Indentation induced local polarization reversal in La doped $BiFeO_3$ ceramics

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ABSTRACT

Stress-induced local polarization reversal was studied in La doped $BiFeO_3$ ceramics under the action of Berkovich-type prism indentation. Piezoresponse force microscopy was used for detailed study of domain structure before and after local polarization reversal. Two mechanisms of domain formation under the action of the mechanical loading were revealed: (1) direct stress-induced and (2) stress mediated by grain clamping. Critical stress value for local polarization reversal was extracted from the dependence of the switched area on the applied loading force.

Keywords: bismuth ferrite, mechanical loading, indentation, polarization reversal, domain structure

Running head: Local switching by indentation in BLFO ceramics

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1. Introduction

Ferroelectric materials are widely used for variety of electromechanical applications such as transducers and actuators [1, 2], where they are protractedly exposed by electrical and mechanical loads. While polarization reversal under the action of electric field has been comprehensively studied for decades, influence of mechanical stress on it is still not totally understood. Mechanical stress was shown to induce phase transitions [3-5], modification of electromechanical properties [6, 7], and polarization reversal [8, 9] in ferroelectric materials. By analogy with electric field induced local polarization reversal, where non-uniform electric field is created by the biased tip of scanning probe microscope (SPM), indentation of a ferroelectric with enough load can induce polarization reversal [10-12]. This method looks attractive to go deeper in understanding of domain wall motion under the action of mechanical loading. Indentation induced polarization reversal was studied in the past in relaxor PMN-PT [10], $BaTiO_3$ [13], tetragonal ZrO_2 [11] and $SrTiO_3$ [14] single crystals, as well as PZT [15] and ZrO_2 [5] piezoelectric ceramics, where it was generally attributed to the direct influence of stress and strains induced by the mechanical loading. Nevertheless, it must be noted that the particular focus of the previous works was on single crystals as more simple systems [13, 16, 17]. In ferroelectric ceramics, specific conditions of domain growth exist, for example, domain wall mobility can be limited by orientation of neighboring grains [18]. Grain boundaries usually concentrate defects and can act both as pinning center for domain walls and as nucleation sites [19, 20]. In addition, specific conditions for the stress propagation exist in ceramics that, for example, hinder the movement of a crack (so-called, “crack grown resistance”) [15]. The stress could have indirect effect on domain structure because of grain clamping that can mediate transfer strain from one grain to another.

In this work, we studied indentation induced local polarization reversal in La doped $BiFeO_3$ (BLFO) ceramics. $BiFeO_3$ (BFO) ceramics are perspective lead-free material for electro-mechanical applications [21], while doping by rare earth elements stabilizes the perovskite phase that decreases amount of secondary phases and, correspondently, leakage current [22, 23]. Moreover, morphotropic phase boundary is realized in some doping concentration range that improves piezoelectric properties through the anti-polar-to-polar phase transition [24-26]. Here, we showed that indentation of BLFO ceramics led to the visible domain structure transformation both under immediate place of indentation and in some area around. Details of the local polarization reversal by indentation were analyzed and switching mechanisms were discussed. Piezoresponse force microscopy (PFM) was shown to be useful technique for study of the switching under the action of mechanical load.

2. Experimental

The investigated samples of BLFO ceramics with molar La concentration 5% were produced using the two-stage solid phase synthesis [27]. The initial high purity oxides were taken in the stoichiometric ratio and thoroughly mixed for about 30 min in a planetary mill RETSCH PM-100 using high purity isopropyl alcohol as a medium. Preliminary synthesis was made at 800°C for 2h, the final synthesis was performed at 900°C for 12h. The samples were quenched from the synthesis temperature down to room temperature. X-ray diffraction (XRD) measurements were made on Rigaku D/MAX-B diffractometer using Cu-Kα radiation. The XRD data were processed by the Rietveld method using the FullProf software.

Since obtained BLFO ceramics were porous, one BFLO sample was permeated by epoxy under vacuum to decrease porosity and to facilitate the realization of the experiments. Further, both as-sintered and permeated by epoxy samples were rigorously polished by the diamond paste with abrasive size decreasing from 6 to 0.25 μm. Fine polishing was performed with colloidal silica (SF1 Polishing Suspension, Logitech, UK). Indentation of investigated samples was realized on scanning nano-hardness tester “NanoScan-4D” (FSBI «TISNCM», Russia) by application of local mechanical loading with diamond indenter of Berkovich type, trihedral pyramid, with 65.3° angle between the axis of the pyramid and face, and 70.32° equivalent angle of the cone. The curvature radius of the indenter was less than 100 nm.

