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Study of ferroelectric domain morphology in PMN–32% PT single crystals

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Abstract

PMN–32% PT relaxor ferroelectric crystals were prepared by Bridgman–ACRT method. Specimens cut in certain direction and from various areas in crystals were ground and polished with carborundum manually. The polished surfaces of specimens were etched by aqua fortis. Subsequently, the ferroelectric domain morphologies at the specimen surfaces were investigated by both optical microscopy and atomic force microscopy. The results indicated that, besides the normal band configuration well known, the ferroelectric domain in PMN–32% PT crystal usually shows abnormal watermark morphology.

Keywords: Ferroelectrics; PMN–32% PT single crystals; Domain morphology

1. Introduction

Recently, much attention has been paid to relaxor-based ferroelectric single crystals, such as $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZN–PT) [1–3] and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT) [4,5] with composition near the morphotropic phase boundary (MPB, $0.08 < x < 0.10$, the later $0.28 < x < 0.36$), because their excellent piezoelectric and dielectric properties. Compared to conventional PZT ceramics [6], PZN–PT and PMN–PT single crystals have ultrahigh piezoelectric constant $d_{33} > 2500$ pc/N, extremely large piezoelectric strain (>1%) and electromechanical coupling factor k_{33} can reach up to 94% with the direction along $\langle 0\,0\,1\rangle_{cub}$, which may replace the PZT ceramics in some application such as ultrasonic imaging, telecommunication, and ultrasonic devices, they are also being considered as the next generation materials for the actuator.

Most of research works concentrated on the growth and characterization of the ferroelectric single crystals, less attention has been paid to study the relationship between crystals internal structure and their high performance properties. It is believed that the outstanding properties such as high electromechanical coupling effect of PMN–PT and PZN–PT crystals are closely related to polarization rotation and phase coexistence near MPB [7], domain structure play an important role in both of two sides. Ye and Dong [8] distinguished mixed phase between rhombohedral $R3m$ and tetragonal 4 mm phases by analyzing the domain morphologies of PMN–PT single crystals with polarized light microscopy (PLM). Xu et al. [9] discovered a third ferroelectric phase in PMN–PT crystals near MPB by investigating of different domain morphologies. Lu et al. [10] confirmed existence of the third ferroelectric phase by another method at same time. Tu et al. [11] observed the successive phase transition with different domain morphologies of PMN–PT crystal upon heating. Yu et al. [12] investigated domain switching in the scale of micron by atomic force microscopy. Most of those works about domain configurations vary between different researchers, and it is difficult to obtain a uniform conclusion. The purpose of this paper is to reveal instinct domain morphologies of PMN–32% PT single crystals and attempts to offer a new procedure to observe the domain morphology.

2. Experiment procedure

The lead magnesium niobate–lead titanate single crystal for this experiment, PMN–32% PT [13] was grown by Bridgman–accelerated crucible rotation technique (ACRT)

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method. The samples were cut into square platelets with the orientation was perpendicular to the pseudo-cubic ⟨0 0 1⟩ direction, which was determined by X-ray diffraction (XRD). The crystal dimensions were 5 mm × 5 mm with a thickness of 1 mm. There were two platelets named sample 1 and sample 2 separately, both of them were ground and finely polished by diamond paste with carborundum manually. Sample 1 was heated to 400 °C (Curie point is 143.5 °C of PMN–32% PT) [13] and then annealed with slow cooling rate of 10 °C/h down to room temperature before etching, while sample 2 was etched by aqua fortis after polishing immediately. Both of them etched at room temperature for 48 h, then the etched surfaces of samples 1 and 2 were investigated by optical reflection microscope and atomic force microscope (AFM), which was operated at non-contact mode (Multi Mode, Digital Instruments Inc., Santa Barbara, CA). Then, we sketched a thin nick in the surface of sample 2 by a nipper; at last, sample 2 was annealed and investigated again.

