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## Effect of surface disorder on the domain structure of PLZT ceramics

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### ABSTRACT

Pb<sub>1-x</sub>La<sub>x</sub>(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)<sub>1-x/4</sub>O<sub>3</sub> (PLZT x/65/35) ceramics were studied by Piezoresponse Force Microscopy in order to understand the origin of domain structure as a function of La content. We show that the domain topology is mainly determined by the composition and grain size. The characteristic correlation length decreases with increasing La content, being sensitive also to the synthesis method. The behavior of the correlation length is linked to the macroscopic properties, showing a strong increase of disorder with La doping. The roughness exponent for the domain wall in PLZT 9/65/35 is close to 2/3 indicating 1D character of domain walls in relaxors.

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Relaxor ferroelectrics; ceramics; domain structure; PLZT; disorder; piezoresponse force microscopy

## 1. Introduction

The unique properties of relaxor ferroelectrics have raised fundamental interest in understanding the mesoscopic domain structures in these materials, including micro- and nanodomain populations, polarization distributions, and their evolution under external electric field and temperature variations. These properties are mainly determined by the existence of small polarization clusters (polar nanoregions, PNRs) due to nanoscale chemical disorder. The interest to relaxors prompted a large number of studies using Scanning Probe Microscopy (SPM) and, later on, Piezoresponse Force Microscopy (PFM) [1]. Abplanalp et al. [2] observed diffuse domains with irregular 180°-domain walls and domain structure that resembled a fingerprint pattern in unpoled Pb(Zn<sub>1/2</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-8% PbTiO<sub>3</sub> (PZN-PT) crystals using both out-of-plane (vertical) and in-plane (lateral) PFM measurements. Ferroelastic domains were also observed and the switching of antiparallel domains was demonstrated with the application of ±30 V. Similar domain patterns were revealed in relaxor PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>-10%PbTiO<sub>3</sub> (PMN-10%PT) crystals by Vakhrushev et al. [3] and, later on, by Bai et al. [4] and Bdikin et al. [5] in PZN-PT. In subsequent studies, Shvartsman and Kholkin [6] and Salak et al. [7] measured the

temperature dependence of the electromechanical response in PMN-20%PT single crystals and in BaTiO<sub>3</sub> ceramics doped with La(Mg<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub>, respectively.

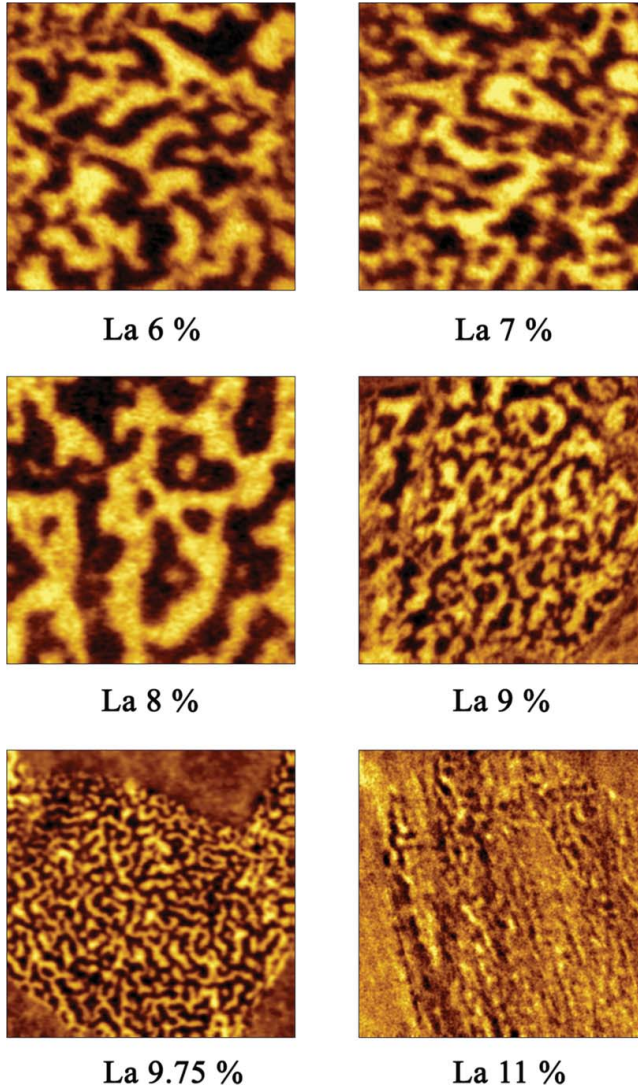
In PMN-20%PT, ferroelectric domains were found to contain PNRs existing above the freezing temperature ( $T_f$ ). Similarly, in doped BaTiO<sub>3</sub>, electromechanical response due to ferroelectric domains disappeared above  $T_C$ , but small residual domains could be observed. Interestingly, even above the transition temperature, local hysteresis loops could still be measured. Vertical and lateral PFM have also been employed to measure the domain structure in PMN-10%PT crystals [8] and in relaxor lead lanthanum zirconate titanate ceramics (PLZT) [9]. Complex domain structure observed in relaxor PLZT (La content 9.75%) was attributed to a La-induced disorder and a correlation length of  $\sim 50$  nm was determined using autocorrelation processing of the PFM images. Grain size effect in PLZT [10] was attributed to inhomogeneous distribution of the correlation length and disorder increasing at the grain boundaries. Surface phase transition observed in PLZT and PZN-PT leads to mesoscale phase at the surface of relaxors with the domain structure that can be considered as agglomerated PNRs [11]. However, these measurements did not consider neither effect of La on the disorder, nor the influence of preparation conditions on the domain structure. This paper fills these gaps.