Domain structure before and after indentation was studied by vector piezoresponse force microscopy (VPFM) realized in scanning probe microscope Asylum MFP-3D (Asylum Research, Oxford Instruments, UK). MikroMasch NSC18/Pt probes with 30 nm tip radius, 75 kHz free resonance frequency and 2.8 N/m spring constant were used. Measurements were done with 20 kHz 5 V_{AC} voltage applied to the tip. R·cosΘ PFM signal was corrected by phase angle rotation in such a way that minimizes R·sinΘ signal and further plotted as image. We further address these images as piezoresponse.

3. Results and discussion

The grain size in BLFO ceramics was about 6-8 μm. VPFM images of BLFO demonstrated mostly piezoelectrically active rhombohedral (*R3c*) phase [28]. Domain structure consisted of prolong lamellar domains converging to one side with non-180-degree domain walls and irregular shaped watermark areas with 180-degree domain walls (Fig. 1). Piezoresponse distribution had discrete values of the measured signal (contrasts) corresponding to the different types of domains allowed by rhombohedral symmetry conditions. Non-180-degree domain walls are clearer seen in the in-plane phase signal, while out-of-plane signal was mostly corresponded to boundaries of watermark areas.

In order to study polarization reversal under the action of mechanical load, we made the indentation within matrix of points with linear growth of applied force from 10 to 50 mN. The scheme of indentation experiments is presented in Figure 2a. During indentation, the loading curves $F = f(h)$ (Fig. 2b) were built. These curves are real experimental analog of stress-strain curve $\sigma = f(\varepsilon)$. It consists of three sections: 1) loading, when polarization switching occurs, 2) delay – holding at the constant load, and 3) uploading, when elastic relaxation of the loaded state occurs. At the uploading stage, backswitching of stress-induced domains can happen [12]. It is speculated that backswitching can give an impact to pop-up event at the finish of uploading [29]. As a result of indentation, Young modulus and hardness of BLFO ceramics were obtained: 80±10 GPa and 2.5±0.2 GPa, correspondently.

Local polarization reversal under the action of indentation results in two principal changes of the domain structure: (1) immediate change in the area of plastic deformation and (2) change in the vicinity of the area of plastic deformation. Example of typical indentation and corresponding domain structure change inside the indentation area is presented in Figure 3. Local polarization reversal led to appearance of a dense net of nanoscale domains in the area of plastic deformation (Fig. 2a, red area). For maximal loading in the corners of the prism, both out-of-plane and in-plane PFM revealed piezoresponse reduction caused by pressure-induced phase transformation to orthorhombic phase [30].

The other part of switching happened out of the area of plastic deformation. Three possible sources of the switching can be considered: (1) strain created by indentation, (2) indirect strain caused by grain clamping by the neighboring grains, and (3) electric field created by charge induced by piezoelectric effect as a result of indentation at the enclosing of plastic deformation area [31]. It was noticed that impact of the charge induced by piezoelectric effect was negligible in our experiment, because we observed mostly the motion of non-180-degree domain walls and shrinkage of in-plane domains (Fig. 4), while electric field was usually created by the irregular shape domains with 180-degree walls [32]. Both other two phenomena were observed in our experiments. Areas with domain switched under the direct stress action were located in the proximity of the indent or indentation induced crack (Fig. 4, blue and green arrows). These domains spread in direction from the region of plastic deformation. It must be noted that usually new domains were formed inside the initial domain structure. Growth of previously formed domain structure was observed rarely for polarization reversal by direct stress. Even domains with one direction of polarization often did not completely merge and residual domains remained (Fig. 4, blue and green arrows). The polarization reversal under the indirect stress by neighboring grains was responsible for shrinking initial ferroelastic domains (Fig. 4, red arrow).

