described in [13]. Rectangular field pulses were generated by DAC board PCI-6251 (National Instruments, United States) controlled by the original software, and amplified by a high voltage amplifier Trek 677B (TREK, United States).

All experiments were carried out at room temperature which is below the freezing temperature for investigated crystal [19]. The thermal depolarization of the samples was performed before the measurements by heating up to 210°C and zero field cooling.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. The Initial Domain Structure

A typical image of the initial domain structure after thermal depolarization obtained by piezoresponse force microscopy is shown on Fig. 1. The light and dark areas correspond to domains with opposite directions of spontaneous polarization. The detailed analysis has shown that the image of the initial domain structure represents a section of a complex three-dimensional quasi-regular self-similar (“fractal”) nanodomain maze. It should be noted that due to the features of PFM method the piezoelectric response is caused by the domain structure not only at the surface, but also in the volume near the surface. Therefore, the observed blurring of the boundaries between domains is due to the fact that the domain structure is a three-dimensional maze.

The characteristic size (“maze period”) used as the statistical characteristic of the maze domain structure was defined as the position of the first maximum of the autocorrelation function, and was found to be 120 ± 40 nm. The fractal dimension of the obtained two-dimensional maze image was measured using islands, Korczak, and cell methods [20, 21] and found to be 1.32 ± 0.08. Thus, the fractal dimension of three-dimensional maze is 2.32 ± 0.08 [21].

It should be mentioned that the similar initial domain structure representing three-dimensional maze formed by thermal depolarization was also observed in single crystals of the uniaxial ferroelectric lead germanate Pb₅Ge₃O₁₁ (PGO) [18]. The fractal dimension in PGO and SBN are practically identical, but the “maze period” in the PGO is above micron, which is much higher than in SBN.
3.2. Single-Domain State Formation

It is known that the application of external electric field allows to enlarge the initial domain structure in ferroelectrics and to create a single-domain state [3]. Therefore, before the domain kinetics study we performed domain structure “forming” by application of a series of 30 to 50 rectangular or triangular ac field with frequency from 0.1 to 0.4 Hz and field amplitude from 250 to 800 V/mm. The uniformity of the single-domain state induced in the surface layer by forming was controlled by PFM, as well as by measurement of surface topography using atomic force microscope after selective chemical etching.

3.3. Formation of the Nanodomain Ensembles after Partial Switching

The single rectangular electric field pulse with duration less than the switching time was applied for the formation of a multidomain state in the surface layer (partial switching). The domain structure was visualized using PFM.

Typical PFM images of the domain structure formed by the field pulse with amplitude 340 V/mm and duration 300 ms are shown on Fig. 2. The obtained images with a relatively low spatial resolution can be considered as a confirmation of the evidence of formation of usual domain structure consisting of micron size “square domains” during polarization reversal in SBN [12]. However, the analysis of PFM images with higher spatial resolution showed that all switched areas presented not the homogeneous domains, but quasi-regular structures consisting of isolated nanometer-sized domains—“nanodomain ensembles” with rough boundary (Fig. 3). Detailed study has shown that typical diameter of isolated nanodomains in ensemble varies from 100 to 200 nm, and the average size of nanodomains increases on the way from the edge of the ensemble to its center (Fig. 3).

Thus, the kinetics of SBN domain structure is not a classical growth of homogeneous domains due to the sideways motion of the domain walls. Increasing of the ensemble area is due to the “discrete switching” in which isolated nanodomains were appeared in the vicinity to the boundary of the ensemble. In the case of the observed discrete switching, the domain wall is substituted by rough boundary of the region covered by formed isolated nanodomains.

It should be stressed that the formation and growth of nanodomain ensembles with the shape close to the shape of usual domains has been observed previously for completely ineffective screening conditions (strongly non-equilibrium switching conditions) in single crystals of lithium niobate and stoichiometric lithium tantalate with artificial surface dielectric layer obtained by proton exchange and by photoresist layer on the crystal surface [22]. It was shown that the average period of the structures (distance between the nearest isolated domains in the ensemble) is equal to the thickness of artificial dielectric layer (dead layer), which is caused by the correlated nucleation effect [22]. Such analogy allows us to assume that the thickness of the intrinsic dielectric gap in SBN is about 100 nm.

