Relaxor-based Ferroelectric Domain Structures on 91PZN-9PT and 68PMN-32PT Single Crystal near a Morphotropic
Phase Boundary Composition

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Abstract: ***Domain structures on the (001) cub surface of the 91PZN-9PT and 68PMN-32PT single crystals were observed in the different phases by Polarizing Light Microscopy (PLM) and confirmed the domain structure by Piezoresponse Force Microscopy (PFM). Due to elastic compatibility, the angles between the domains are well defined and determined by the symmetry of the ferroelectric phase. The electric field-induced nanotwin and dot like related domains were investigated in 91PZN-9PT and 68PMN-32PT single crystals. Twin-related alternative micron-sized domain structures were found to be of ~1μm in length as revealed as dark and bright domains in the different phases. Dot like patterns within the dark or bright domains were found to correspond to nano domains in size range 5 -100 nm length scales. Alternative related striated-shaped domain patterns were found to have coarse domains of ~5μm in length oriented along {010}. Each coarse domain has fine domains of ~1μm in length oriented along {100}.***

Keywords: Ferroelectric 91PZN-9PT and 68PMN-32PT single crystal, Nanometer-sized twin domain, Piezoresponse force microscopy.

1. Introduction

Relaxor-based ferroelectric single crystal solid solution (1-x) Pb $(Zn_{1/3}Nb_{2/3})$ $O_{3-x}PbTiO_3$, abbreviated (1-x) PZN_{-x} PT, binary system with compositions near a morphotropic phase boundary (MPB) have attracted much attention for applications in high performance actuator, non-destructive testing and ultrasonic devices, making use of its superior piezoelectric properties. 0.91Pb $(Zn_{1/3}Nb_{2/3})$ $O_{3-0.09}PbTiO_3$ (91PZN-9PT) single crystal exhibits excellent piezoelectric constant (d33~2500pC/N) and high electromechanical coupling coefficient

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(k33~94%) on (001) cub surface in the rhombohedral (R) phase in engineered domain state [1-3]. Such superior properties were reported to be related to intermediate monoclinic (M) phase between R and tetragonal (T) phase near the MPB [4-7]. It was also reported to be a mixed state of nanometer-sized twin (nanotwin) related domains of the T phase. Such nanotwins due to the small domain size and small ferroelastic strain were reported to play an essential role in the ultrahigh electromechanical responses [5-6]. A pure compound, lead titanate, was very recently reported to display a MPB under pressure [7], while pressure-induced suppression in piezoresponse was also reported in 91PZN-9PT single crystal [8]. The electric field-induced domain wall movement and the high-density domain walls associated with the nanotwin related domains were reported to have a significant contribution to the superior piezoelectric properties near the MPB [6]. In this work, the electric field-induced nanotwin and dot like related domains was investigated in 91PZN-9PT and 68PMN-32PT single crystals by scanning force microscopy in the piezo response mode (PFM). The remarkable differences in its process on (001) cub surfaces were found. In this paper, electric field-induced nanotwin related domain structure of the 91PZN-9PT and 68PMN-32PT single crystal observed with PFM is presented and discussed.

2. Experimental Procedure

Single crystals of 91PZN-9PT were grown by a modified Bridgman technique [9]. The crystals obtained from JFE Mineral Company Ltd., was used for this work. The crystals were cut into plates with (001)cub and (111)cub orientation, confirmed by X-ray diffraction and from Laue photographs. Both surfaces were polished to optical quality using diamond paste with the final particle size of 0.1µm and down to 80µm. The domain structures were analyzed by means of a polarizing light microscopy (PLM) (Olympus BX51) with a heating/cooling stage (Japan High Tech LK600). PFM studies of 91PZN-9PT single crystals were performed using a commercial PFM (SPA300/SPI3800N, SeikoInc, Japan) [10, 11]. An external voltage was applied to one crystal surface through the Al coated cantilever (SI: DF3-R, f=27 KHz, C=1.6N/m) with a tip apex radius of ~10 nm as a top electrode. The other surface was electroded by silver paste and glued to the sample holder as a bottom electrode. The PFM images were taken over 20µm length scales on (001) cub and (111) cub faces at room temperature. When an ac voltage $V_{ac}=V_0\sin\omega t$ is applied between the tip top electrode and the bottom one of the sample, the alternating external electric field gives rise to the piezoelectric vibration of the sample, or a change in the sample thickness due to the converse piezoelectric effect. The domain structure can be visualized by monitoring the first harmonic signal (piezoresponse) caused by the piezoelectric effect, since the phase of this signal depends on the sign of the piezoelectric coefficient and on the polarization direction. In this experiment, an imaging ac voltage with amplitude V_0 between 2 and 20V and a frequency $\omega/2\pi$ of 5 KHz was applied.