Noticeable change of the domain structure was obtained at loads above 10 mN, strong destruction of ceramics began for loads above 30 mN. Linear increase in the indentation force from 10 up to 30 mN led to linear increase in switching area (Fig. 5, red line). Critical value of stress can be found by the analysis of the switching area dependence on the load force (Fig. 5). From linear fitting, critical force necessary for polarization reversal was found $F_c = 1.9$ mN. This load force corresponded to penetration of the indenter about 75 nm into the ceramics surface and 0.13 μm^2 indentation area. Thus, critical stress $\sigma_c = 14.6$ MPa can be evaluated. This value is close to those obtained for single crystals and calculated from the first principals [6]. It must be noted that partial backswitching can happen after indenter uploading and thereby critical stress can be slightly different from one extracted from the fitting [12].

BLFO embedded in epoxy glue behave significantly different as compared with initial BLFO (Fig. 5). Local polarization reversal by indentation can be realized only by 30 mN, but more stress could be applied without complete grain destroying, up to 50 mN. Domain structure after indentation was significantly less modified under the action of mechanical load (Fig. 5). That fact can be attributed to grain clamping, that is produced due to compression of epoxy and mediates stress to the grains of the ceramics. Stress-induced domains must change their size due to the piezoelectric effect and consequently overcome stress created by the grain clamping.

Significant increase in the force necessary for local polarization reversal can be attributed to backswitching under the action of compressive strain of epoxy binder. That is why real critical force is hard to be evaluated in that case. Both switching mechanisms were observed in epoxy embedded ceramics as well: switching by direct stress (Fig. 5, blue arrows) and switching by indirect stress from neighboring grain (Fig. 5, red arrows). Due to the fact that polarization reversal was realized immediately near the grain boundary, nucleation of the new domains at the grain boundary under the action of clamping stress was observed (Fig. 5, red arrows).

4. Conclusion

Local polarization reversal under the action of mechanical load realized by Berkovich type prism indentation was studied in BLFO ceramics. Nanoscale domain structure and polar-to-nonpolar phase transition was observed in the area of plastic deformation. In the vicinity of the area of plastic deformation stress-induced ferroelastic domains appeared driving by conditions of mechanical energy minimization. Indirect action of grain clamping by neighboring grain resulted in shrinkage of existed ferroelastic domains and nucleation of new domains in the area of grain boundaries. Area of switching was found dependent linearly on the applied load force. The value of the critical stress σ_c = 14.6 MPa for indentation induced local polarization reversal was evaluated from fitting. Obtained experimental results are significant for understanding mechanical stress mediated depolarization effects in ferroelectric ceramics.

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Figure captions

Figure 1. PFM images of the initial domain structure in BLFO ceramics: (a) topography; (b) deflection; amplitude: (c) out-of-plane and (d) in-plane; phase: (e) out-of-plane and (f) in-plane; piezoresponse: (g) out-of-plane and (h) in-plane.

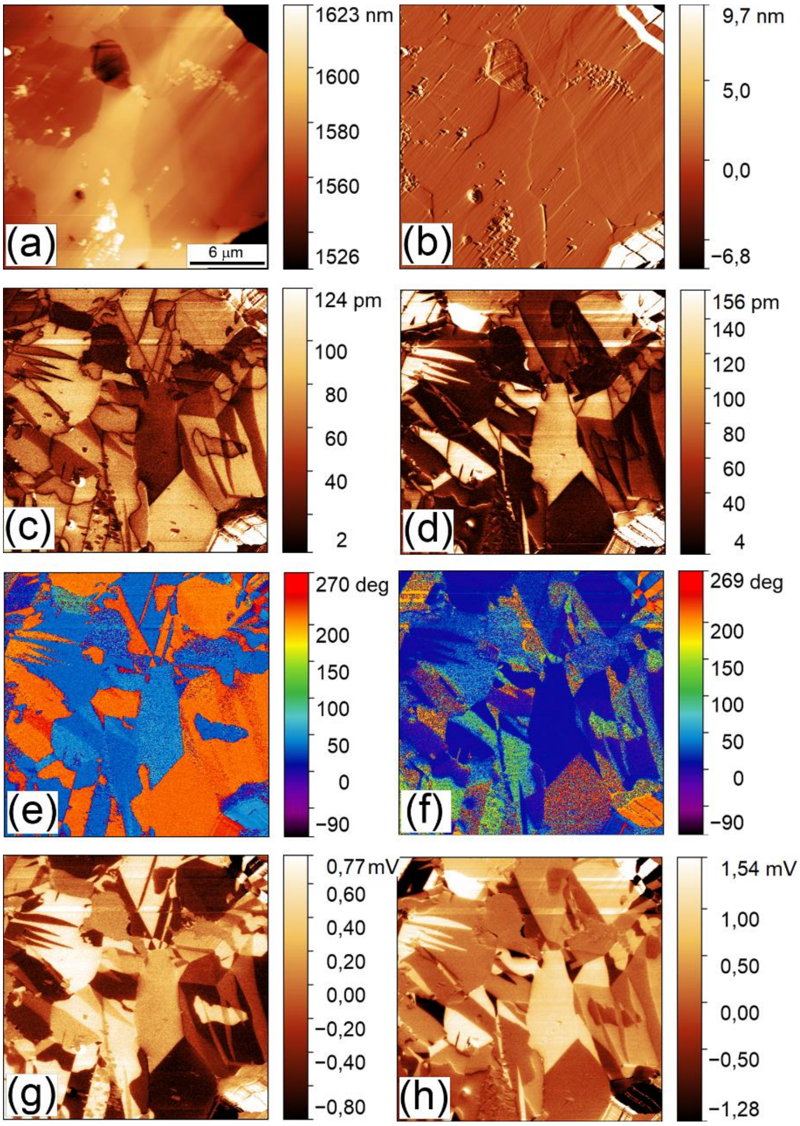
Figure 2. (a) Scheme of indentation by Berkovich type indenter. F – load force, h – penetration depth of indenter. Red semi-circle corresponds to the region with plastic deformation. (b) Typical loading curve for BLFO with 20 mN loading force.