## 2. Experimental

Pb<sub>1-x</sub>La<sub>x</sub>(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)<sub>1-x/4</sub>O<sub>3</sub> ceramics was sintered by the hot pressing method at the Institute of Solid State Physics, University of Latvia, Riga. Platelet-shaped samples of 0.3-1.0 mm thickness were polished to the optical quality. Domain images were obtained by the PFM method using a commercial atomic force microscope (MFP-3D, Asylum Research, Oxford Instruments, UK). The detailed description of the technique can be found elsewhere [12]. The PFM method is based on the detection of the thickness oscillations of ferroelectric materials under a weak *ac* voltage applied between the conductive tip and the bottom electrode in a regular contact mode. The amplitude of the measured vibration is proportional to the effective piezoelectric coefficient, while its phase depends on the orientation of the out-of-plane component of the polarization. Measurements of the domain wall roughness were done on as-grown domains using proprietary software. We used the probes ASYLEC-01 with titanium-iridium conductive coating (Asylum Research, Oxford Instruments, UK) with a radius of curvature  $R = 28$  nm, resonance frequency  $f = 70$  kHz, and spring constant  $k = 2$  N/m and the probes DPER-18 (MikroMash, Estonia) with a platinum conductive coating and typical radius of curvature about 20 nm, resonance frequency about 280 kHz, and spring constant about 3 N/m.

## 3. Results and discussion

Fig. 1 shows the nanoscale structures in PLZT x/65/35 ceramics with varying  $x$  visualized by PFM. The size for all images is  $4 \times 4 \mu\text{m}^2$ . It is clearly seen that the domain size progressively decreases with increasing La content except of the composition with La 8%. This is attested to increasing disorder due to a larger La content. It is well known that La<sup>3+</sup> (added as La<sub>2</sub>O<sub>3</sub>) replaces Pb<sup>2+</sup> in pure PZT composition and charge balance is maintained by the creation of lattice site vacancies.



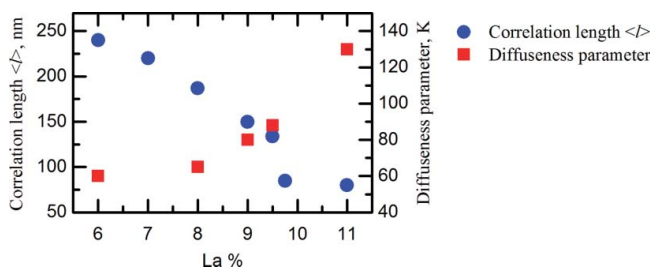
**Figure 1.** PFM images of nanoscale domains in PLZT x/65/35 ceramics. Size of all images is  $4 \times 4 \mu\text{m}^2$ . All measurements were done at the room temperature.

These, depending on the method of preparation, can be compensated by the vacancies both in  $\text{A}^{2+}$  and  $\text{B}^{4+}$  sites. This leads to the complex structure with different concentrations of vacancies (Y denotes the amount of vacancies) in accordance with formulas:

$$\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{Y}_{x/4}\text{O}_3 \text{ for B-site compensation} \quad (1)$$

$$\text{Pb}_{1-3x/2}\text{La}_x\text{Y}_{x/2}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3 \text{ for A-site compensation} \quad (2)$$

It is well-known that both A- and B-site vacancies are indeed present in the lattice [13], thus making the chemical composition extremely complicated. The ratio between



**Figure 2.** The dependence of the correlation length (circles) and diffuseness parameter (squares) as a function of La content in PLZT x/65/35 ceramics.