3.4. Partial Merging of the Nanodomain Ensembles

PFM measurements allowed also to reveal partial merging of the growing ensembles and decreasing of the isolated nanodomains concentration along the line...
of ensemble contacts (Figs. 2 and 4). This effect is similar to the effect of residual domains formation during coalescence, observed in lithium niobate single crystals with a surface layer modified by proton exchange [22]. This fact indicates the interaction between approaching isolated nanodomains with charged domain walls.

It is known that the effect of shape persistence is observed in lithium niobate single crystals. It represents the recovery of the hexagonal domain shape after merging of two isolated hexagonal domains and formation of the polygon with concave sides due to accelerated motion of “concave domain walls” [22]. The absence of such effect in SBN is a consequence of incomplete merging of the nanodomain ensembles (Figs. 2 and 4).

3.5. Shape of the Nanodomain Ensembles

The enlarging of the nanodomain ensembles in SBN is similar to the “classic growth” of macroscopic isolated domains, and ensemble shape is similar to the shape of domains determined by the crystal symmetry [1, 22]. It was found that the increase of domain size leads to change of the nanodomain ensembles shape (geometry) from “circular” (for submicron sizes) to “square” with barrel distortion [23] (Fig. 2).

The observed effect can be attributed to change of the relative contribution of competing stochastic and determined nucleation mechanisms [22]. Stochastic nucleation leads to the isotropic growth of “circular” nanodomain ensembles, and determined—to the anisotropic growth of “square” ensembles. Obtained “square” shape of ensembles is similar to the classical domains shape in barium titanate [24] and is defined by the symmetry of the SBN crystal in the ferroelectric phase—\( C_{4v} \).

The visualization of all obtained domain structures on the opposite polar surface of the plate demonstrated that the formed domain structure is non-through and, therefore, consists of needle-like domains with charged walls. It is important to note that the formed structure remained constant for several months, despite the fact that it is clearly metastable, because the presence of charged domain walls increases considerably the depolarizing energy.

3.6. Field Dependence of Shape and Structure of the Nanodomain Ensembles

Increase of the amplitude of the applied field pulses resulted not only in acceleration of the switching process (decrease of the switching time), but also in decrease of the concentration of nanodomains in the ensemble and a significant increase of “roughness” of the domain wall from 20 nm for pulse amplitude 340 V/mm to 100 nm for pulse amplitude 680 V/mm (Fig. 3). The value of roughness \( R_y \) was calculated as the arithmetical mean of absolute deviations of the domain wall \( y_i \) in the range of basic line determined by the least square method: 

\[
R_y = \frac{1}{n} \sum_{i=1}^{n} |y_i|, \text{ where } n \text{ is the number of points at the base line [25].}
\]

In addition, in higher fields the ensemble shape became closer to the circle, which indicates the dominant role of isotropic growth.

The observed effects may be caused by ineffective screening of depolarizing fields during switching time decrease [26]. It is known that inefficient screening leads to deceleration of domain wall motion and formation of isolated nanodomains in front of a moving domain wall [22]. In this case, the merging of isolated nanodomains with a moving domain wall results in the equiprobable generation of steps (stochastic nucleation), which leads to isotropic domain growth.

4. CONCLUSIONS

The investigation of the formation of nano- and micro-domain structures in single crystals of relaxor ferroelectric strontium barium niobate \((Sr_{1.5}B_{0.79}N_{1.5}O_{6})\), doped with cerium was performed. Initial nanodomain structure formed after thermal depolarization is a three-dimensional maze with an average period about 120 nm and a fractal dimension of 2.32. The single-domain state was created in the surface layer by application of series of ac electric field pulses. It was shown that the structures formed as a result of polarization reversal from single-domain state in SBN differ qualitatively from the classical domains and represent quasi-regular ensembles of isolated needle-like nanodomains with charged domain walls. Increasing of the ensemble area is due to the formation of isolated nanodomains in the vicinity of the ensemble boundary. It was shown that enlarging of the nanodomain ensembles leads to changes of their shape from “circular” to “square” with barrel distortion. Moreover the increasing of applied field decreases the concentration of nanodomains in the ensemble and increases the domain wall “roughness”.
thus leading to isotropic ensemble growth. The observed effects are attributed to increasing of the screening inefficiency with decreasing of the switching time.

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