According to the Martensite theory developed thermodynamically and crystallographically, the typical domain size λ is given by the following relation. Where β is a dimensionless constant, D the thickness of the polydomain plate, γ the domain wall energy, μ

$$\lambda = \beta\left[\gamma D / \mu\varepsilon_o^{\,2}\right]^{1/2}$$

the shear modulus, $\square_o$ the twinning strain. The decrease in domain size leads to the increase in piezoelectric load with both the increase in $\square_r$ and the increase in elastic compliance.

3. Results And Discussion

The domain structures of a (001) cub 91PZN-9PT and 68PMN-32PTsingle crystal were analyzed at room temperature by means of PLM. This domain structure reveals that the R phase with extinction directions along <110>cub and the T phase with extinction directions parallel to <100>cub are intimately mixed up in the morphotropic 91PZN-9PT crystal [12], in which furthermore, the M phase with extinction directions crossing <001>cub at the variable angles of δ= 5-35°except 0°(=90°) and 45°is revealed to coexist. In a tetragonal ferroelectric phase, the angles are either 90° or 180°, whereas in a rhombohedral (R) phase, they can be 71°, 109° or 180°. Generally, 180° domains can be reversed with only minimal structural strains. However, switching of 71°, 90° or 109° domains require significantly larger deformations [4, 6, 13-16].

Domain structures on the (001) cub surface of the 91PZN-9PT single crystals were observed in the R phase as shown in Fig.1 (a) by PLM. Twin- related zigzag-shaped domain patterns were found to have coarse domains in ~20μm length oriented along {1-10} with fine domains (marked withλ) in ~1μm length oriented along {010} and {100}. Fig.1 (b) shows twin-related alternative micron-sized domain structures to be ~1μm length (marked withλ) as revealed as dark and bright domains in the T phase, which have some preferential orientations along {010} and {100}. Domain structures on the (001) cub surface of the 91PZN-9PT single crystal were observed in the M phase as shown in Fig.1 (c) by PLM. Twin- related striated-shaped domain patterns were found to have coarse domains (marked with D1) of ~15μm length oriented along {1-10} and coarse domains (marked with D2) of ~5μm length oriented along {100}. Both coarse domains have fine domains (marked withλ) of ~2μm length oriented along {010}. Fig.1(d) shows the domain structure of 68PMN-32PT single crystal on (001) surface observed in the M phase by PLM. Alternative related striated-shaped domain patterns were found to have coarse domains (marked with D) of ~5μm length oriented along {110}. Each coarse domain has fine domains (marked withλ) of ~1μm length oriented along {100}.

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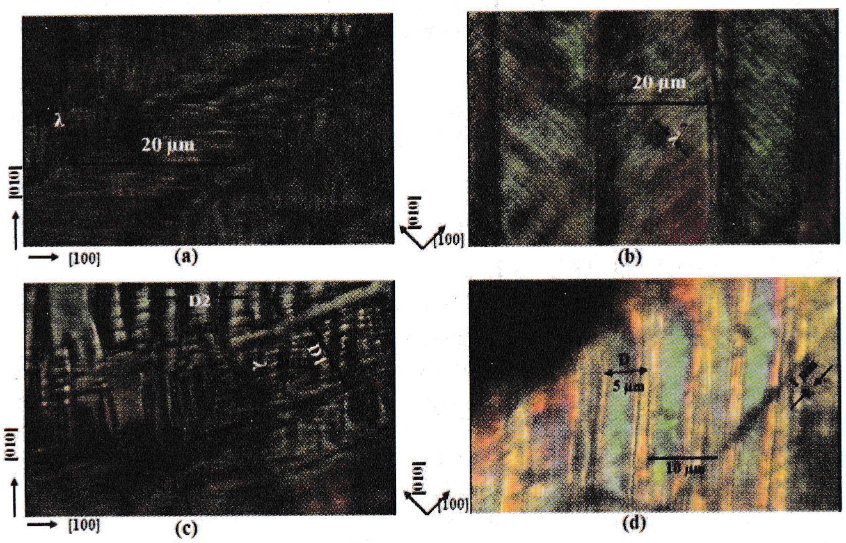

Fig.1. (a), (b) and (c) show the domain structure in R, T and M phases of 91PZN-9PT single crystal and (d) in R phase of 68PMN-32PT single crystal.

