AIP Applied Physics Letters

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Citation: Applied Physics Letters **103**, 242903 (2013); doi: 10.1063/1.4846015
View online: http://dx.doi.org/10.1063/1.4846015
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/103/24?ver=pdfcov
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Shape of isolated domains in lithium tantalate single crystals at elevated temperatures

V. Ya. Shur,[1,2,a)] A. R. Akhmatkhanov,[1,2] D. S. Chezganov,[1] A. I. Lobov,[1] I. S. Baturin,[1,2] and M. M. Smirnov[1]
[1]*Ferroelectric Laboratory, Institute of Natural Sciences, Ural Federal University, 620000 Ekaterinburg, Russia*
[2]*Labfer Ltd., 620014 Ekaterinburg, Russia*

(Received 30 October 2013; accepted 23 November 2013; published online 10 December 2013)

The shape of isolated domains has been investigated in congruent lithium tantalate (CLT) single crystals at elevated temperatures and analyzed in terms of kinetic approach. The obtained temperature dependence of the growing domain shape in CLT including circular shape at temperatures above 190 °C has been attributed to increase of relative input of isotropic ionic conductivity. The observed nonstop wall motion and independent domain growth after merging in CLT as opposed to stoichiometric lithium tantalate have been attributed to difference in wall orientation. The computer simulation has confirmed applicability of the kinetic approach to the domain shape explanation. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4846015]

Lithium tantalate ($LiTaO_3$, LT) and lithium niobate ($LiNbO_3$, LN) exhibit unique electro-optical, pyroelectric, and piezoelectric properties[1,2] combined with good mechanical and chemical stability, wide transparency range,[3] and high optical damage threshold.[4] The LT crystals are very promising materials for nonlinear optical applications, such as frequency conversion of coherent light.[5–7] Such applications require creation of regular domain structures in LT crystals using electrical field poling techniques,[8] which are quite challenging due to high values of coercive fields at room temperature (RT); however, the strong decrease of threshold fields for polarization reversal at elevated temperatures was reported earlier.[9,10] Therefore, the growing interest to domain kinetics and domain shape in LT crystals at elevated temperatures is observed.[9–12]

The paper contains the information about domain shape evolution in congruent lithium tantalate (CLT) and stoichiometric lithium tantalate (SLT) crystals at temperatures up to 250 °C. The domain shapes have been studied at two stages of the domain evolution: growth of isolated domains and domain merging.

The studied samples represent Z-cut optical grade 0.4-mm-thick CLT single crystals grown by Czochralski method (Yamaju Ceramics, Japan) and 0.5-mm-thick SLT single crystals grown by double crucible Czochralski method (Oxide Co, Japan).[3] The circular shape sputtered electrodes of 50 nm-thick Cr with 2 mm diameter were deposited on Z+ polar surface and solid electrodes—on Z-surface. The polarization reversal was performed by application of the single field pulse using high voltage amplifier TREK Model 20/20C. The switching pulse waveform consisted of: (1) field increasing stage—from zero to sub-threshold field E_{min} during 0.5 s, (2) switching stage—with field increasing rate 500 V/(mm s) from E_{min} to E_{max} ranged from 10 to 22 kV/mm, (3) field decreasing stage—from E_{max} to zero during 0.5 s (Fig. 1).

The sample was clamped between spring-loaded aluminum rod and copper plate. The rod diameter was smaller than that of the deposited round electrode. Such assembly was immersed in a silicon oil bath with an electrical heater driven by proportional-integral-derivative temperature controller Owen TPM151. Before polarization reversal, the sample was heated slowly up to the given temperature ($dT/dt = 10\,°C/min$).

The domain structures formed after partial polarization reversal were revealed by selective etching in pure hydrofluoric acid (HF) at room temperature for 30–40 min after chemical removal of the electrodes. The shallow surface relief corresponding to static domain patterns was visualized by optical microscopy in transmitted and dark field modes (Olympus BX-51, Japan) and by scanning electron microscopy (Auriga Crossbeam, Germany). The estimated lateral resolution was about 300 nm and 2 nm, correspondingly.

The hexagonal shape of the isolated domain in SLT for switching at RT is similar to the domain shape in LN crystals (Fig. 2(a)). Such domain type with six domain walls strictly oriented along Y crystallographic directions was denoted by us as **6Y**[13,14] in contrast with the triangular shape of isolated domains with X oriented walls (**3X**) observed in CLT (Fig. 2(b)).