A- and B-vacancies should also depend not only on the initial formulation, but also on the excess of PbO either as raw material, or as PbO pressure. The formation of B-site vacancies is favored under increased PbO vapor pressure, but preparation of PLZT-perovskite phases with B-site vacancies only is impossible since the increase in the partial pressure of PbO is naturally limited by the condensation of liquid PbO at the grain boundaries of the ceramics. All in all, the defect structure and random electric fields that destroy the normal phase transition are critically dependent on La concentration [14, 15]. This is directly reflected in their mesoscale structure. We calculated the average correlation length for each composition shown in Fig. 1 using the procedure described in Ref. [9]. For this purpose, we used autocorrelation function averaged over all directions for images shown in Fig. 1 and fitted it with the formula:

$$C(r) \propto \exp \left[ (r/l)^{-2h} \right], \quad (3)$$

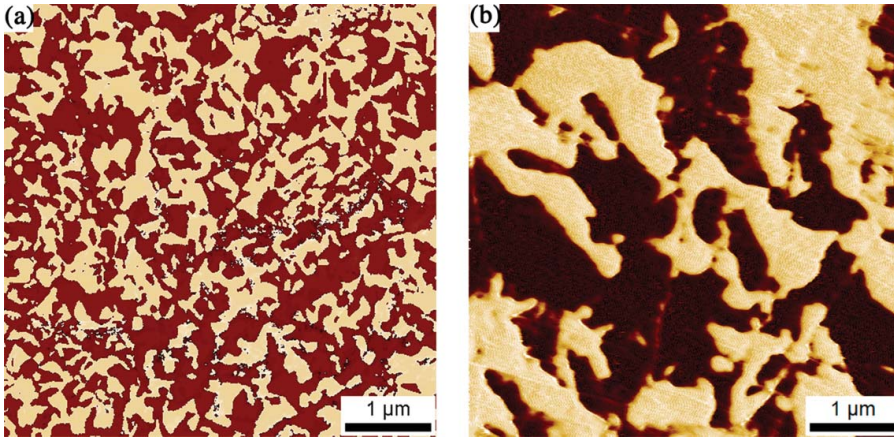
where  $r$  is the radius,  $l$  is the correlation length, and  $h$  is the parameter.

The dependence of the correlation length as a function of La content is shown in Fig. 2. It is clear that increasing the number of defects (in general governed by  $x$ ) leads to the gradual decrease of the correlation length. This is accompanied by the gradual increase of the diffuseness of the phase transition calculated as a half width of the normalized temperature maximum (diffuseness parameter). It is commonly used as a measure of the disorder caused by the random distribution of electric fields due to  $\text{La}^{3+}$  and compensating A- or B-site vacancies.

We suggest that the liquid sintering effect occurring at high concentrations of  $\text{La}^{3+}$  may also play a role. It is also worth to note a monotonous behavior of the percentage of A-site vacancies as a function of La content in PLZT x/65/35 series [16]. It is important that the hysteresis loops measured at room temperature are becoming slimmer with increasing La concentration [17], which is a manifestation of the gradual transformation of normal ferroelectric to the non-ergodic relaxor. All in all,  $\text{La}^{3+}$  addition causes the decrease of the correlation length at the surface of relaxors of the x/65/35 series, which is related to the increase of disorder as confirmed by the macroscopic measurements.

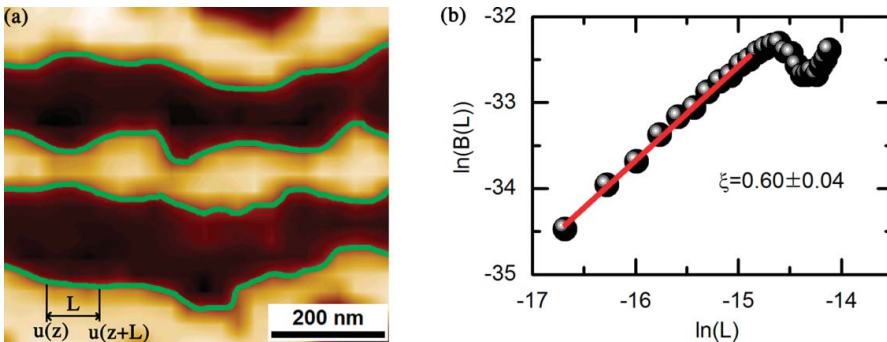
We tested 6/65/35 PLZT ceramics sintered in different laboratories in order to understand the effect of the preparation conditions on the correlation length, which is the signature of the disorder in the material. The results are shown in Fig. 3. Both samples were hot pressed,