Domain structures on the (001) cub surface of the 91PZN-9PT single crystals were observed in the R, T and M phase as shown in Fig. 2 by PFM. Fig.2 (a) shows the piezo response (Acosθ) image taken over 20μm length scales in the imaging ac voltage at 20V by PFM. Twin-related alternative micron-sized domain structures were found to be ~1μm length as revealed as dark and bright domains in the R phase, which have some preferential orientations along {110} and {010}.Furthermore, dot like patterns were found to be within the dark or bright domain patterns. Fig. 2(b) shows the piezoresponse image taken over ~3μm length in the imaging ac voltage 20V. Dot like patterns within the dark or bright domains in Fig. 2 (b) were found to correspond to nano domains in size range ~100 nm. Fig. 2 (c) shows the piezo response image in the imaging ac voltage at 20V in the T phase. Twin-related alternative nanometer-sized domains were found to be ~ 200nm length (marked with λ) oriented along {100}.Nanometer-sized domains were found to be ~ 100nm length show in the Fig.2 (d). Fig.2 (e) shows the piezo response image in the imaging ac voltage at 20V by PFM in M phase. Twin-related alternative micron-sized domain structures with ~1μm (marked withλ) length were found as revealed as dark and bright patterns, which have some preferential orientations along {010}, {110} and {100} by PFM. Micron-sized domains were found to be ~ 1-2μm length show in the Fig.2 (f).

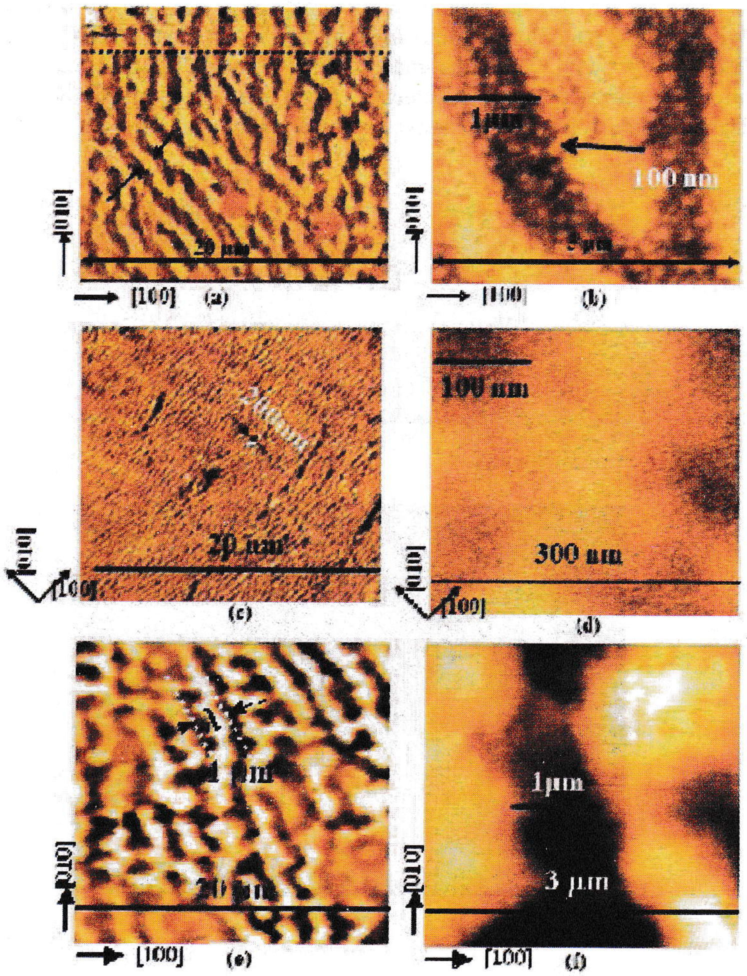

Fig.2. (a), (b), (c), (d), (e) and (f) show the domain structure in R, T and M phases of 91PZN-9PT single crystal.