3. Results and discussion

Fig. 1(a) shows the surface domain configurations of sample 1, straight band domain configuration can be observed from this photograph. Contrasted to the simple configuration of sample 1, Fig. 1(b) shows another complicated watermark domain configuration of sample 2, but we can also recognize the general band orientation which from down to up. Devries and Burke [14] have pointed out that the effect of different polishing treatments on $BaTiO_3$ ceramics could result different domain configurations, but samples 1 and 2 were polished along same directions and etched by the same enchant, the only difference was sample 2 etched without annealing. Fig. 1(c) shows the surface domain morphologies of sample 2 after annealing, thinner band domain can be observed although its domain wall is not straight as in sample 1, and its domain configuration is complicated contrasted to sample 1 but it is much simple than sample 2. Fig. 1(d) shows the same morphologies as Fig. 1(b) except the thin

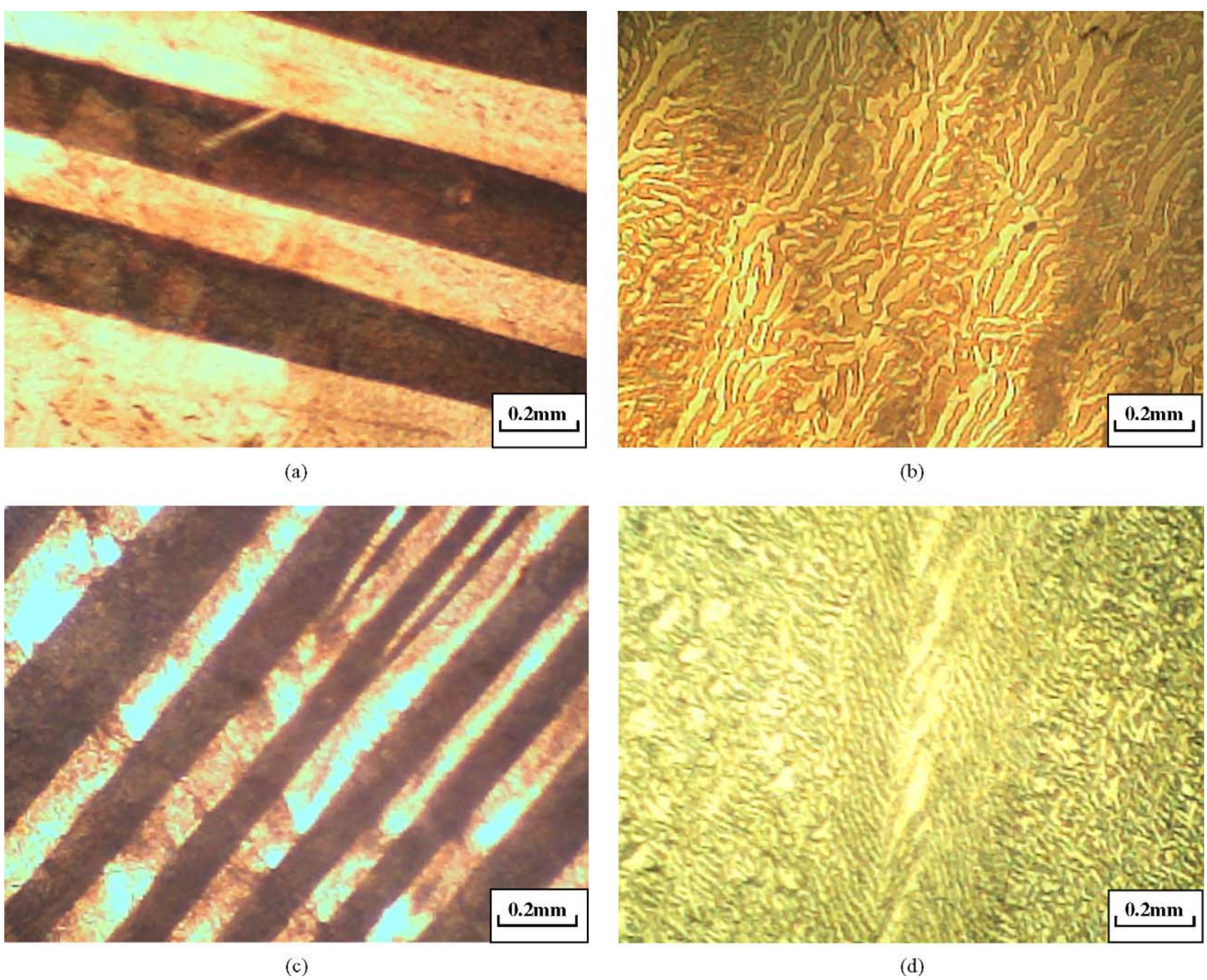

Fig. 1. Optical photographs of PMN–32% PT single crystal surface domain structures: (a) sample 1, (b) sample 2 before annealing, (c) sample 2 after annealing and (d) sample 2 (the thin nick was sketched by a nipper).