The regular hexagonal domain shape changes drastically during merging and recovers back in short time.[15] Three

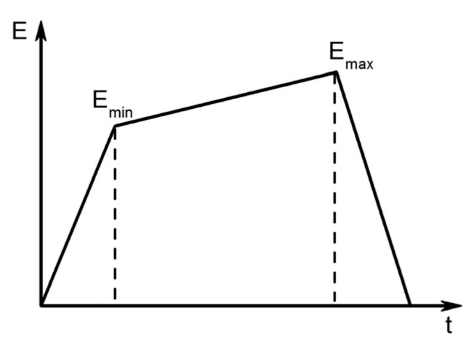

FIG. 1. External electric field waveform used for polarization reversal.

[a)]Author to whom correspondence should be addressed. Electronic mail: vladimir.shur@usu.ru

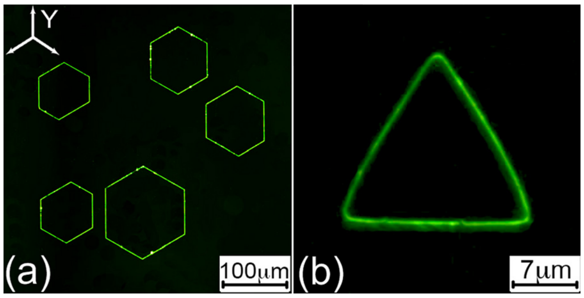

FIG. 2. Typical domain shapes in LT at RT. (a) Hexagonal domains with Y oriented domain walls (6Y) in SLT. (b) Triangular domain with X oriented domain walls (3X) in CLT. Domain images revealed by chemical etching and visualized by optical microscopy in dark field mode.

stages of domain shape evolution can be separated. The first stage represents formation of the polygon with two concave angles, ten Y walls, and two X walls (**10Y + 2X**) just after domain merging (Fig. 3(a)). At the second stage, the concave angles disappear and domain shape changes to the polygon with convex angles only (**6Y + 2X**), because the sideways motion of X oriented domain walls is essentially faster than that of Y oriented walls (Fig. 3(b)). Finally, the hexagonal domain shape (**6Y**) recovers (Fig. 3(c)). Such evolution of the domain shape leads to domain shape stability.[15] Eventually, the hexagonal domain shape with Y oriented walls prevails in SLT even during domain merging.

The main feature of domain shape evolution during merging of isolated triangles in CLT as compared with SLT is conservation of the arisen concave angles (Fig. 4(a)). The merged domains continue to grow almost independently (Fig. 4). Thus, the domain shape stability effect is absent in CLT. This fact leads to formation of the domain structures with zigzag domain walls with X oriented fragments during domain merging in CLT (Fig. 4(a)). The independent domain growth leads to formation of isolated triangular shaped non-switched domains surrounded by growing ones (Fig. 4(a)).

The static domain patterns formed at various temperatures were analyzed. It was demonstrated that the shape of isolated domains was essentially temperature dependent.

The domain structure evolution observed in CLT at temperatures up to 130 °C is similar to RT scenario (Fig. 4).[13,16–18] The appearance of new domains takes place during the whole switching process. The absence of the local acceleration of the domain wall motion after merging is in contrast with domain evolution in SLT.

In the temperature range from 130 °C to 190 °C, the shape of isolated domains changed qualitatively from triangular to hexagonal; however, the walls orientation along X directions remains (6X) (Fig. 5(a)). This wall orientation in CLT results in distinct evolution of the domain structure

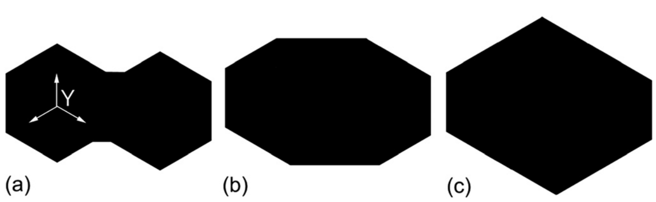

FIG. 3. Domain shape stability effect. The scheme of the domain shape transformation after merging.

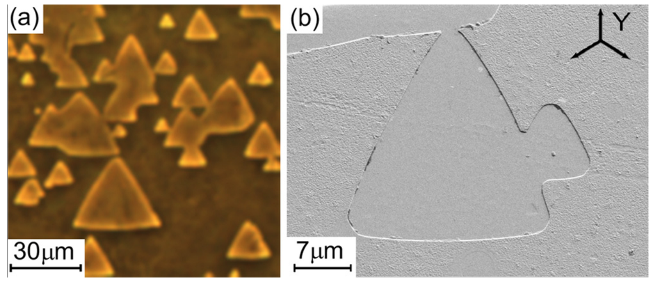

FIG. 4. Typical domain patterns in CLT at RT during merging. Domain images revealed by chemical etching and visualized by: (a) optical microscopy in phase contrast mode and (b) scanning electron microscopy.

accompanied by nonstop wall motion and independent domain growth after merging (Fig. 5(b)) in contrast with jerky wall motion and the domain shape stability effect for Y walls in SLT (Figs. 2(a) and 3).