**Figure 3.** PFM images of 6/65/35 PLZT ceramics sintered in: (a) Institute of Solid State Physics, University of Latvia, Riga, Latvia and (b) Jozef Stefan Institute, Ljubljana, Slovenia.

but in the case of ceramics sintered in Institute of Solid State Physics, University of Latvia, powder synthesis was done via a 2-stage chemical coprecipitation method and final ceramic densification was performed in oxygen atmosphere [18], while in the ceramics from Jozef Stefan Institute standard solid-state synthesis was done and samples were hot pressed in PbO-rich atmosphere. This, obviously, not only changed the grain size, but also drastically altered the ratio between A- and B-vacancies. The results of the PFM mapping in both ceramics are shown in Fig. 3. The correlation length was 60.4 nm in the case of the first ceramics, while it was almost 100 nm in the ceramics sintered using standard solid-state sintering. We thus infer that defect structure favors much stronger random field in the first case, probably due to lead evaporation and creation of A-site vacancies. Fractal nature of polar nano regions in PLZT ceramics was demonstrated earlier [19]. The fractal dimension ( $D$ ) characterizing the roughness of domain walls was much larger in the first case (1.79 vs. 1.45). It seems that degree of order caused by different structures also affects the ruggedness of the domain walls in PLZT ceramics:  $D = 1$  for smooth domain walls, otherwise  $1 < D < 2$ . We note that a substantial deviation of  $D$  from the topological dimension,  $D = 1$ , is observed even in ferroelectric PLZT 6/65/35[17].



**Figure 4.** (a) As-grown ferroelectric domain structure of the bulk PLZT 9/65/35 ceramics. (b) Representative correlation function  $B(L)$  and fitting of the linear part of the curve yielding the exponent  $2\xi$ .

In order to further understand the effect of defects on the topology of domain walls in PLZT, we studied the roughness of the domain walls in PLZT 9/65/35 using the method described by Paruch and co-workers [20]. We studied the roughness of walls between as-grown domains with the polarization vector orthogonal to the sample surface (Fig. 4a). Four walls with average length of about 1  $\mu\text{m}$  and effective width around 150 nm were analyzed using the pair-correlation method described in Ref. [20].

The correlation function  $B(L)$  of relative displacements  $u(z)$  shown in Fig. 4b measures the local variance of the wall position from an ideal flat configuration as a function of the distance  $L$  along the wall. For equilibrium configurations  $B(L)$  is predicted to display a power-law growth at short length scales, which is governed by a characteristic roughness exponent  $\zeta$  via the relation:

$$B(L) = \langle [u(z+L) - u(z)]^2 \rangle \sim \left( \frac{L}{L_c} \right)^{2\zeta}, \quad (4)$$

where  $L_c$  is the characteristic collective pinning length (the so-called Larkin length) [21].

As shown in Fig. 4b, the linear fit of  $\ln B(L)$  plotted versus  $\ln(L)$  can provide the exponent  $2\zeta$  with a high accuracy. By averaging the results obtained for all four domain walls, we found  $\zeta = 0.60 \pm 0.04$ , which is close to the theoretical value  $2/3$  corresponding to either one-dimensional walls in ferroelectrics with random-bond disorder or two-dimensional walls in materials with random-field disorder [20]. The same result was obtained earlier for the PLZT 9.5/65/35 [22]. At the same time, our roughness exponent is more than two times larger than  $\zeta = 0.26$  obtained for artificial domains in  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin films [18]. The exact origin of the domain-wall roughness in PLZT ceramics is yet unknown, although the intrinsic disorder associated with aliovalent substitution of lead cations by  $\text{La}^{3+}$  accompanied by the formation of compensating vacancies seems to be the most probable. An “extrinsic” disorder caused by impurities not related to La substitution and other defects cannot be ruled out. However, all set of data presented in this work hints to the La-induced defects such as A- and B-site vacancies responsible for the peculiar domain structure in PLZT ceramics.

## 4. Conclusion

In summary, we studied PLZT  $x/65/35$  ceramics with La content  $x$  and different preparation methods. We found that the correlation length describing the degree of disorder and random electric fields depended on the amount of La incorporated in the lattice. Correlation length was found also to depend on the preparation method and supposedly varied with different amount of A- and B-site vacancies. At the same time, our roughness exponent is more than two times larger than  $\zeta = 0.26$  obtained for artificial domains in  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  thin films [18] and can be assigned to close to the theoretical value  $2/3$  corresponding to one-dimensional walls in ferroelectrics with random-bond disorder [20].

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