In situ visualization of domain structure evolution during field cooling in 0.67PMN-0.33PT single crystal

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Abstract. The evolution of the domain structure during in-field cooling was *in situ* studied in [001]-cut single crystals of relaxor ferroelectric (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN-PT) with x = 0.33 with maximum of dielectric permittivity at 150°C. The main stages of domain evolution have been separated. The visualization of the static as-grown and polarized domain structures with high spatial resolution by piezoresponse force microscopy and scanning electron microscopy allowed measuring the characteristic features of maze and needle-like domain structures.

1. Introduction

Relaxor ferroelectric single crystals, such as *(1-x)*$Pb(Mg_{1/3}Nb_{2/3})O_3$-*x*$PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT), have attracted extensive attention over the last 20 years due to their superior piezoelectric properties leaving far behind polycrystalline ceramics $Pb(Zr_xTi_{1-x})O_3$ (PZT) [1-3]. Comprehensive studies have been focused on the piezoelectric response of domain engineered crystals. PMN-PT is the most widely used relaxor single crystal due to its broad morphotropic phase boundary (MPB) and comparatively simple growth procedure [4]. Increase of PT concentration allows changing the phase of PMN-*x*PT at room temperature from the rhombohedral *R3m* (for x < 0.32) to intermediate monoclinic *Cm* (for 0.32 < x < 0.37) and tetragonal *P4mm* (for x > 0.37). At present, the investigators focus their interests on the domain engineered PMN-PT single crystals with various compositions near or far from MPB [5, 6]. However, the high resolution observation of the poling process in PMN-PT crystals is rarely reported.

The domain engineering in ferroelectric crystals represents the modern method of creation of the stable domain configurations with desired geometrical parameters for enhancement of the proper crystal properties [7, 8]. Artificially created high concentration of the domain walls leads to high piezoelectric properties in PMN-PT. The tailored domain structure with precise periodicity will allow realizing the quasi-phase matching effect in PMN-PT, thus obtaining the efficient frequency conversion of the coherent light.

We investigated the 0.67PMN-0.33PT single crystal, which is a typical MPB composition, in which coexistence of *Ma* and *Mc* phases has been confirmed experimentally [9]. We carried out an experimental observation of the domain structure evolution during the field cooling procedure using

the optical microscopy and separated the main stages of the process. The static domain structures before and after field cooling were visualized using piezoresponse force microscopy (PFM) and scanning electron microscopy (SEM). The synergy of the combination of the used experimental methods allowed studying the process of domain structure evolution in multiaxial relaxor ferroelectric single crystals PMN-PT.

2. Experiment

Lead magnesium niobate-lead titanate *(1-x)*$Pb(Mg_{1/3}Nb_{2/3})O_3$–*x*$PbTiO_3$ (PMN-PT) single crystals with x = 0.33 corresponding to tetragonal phase at room temperature were grown from the melt by modified Bridgman technique [10]. The [001]-cut plates with dimensions 40×40×0.8 mm^3 were mechanochemically polished to optical grade using silica compound (SF1 suspension, Logitech Ltd.), then sliced to 5×1×0.8 mm^3 samples using DAAD 3220 dicing saw (Disco Co., Japan). The electrodes were formed on (100) sample surfaces.

The used experimental setup consisting of polarizing optical microscope Olympus BX51 (Olympus Corporation, Japan) with CCD-camera and heating stage THMSE600 (Linkam Scientific Instruments Ltd., UK) allowed recording the instantaneous domain patterns field treatment including: (a) zero field heating, (b) in-field annealing, and (c) field cooling. The procedure was realized by four consequent stages: (1) zero field heating to 200ºC with rate 3ºC/min, (2) in field annealing at constant temperature 200ºC for 10 min, (3) slow cooling to 150ºC with rate of 1ºC/min, and (4) in-field cooling down to room temperature with rate of 10ºC/min. The electric field with amplitude 300 V/mm was applied to the sample in [100] direction by voltage amplifier TREK 677B (Trek Inc., USA). Dielectric properties have been measured using impedance bridge QuadTech RLC 7600 (IET Labs Inc., USA). Frequency and amplitude of testing signal were 100 Hz and 1 V, respectively.

The shallow surface relief (about few nanometers) corresponding to domain patterns revealed by selective etching during mechanochemical polishing was visualized by SEM in detection of secondary electron mode using Merlin (Carl Zeiss, Germany) [11]. The static domain structures were visualized by scanning probe microscope NTEGRA Aura (NT-MDT, Russia) using PFM mode [12].

3. Results and discussion

Temperature and field profiles used for field cooling are shown in Figure 1a. We use a quite slow cooling rate through the Curie temperature to decrease internal stress and prevent the formation of non-180º domains. The temperature dependences of dielectric permittivity during heating and subsequent cooling measured for non-poled sample (Fig. 1b-c) showed a maximum around 150 ºC. The single peak was observed during heating in the dielectric measurement of the non-poled sample. However, in the cooling stage one additional peak appeared around 55 ºC. Generally, such two dielectric peaks, which correspond to the *Ma* to *Mc* and *Mc* to *C* phase transitions, respectively, are observed usually in the heating measurement of poled samples. The obtained temperature hysteresis with essentially higher value of dielectric permittivity for cooling stage could be attributed to input of the appeared mobile domain walls.