It is necessary to point out the additional noticeable effect of the domain shape rounding with temperature increase (Fig. 6). For temperatures above 190 °C, the rounding effect results in formation of circular shaped isolated domains (Figs. 6 and 7(a)). The independent growth of merged circular domains leads to formation of the disordered shapeless domain structure (Fig. 7(b)).[9]

We have obtained the variety of the isolated domain shapes in CLT by varying the temperature. This experimental fact can be explained in the framework of our approach. As a rule, the static domain structures in ferroelectrics are metastable and domain shape is defined by growth kinetics. Existence of the domain configurations being far from equilibrium state is possible due to screening of depolarization field. The absence of screening mechanism in ferromagnetics leads to prevailing of the equilibrium domain structures.

In analogy to the first order phase transition, the mechanism of ferroelectric domain growth is defined by nucleation process.[19–21] Three types of nucleation can be distinguished: 3D nucleation—formation of new domains, 2D nucleation at the domain wall—step generation, and 1D nucleation at the step edge—step propagation. Thus, the sideways wall motion is a result of step generation and step propagation along the wall.[22]

It has been shown experimentally that in LN and LT crystals with C_{3v} symmetry the steps move strictly along one of the three Y crystallographic directions. The growth of polygon domains at RT is a result of determined nucleation effect, which represents the generation of elemental steps at three nonadjacent polygon vertices and step growth along

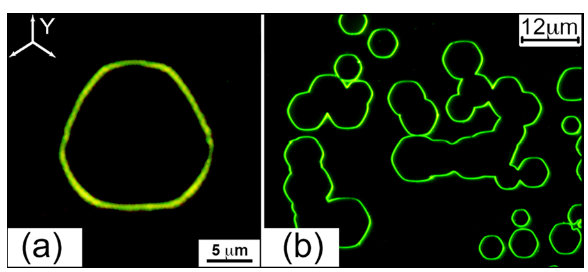

FIG. 5. Typical domain patterns in CLT at 150 °C: (a) isolated hexagonal domain with X oriented domain walls (6X); (b) domain merging. Domain image revealed by chemical etching and visualized by optical microscopy in dark field mode.

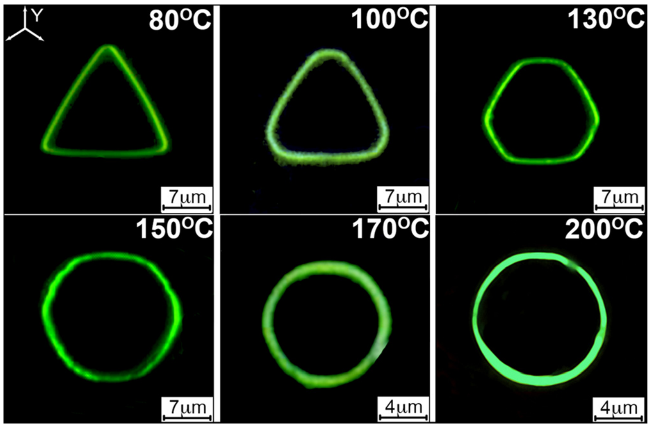

FIG. 6. Effect of the domain shape rounding with temperature increase in CLT. Domain image revealed by chemical etching and visualized by optical microscopy in dark field mode.

three Y+ directions.[22] This effect can be attributed to anisotropy of the bulk screening of the depolarization field governed by anisotropic hopping bulk conductivity, which dominated in both crystals at low temperatures. The domain wall motion is limited by step generation process. Effective bulk screening in SLT in usual switching conditions leads to formation of the hexagonal domains and jerky wall motion similar to LN.[17,23,24]

In CLT, essential increase of the step concentration at the walls up to the limiting value for X oriented ones takes place due to the considerably slower bulk screening and realization of non-equilibrium switching conditions (Fig. 8).[25,26] The X wall growth velocity is defined by step growth only and is completely independent on the step generation process. This feature of X walls results in nonstop wall motion without essential interaction with defects, absence of the domain wall local acceleration after domain merging, and independent growth of the merged domains.

The obtained change of the domain shape at the elevated temperatures can be attributed to the input of the competing isotropic ionic mechanism of the bulk conductivity,[27] which provides the stochastic step generation with equal nucleation probability along the whole wall.[28] The domination of the stochastic nucleation at high temperatures (above 190 °C) leads to isotropic domain growth and formation of the circular-shaped domains.