Domain structures on the (001) $_{cub}$ surface of 68PMN-32PT single crystals were observed by PFM shown in Fig.3. Fig. 3 (a) shows the piezo response (Acosθ) image taken over 20μm length scales in the imaging ac voltage at 20V. Dot like micron-sized domain structures were found to be ~1μm (marked with λ) length as revealed as dark and bright domains, which have some preferential orientations along {110} and {100}. Fig.3 (b) shows the piezo response (Acosθ) image taken over 3μm length scales. Dot like micron-sized domain structures were found to be ~ 0.5 μm. Fig. 3 (c) shows the enlarged three-dimensional piezo response image. There are nanometer-sized island like domains of ~5-

10nm width. Then the nano domains in size range from 10 to 100nm were confirmed. These nano domain sizes are compared with those of 20 to 100nm for 95.5PZN-4.5PT [11]. This nanometer sized domains have attracted much attention to enhance the piezoelectric properties for applications in high performance actuator, non-destructive testing and ultrasonic devices.

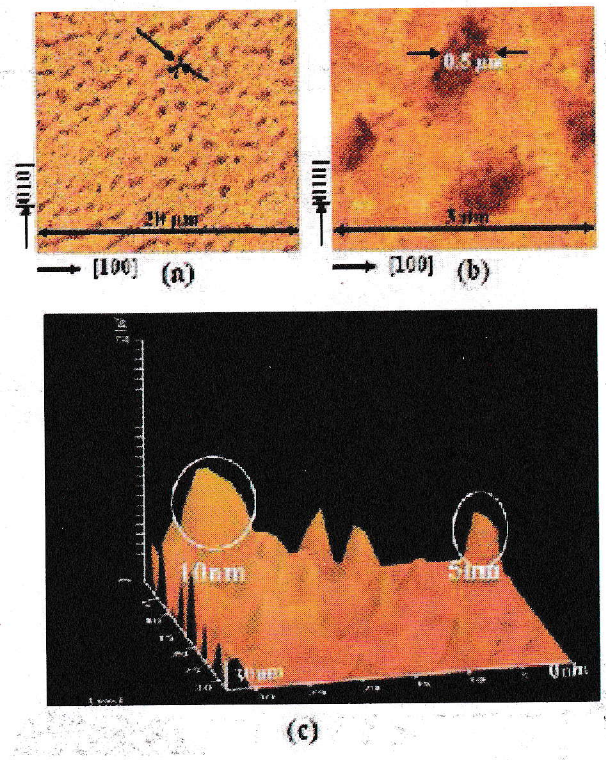

Fig. 3 (a), (b) and (c) show the piezoresponse image taken over 20µm, 3µm and 5-10nm width.

4. Conclusions

Domain structures on the (001) cub surface of the 91PZN-9PT and 68PMN-32PT single crystals were observed in the different phases by PLM and confirmed the domain structure by PFM to enhance the piezoelectric properties for applications in high performance actuator, non-destructive testing and ultrasonic devices. The electric field-induced nanotwin and dot like related domains were investigated in 91PZN-9PT and 68PMN-32PT single crystals. Twin-related alternative micron-sized domain structures were found to be ~1µm length as revealed as dark and bright domains in the different phases. Dot like patterns within the dark or bright domains were found to correspond to nano domains in size range 5-100 nm length scales. Alternative related striated-shaped domain patterns were found to have coarse domains of ~5μm length oriented along {010}. Each coarse domain has fine domains of ~1μm length oriented along {100}.Such results of hierarchal domains in the engineered states in the (001) cub oriented 91PZN-9PT single crystal are similar to those in the (001) cub oriented 68PMN-32PT.

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References

[1]. J. Kuwata, K. Uchino, and S. Nomura (1981), "Phase transitions in the $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ system" Ferroelectrics, Vol. 37, pp. 579-582.

[2]. S.E. Park and T.R. Shrout (1997), "Ultrahigh strain and piezoelectric behavior in relaxorbased ferroelectric single crystals" J. Appl. Phys. Vol.82, pp. 1804-1811.