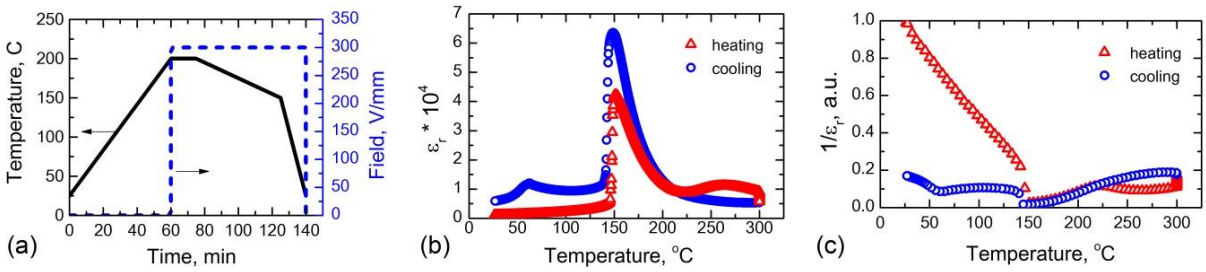

Figure 1. (a) Temperature and field profiles used for poling procedure. Temperature dependences of (b) dielectric permittivity and (c) reversed dielectric permittivity for heating and cooling stages.

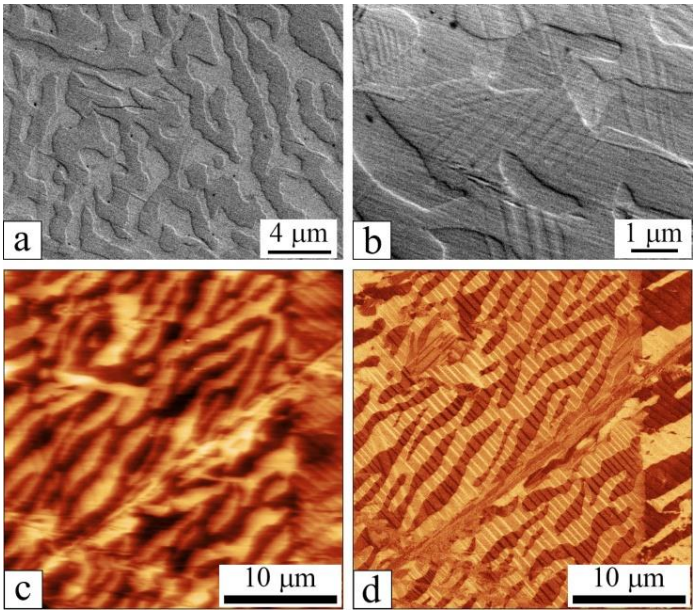

Figure 2. Images of as-grown domain structure after mechanochemical polishing: (a), (b) SEM and PFM: (c) topography and (d) amplitude.

3.1. As-grown domain structure

SEM images of the 0.67PMN-0.33PT single crystal etched during mechanochemical polishing are shown in Figure 2a,b. It is known that the etching allows revealing both in plane and out of plane domains. Maze adjacent domains and needle-like domains were revealed similar to that reported by Yu *et al.* [13]. The width of needle-like domains is about 150 nm and that of maze domains ranged from 0.5 to 3 microns. The formation of micro-sized domains is due to destruction of the long range ordered polar structure caused by random fields. The maze adjacent and needle-like domains were visualized also by PFM (Fig. 2c,d). The maze adjacent domains were separated by 180° walls. The needle-like domains were more regular and narrow. It is worth noting that two kinds of domain walls with different orientations can also be obtained and are in contact at the interfaces close to the (110) planes. Generally, this plane is considered as the allowed orientation of the domains wall between certain ferroelectric-ferroelastic domain states. Thus, the needle-like shape corresponds to ferroelastic domains [14].