The computer simulation of the domain growth by step generation and growth on hexagonal lattice of individual elements (nanodomains) has been used for explanation of the domain shape change with temperature increase from triangular to circular through hexagonal with X-oriented walls.[29,30] Two main aspects were taken into account: (1) competition between determined and stochastic nucleation mechanisms and (2) incomplete screening of depolarization field. In the framework of this model, the bulk screening efficiency has significant influence on domain kinetics.[29]

The domain kinetics with determined nucleation only and incomplete screening realized at RT in usual switching conditions resulted in **3X** domain shape (Fig. 9(a)). The faster bulk screening at elevated temperatures (about 150 °C) due to input of isotropic ionic conductivity leads to increase of stochastic nucleation probability and effective screening of depolarization field, resulting in **6X** domain shape (Fig. 9(b)). The further increase of isotropic ionic conductivity at temperatures above 200 °C leads to prevalence of stochastic nucleation and circular domain shape (Fig. 9(c)).

The shape of isolated domains and the domain shape evolution after merging during polarization reversal in uniform electric field have been investigated in single crystals of SLT and CLT from room temperature up to 250 °C. The change of the growing domain shape during heating in CLT from triangular (3X) to circular through hexagonal (6X) has been attributed to increase of the relative input of isotropic ionic conductivity resulting in increase of the stochastic nucleation probability and the effective screening of depolarization field. The orientation of domain walls in CLT along X crystallographic directions at temperatures below 190 °C results in nonstop wall motion and independent domain growth after merging in contrast to jerky wall motion and the domain shape stability effect obtained in SLT. The computer simulation of the domain growth taking into account competition between determined and stochastic nucleation mechanisms and incomplete screening of depolarization field has

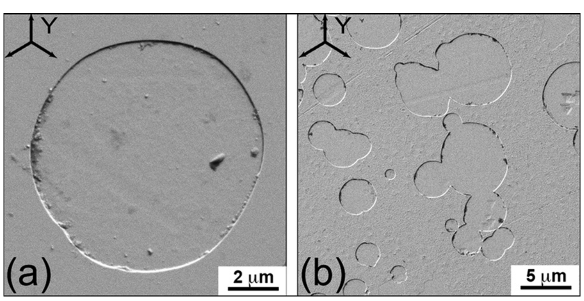

FIG. 7. Typical domain patterns in CLT at 200 °C: (a) isolated circular domain; (b) domains merging. Domain images revealed by chemical etching and visualized by scanning electron microscopy.

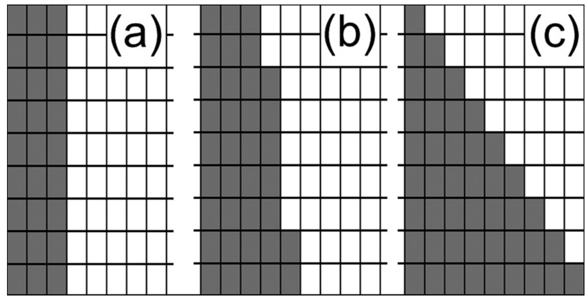

FIG. 8. The schemes of the domain walls microstructure: (a) static flat Y oriented wall without steps, (b) moving Y oriented wall with growing steps, and (c) static X oriented wall with maximum step concentration.

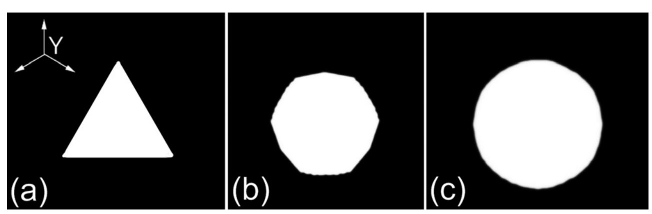

FIG. 9. Domain shapes obtained by computer simulation for various switching conditions: (a) **3X** for determined nucleation only and ineffective bulk screening; (b) **6X** for determined nucleation with low stochastic nucleation and effective bulk screening; (c) circles for stochastic nucleation only and effective bulk screening.

been used for explanation of the domain shape change in CLT with temperature increase. The obtained results confirmed the applicability of the kinetic approach to explanation of the domain shape.

The equipment of the Ural Center for Shared Use "Modern Nanotechnology," Institute of Natural Sciences, Ural Federal University has been used. The research was made possible in part by RFBR and the Government of Sverdlovsk region (Grant No. 13-02-96041-r-Ural-a), by RFBR (Grant Nos. 11-02-91066-CNRS-a and 13-02-01391-a) and with the financial support of young scientists in terms of Ural Federal University development program.

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