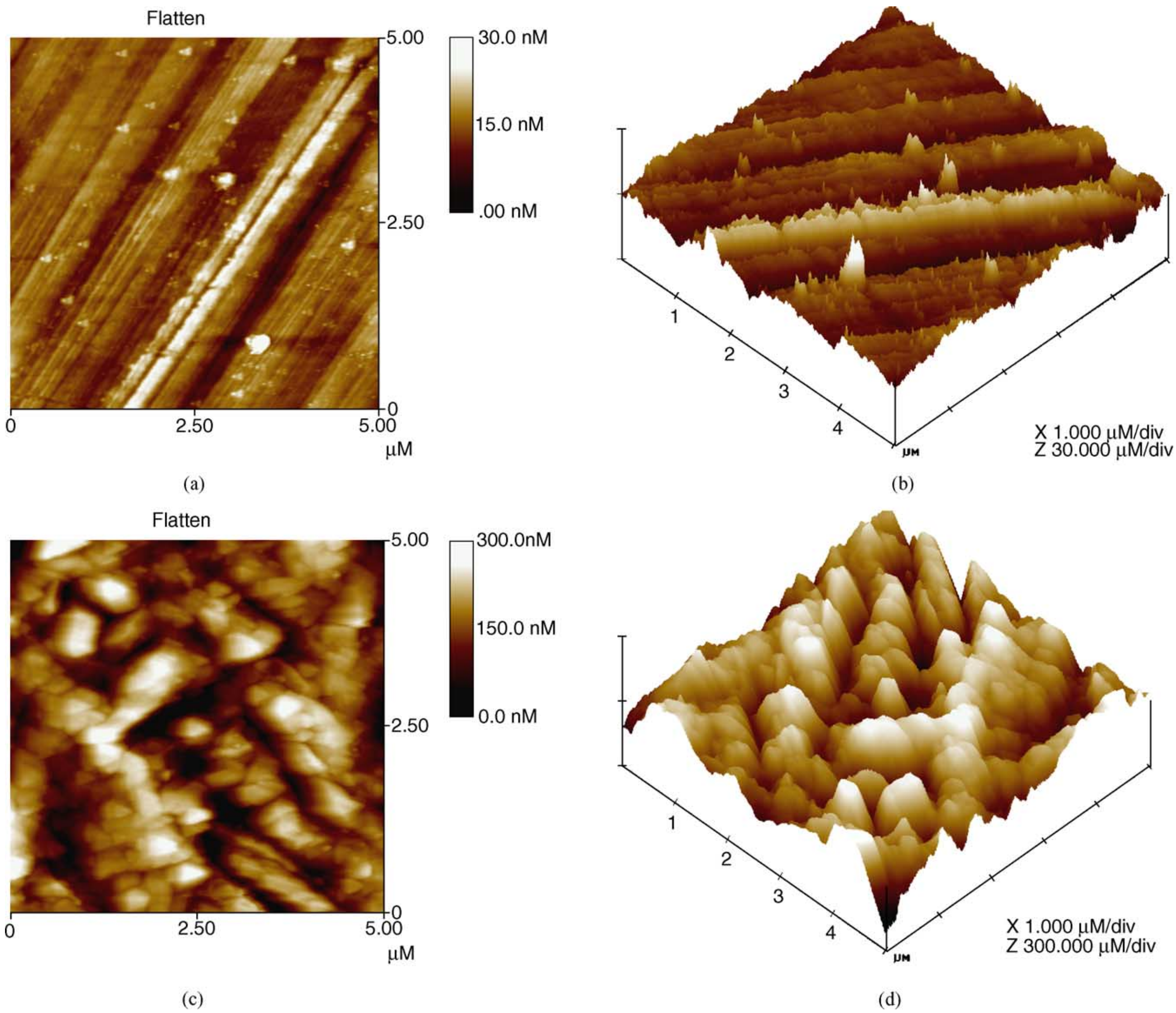

Fig. 2. AFM domain morphologies: (a) sample 1 (flatten), (b) sample 1, (c) sample 2 (flatten) and (d) sample 2.

nick in the middle of this photograph, which was sketched by a nipper.

In suit investigation of samples 1 and 2 by the AFM revealed the surface microstructures of PMN–32% PT single crystals. Hooton and Merz [15] have discovered that the positive end of the electric polarization was etched much faster than the negative one, the white stripe according to higher area and the black one according to the lower. Fig. 2(a) and (b) show sample 1 domain microstructure, which was composed by order arranged strips. Fig. 2(c) and (d) show another domain microstructure, as can be seen that the watermarks of sample 2 are made up of these disorder arrangement dipoles.

What the watermarks are we suspect those as tetragonal phase 180° domain. Because we can confirm the band domain as 90° domain by optical method of sample 2 after annealing, before and after annealing sample 2 should keep its primary phase, if the watermark is rhombohedral phase domain, we can not observe the tetragonal 90° band domain configuration in Fig. 1(c), and in tetragonal phase there were two domains, one is 90° domain the other is 180° domain. Therefore, we believe those irregular watermarks as tetragonal phase 180° domain. Devries and Burke [14] have observed similar domain configuration in $BaTiO_3$ single crystals.

Merz [16] has calculated the 180° domain wall energy and thickness of $BaTiO_3$, and found that the 180° domain wall thickness is small, of the order of one to a few lattice constants, contrasted to 20–30 lattice constants of the 90° domain wall thickness. Therefore, in PMNT crystal 180° domain configuration is much sensitivity to mechanical and thermal energy by the effect of polishing and annealing treatment. Fig. 1(d) shows the changes caused by stress, which indicated that effect of polishing lead much change of the domain configuration, in order to get out of polishing effect, and annealing treatment is the best choice. Above 143.5 °C

(Curie point), PMN–32% PT crystals has the cubic perovskite structure which belongs to paraelectric phase, upon slow cooling below 143.5 °C, PMN–32% PT takes phase transformation from cubic paraelectric phase to tetragonal ferroelectric phase, and forms domain configuration at the same time. Domain configuration is close relation to the thermal energy, those dipoles which spontaneous polarization direction was changed by stress can rearrange freely as the domain growth at ferroelectric phase transition by annealing treatment. After etching the surface of PMN–32% PT crystals is not flat as before, in this case annealing need not only overcome the domain wall but also the configuration which exist larger distance between the higher end and the lower one. The later one could not overcome unless the temperature is high enough near to the melting point. By this disposal procedure, we can get an instinct domain configuration which is almost the same domain configuration as generation by ferroelectric phase transition without any external affects.

4. Conclusion

The PMN–32% PT single crystals domain morphologies have been investigated with optical reflection microscope and atomic force microscope (AFM) by etching method; two different domain configurations were observed, one is board band while the other is watermark. Watermark maybe the 180° domains, which were not the instinct domains in PMN–32% PT crystals. In order to investigate PMN–32% PT crystals instinct domain morphologies, annealing is important and necessary. The best experimental procedure is polishing, annealing and etching in sequence.

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