Figure 3. PFM images of the domain structure change in the indentation area. Topography: (a) before indentation and (b) after indentation; piezoresponse: out-of-plane (c) before indentation and (d) after indentation; in-plane (e) before indentation and (f) after indentation.

Figure 4. PFM images of the domain structure change in the vicinity of the indentation area. Topography: (a) before indentation and (b) after indentation; piezoresponse: out-of-plane (c) before indentation and (d) after indentation; in-plane (e) before indentation and (f) after indentation.

Figure 5. Dependence of the switching area on the load force for the initial BLFO ceramics (red color) and BLFO ceramics embedded in epoxy glue (blue line). Dots are responsible for the experimental data, while lines are fitting by linear function.

Figure 6. PFM images of the domain structure change in BLFO ceramics permeated by the epoxy. Topography: (a) before indentation and (b) after indentation; piezoresponse: out-of-plane (c) before indentation and (d) after indentation; in-plane (e) before indentation and (f) after indentation.



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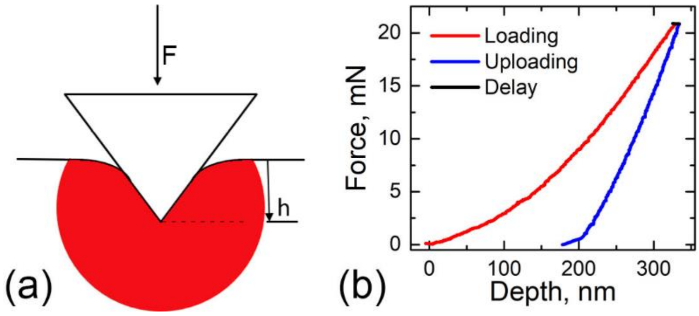

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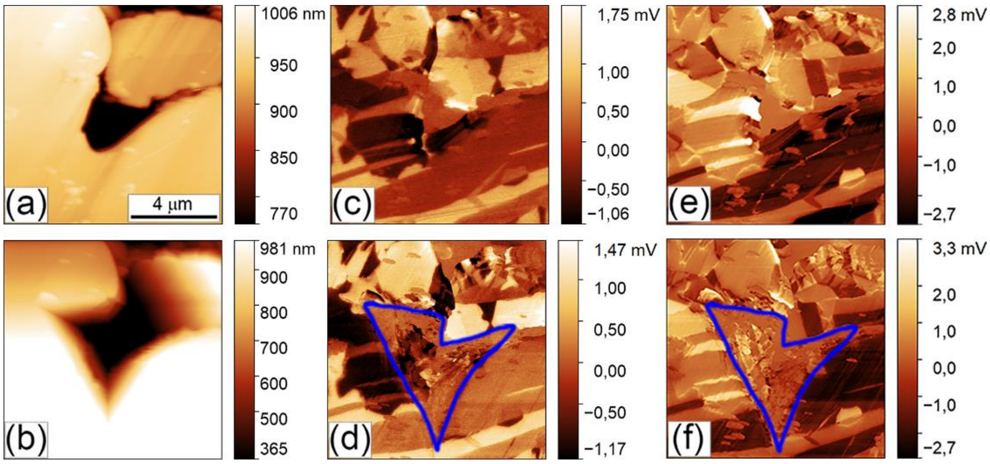