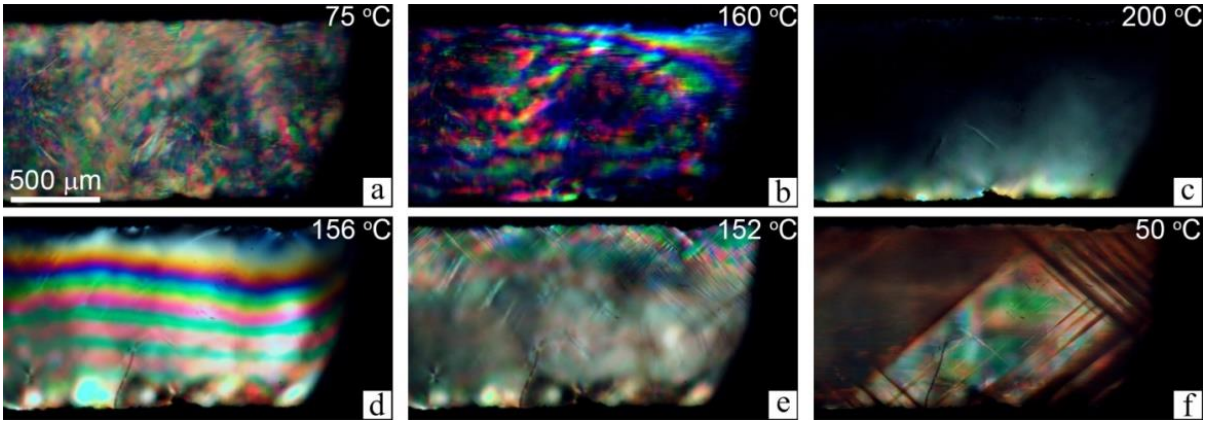

Figure 3. Main stages of domain structure evolution: (a), (b) zero field heating, (c) field annealing, (d), (e), (f) field cooling.

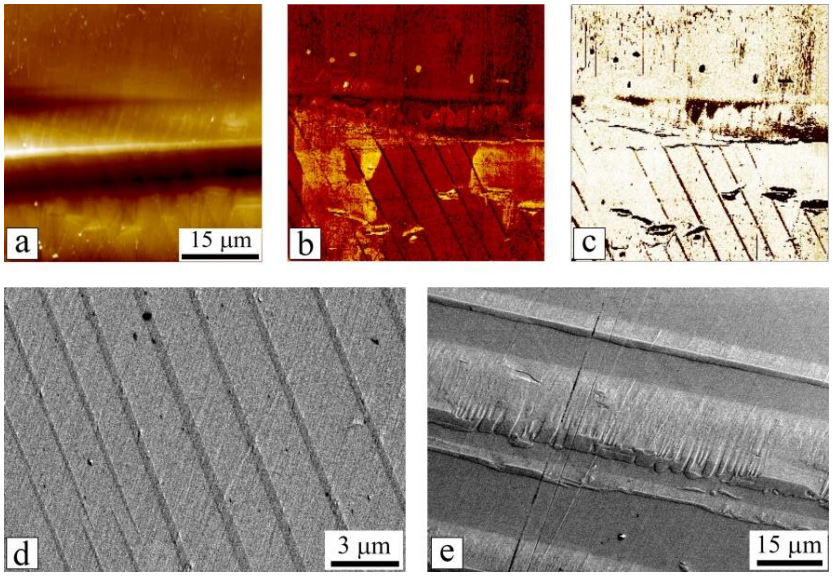

Figure 4. Sample after field treatment. PFM images: (a) topography, (b) amplitude, (c) phase. SEM images of (d) stripe and needle-like domains, (e) single domain regions.

3.2. The domain structure evolution during field treatment

The evolution of the domain structure in as-grown PMN-0.33PT sample was visualized *in situ* during consequent zero field heating, annealing in field, and field cooling by optical microscopy with crossed polarizers. The main stages of the process were defined (Fig. 3). First, destruction of as-grown microdomain structure in the temperature range of 75-90ºC (Fig. 3a) and slow extinction of birefringent patterns up to 200ºC (Fig. 3b) was obtained during zero field heating. Second, retention of the appeared transparent state was observed during field annealing at 200 ºC (Fig. 3c). Third, slow appearance of birefringent patterns oriented in direction of the applied field was visualized during field cooling from 200 to 156ºC (Fig. 3d). Fourth, the appearance and growth of needle-like domains was revealed during subsequent cooling from 156 to 150ºC (Fig. 3e). Finally, the intensive domain growth from the sample edges (Fig. 3f) was observed. The observed non-180º in-plane domains balanced the inner strain during cooling. The amount of needle-like domains was quite small in the temperature range from 156 to 150 ºC and cooling rate 0.1 ºC/min, while the cooling rate increase for the temperatures below 120 ºC led to fast increasing of the domain number. It is worth noting that highlighted stages do not fit perfectly to the dielectric permittivity maxima shown in Figure 1b. It could be explained by the shift of phase transition temperatures under the applied electric field [15].

3.3. Domain structure of poled sample

The sample after field treatment was polished with silica compound and the domain structure was visualized with PFM (Fig. 4a-c) and SEM (Fig. 4d-e). The domain structure after treatment became more uniform and regular. The stripe domains (width about 3 μm) and single domain regions (width about 20 μm) were formed. The needle-like domains became wider (width about 600 nm). The obtained increasing of the domain sizes as a result of field treatment allowed predicting achievement of the single domain state in (001) oriented tetragonal and (111) oriented rhombohedral PMN-PT crystals. Whereas, in studied 0.67PMN-0.33PT crystal the coexistence of *Ma* and *Mc* phases did not allow producing the desired single domain state.

4. Conclusion

The presented work demonstrated the effectiveness of application of complementary experimental methods of domain visualization for investigation of the domain structure evolution in multiaxial

relaxor ferroelectric PMN-PT with high spatial resolution. The coexistence of maze adjacent 180° domains with antiparallel polarization and needle-like ferroelastic domains was revealed. Main stages of domain structure evolution during field treatment consisting of zero field heating, field annealing, and field cooling were defined. The transformation of as-grown domain structure to a more regular one as a result of field treatment was demonstrated.

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