[3]. P.W. Rehrig, W.S. Hackenberger, S.E. Park and T.R. Shrout (2002), "Piezoelectric Materials in Devices", EPFL 2002, pp. 433.

[4]. B. Noheda and D.E. Cox (2006), "Bridging phases at the morphotropic boundaries of lead oxide solid solutions", Journal of Phase Transition, Vol. 79, pp. 5–20.

[5]. Y.M. Jin, Y.U. Wang, A.G. Kachaturyan, J.F. Li and D. Vielhland (2003), "Conformal Miniaturization of Domains with Low Domain-Wall Energy: Monoclinic Ferroelectric States near the Morphotropic Phase Boundaries", Phys.Rev.Lett. Vol. 91, pp. 197601-197604.

[6]. Y.U. Wang (2006), "Three intrinsic relationships of lattice parameters between intermediate monoclinic MC and tetragonal phases in ferroelectric $Pb[(Mg_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ and $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ near morphotropic phase boundaries", Phys. Rev. B. Vol. 73, pp. 014113.

[7]. M. Ahart, M. Somayazula, R.E. Cohen, P. Ganesh, P. Dera, H. Mao, R.J. Hemley, Y Ren, P. Liermann and Z. Wu (2008), " Origin of morphotropic phase boundaries in ferroelectrics", Nature. Vol. 451, pp. 545-548.

[8]. N. Yasuda, M. M. Rahman, H. Ohwa, M. Matsushita, Y. Yamashita, M. Iwata, H. Terauchi and Y. Ishibashi (2006), "Pressure-induced suppression of piezoelectric response in a $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ binary system single crystal near a morphotropic phase boundary", Appl.Phys.Lett. Vol. 89, pp. 192903-192906.

[9]. M. Matsushita, Y. Tachi and K. Echizenya (2001), "Poling and depoling effects on dielectric properties and domain structures in relaxor 24Pb $(In_{1/2}Nb_{1/2})O_{3-46}Pb(Mg_{1/3}Nb_{2/3})\ O_{3-30}PbTiO_3$ near a morphotropic phase boundary composition". 103rd Annual Meeting of the American Ceramic Society, Indiana, pp. 247–248.

[10]. A. Gruverman, O. Auciello and H. Tokumoto (1996), " Nanoscale investigation of fatigue effects in $Pb(Zr,Ti)O_3$ films", Appl.Phys.Lett.Vol. 69, pp. 3191-3193.

[11]. I.K. Bdikin, V. V. Shvartsman and A.L. Kholkin (2003), "Nanoscale domains and local piezoelectric hysteresis in $Pb(Zn_{1/3}Nb_{2/3})O_{3\text{-}4.5\%}PbTiO_3$ single crystals". Appl. Phys. Lett. Vol. 83. pp. 4232-4234.

[12]. L. Zhang, M. Dong and Z.G. Ye(2000), "Flux growth and characterization of the relaxor-based $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ [PZNT] piezocrystals". Material Science Engineering B Vol. 78, pp. 96–104.

[13]. Y. Uesu, M. Matsuda,Y. Yamada, K. Fujishiro, D.E. Cox, B. Noheda and G. Shirane (2002), "Symmetry of High-Piezoelectric Pb-Based Complex Perovskites at the Morphotropic Phase Boundary: I. Neutron Diffraction Study on $Pb(Zn_{1/3}Nb_{2/3})O_{3-9\%}PbTiO_3$". J. Phys. Soc. Jpn. Vol. 71. pp. 960-965.

[14]. K. J. Hyeon, D. H. Kim and S. Kojima (2003), "Elastic responses to different electric-field directions in relaxor ferroelectric $Pb[(Zn_{1/3}Nb_{2/3})0.91Ti_{0.09}]O_3$ single crystals". Applied Physics Letter,Vol. 83, pp. 2037–2039.

[15]. R.R. Chien, V.H. Schmidt,C. S. Tu and F.T. Wang (2006), "Direct observation of ferroelectric domains and phases in (001)-cut $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ single crystals under electric-field polin". Journal of Crystal Growth, Vol. 292, pp. 395–398.

[16]. G. Xu, H. Luo, H. Xu and Z. Yin (2001), "Third ferroelectric phase in PMNT single crystals near the morphotropic phase boundary composition", Physics Review B, Vol. 64, pp. 020102.