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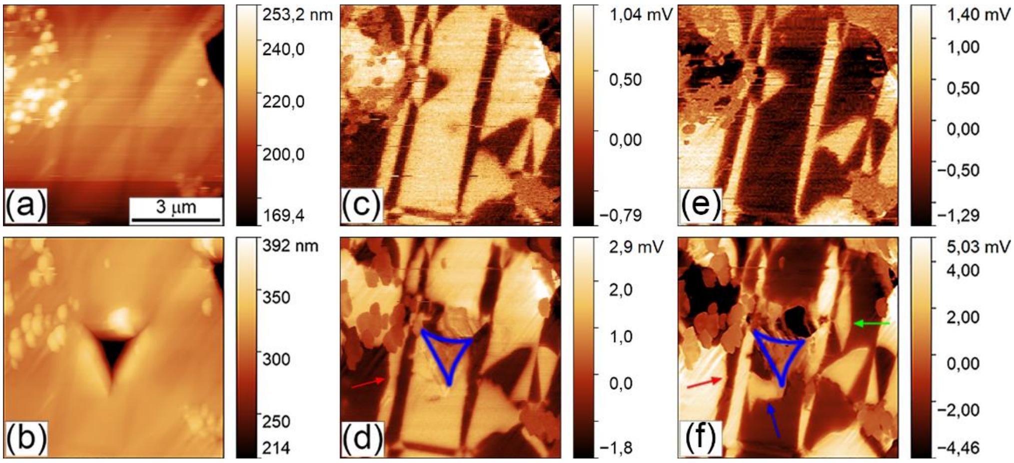

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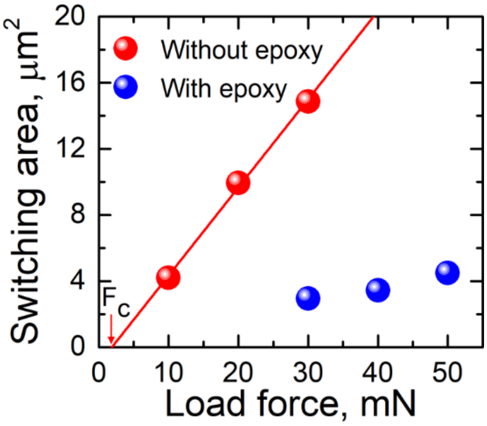

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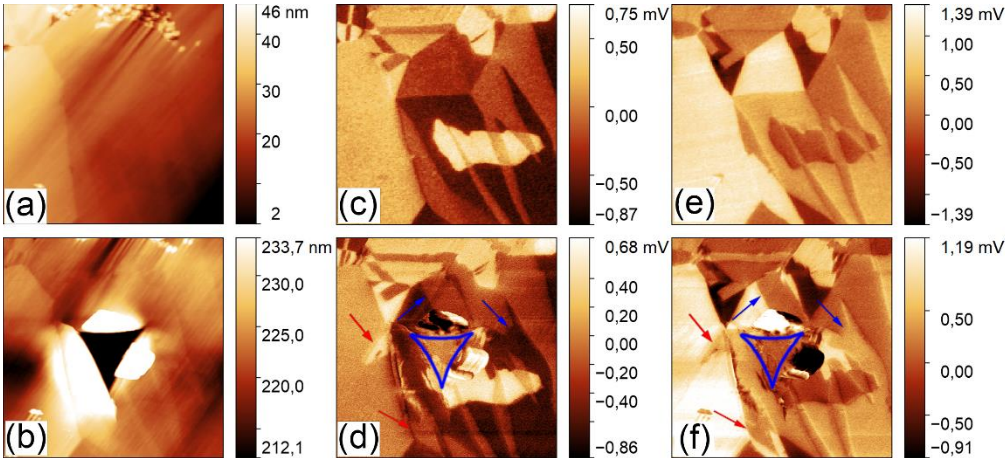

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