A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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STUDY OF DOMAIN STRUCTURE IN (211)-CUT $(Pb(Mg_{1/3}Nb_{2/3})O_3)_{0.7}(PbTiO_3)_{0.3}$ SINGLE CRYSTAL BY TEMPERATURE-DEPENDENT PIEZORESPONSE FORCE MICROSCOPY [1)]

BADANIE STRUKTURY DOMEN W PRZEKROJU (211) MONOKRYSZTAŁU $(Pb(Mg_{1/3}Nb_{2/3})O_3)_{0.7}(PbTiO_3)_{0.3}$ METODĄ MIKROSKOPII SIŁ Z CZUJNIKIEM PIZOELEKTRYCZNYM

PMN-xPT is relaxor ferroelectrics with great potential in the application of novel devices. At the morphotropic phase boundary with x ~28%–36% of PT, PMN-xPT exhibits complex crystal structure and phase transformation, which are not fully understood yet. The ferroelectric domain evolution study may reveal the mechanism of phase transformations induced by temperature or electrical field. In this work, we report the study of domain evolution of PMN-30% PT single crystal by means of temperature-dependent piezoresponse force microscopy (PFM) and electrical measurement. Observation of poled (211)-cut sample revealed that lamellar domains are developed from an unstable single domain structure generated by poling. Temperature-dependent PFM of the poled sample revealed a domain evolution. During temperature increase, the lamellar domains become smaller, and the phase transformation from rhombohedral-orthorhombic or monoclinic-tetragonal phase is progressing according to polarization rotation. When temperature is higher than T_m, the domain contrast becomes very weak and finally disappears. After heating and cooling cycle, the PNRs and speckle-shaped microdomains with random arrangement can be observed in the PFM image.

PMN-xPT jest ferroelektrykiem posiadającym duże potencjalne możliwości zastosowań w nowoczesnych urządzeniach. Na morfotropowej granicy fazowej zawierającej z ~28%–36% PT, PMN-xPT wykazuje złożoną strukturę krystaliczną i przemianę fazową, która nie była dotychczas wyjaśniona. Badanie zmian zachodzących w domenach ferroelektrycznych może wyjaśnić mechanizm przemian fazowych wywołanych temperaturą lub polem elektrycznym. W pracy przedstawiamy badania zmian domen monokryształu PMN-30% PT przy użyciu mikroskopii sił z czujnikiem piezoelektrycznym przy zmiennej temperaturze (PFM) oraz pomiarów elektrycznych. Obserwacje ukierunkowanej próbki o przekroju (211) wykazały, że płytkowe domeny powstają z niestabilnej struktury pojedynczych domen na skutek biegunowości. PFM w zmiennej temperaturze dla próbki biegunowej ujawnił zmiany domen. Wraz ze wzrostem temperatury płytkowe domeny rosną i następuje przemiana fazowa z fazy romboedrycznej-ortorombowej lub jednoskośnej-tetragonalnej zgodnie z rotacją polaryzacji. Gdy temperatura jest wyższa niż T_m kontrast domenowy staje się bardzo słaby i ostatecznie zanika. Po cyklu wygrzewania i chłodzenia obserwowano na obrazach PFM PNRs i chaotycznie rozłożone mikrodomeny o kształcie cętek.

1. Introduction

The complex perovskite structure $(Pb(Mg_{1/3}Nb_{2/3})O_3)_{1-x}(PbTiO_3)_x$ (PMN-xPT) exhibits typical relaxor ferroelectrics properties which is attracting a great deal of attention for both practical and fundamental investigations due to their high piezoelectric coefficient (d_{33} ~2000pC/N) and electromechanical coupling factor (k_{33} ~92%)[1, 2]. Therefore, it has been studied for application of novel devices such as electro-mechanic sensors, high performance ultrasound transducers, and actuators. It has been found that the morphotropic phase boundary of PMN-xPT system between rhombohedral (R) and tetragonal (T) phases is around x~28%–36% [3], and exhibits temperature, electric-field, and stress-induced phase transitions which are attributed to polarization rotation through intermediate monoclinic (M) or orthorhombic(O) phases. The existence of polar

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nanosized regions (PNRs) are closely related to the local random field due to random distribution of Mg^{2+} and Nb^{5+} cations in PMN-xPT system.

In the past, the domain structure and phase transition in ferroelectric material is commonly investigated by means of polarizing optical microscopy [4-7], but has a drawback of limited resolution. Recently, the development of piezoresponse force microscopy (PFM) has received a great deal of the attention on the investigation of ferroelectric material due to high spatial resolution and sensitivity to local polarization [1, 8-12].

Piezoresponse force microscope (PFM) is a powerful tool for the study of ferroelectric domains by visualizing the domain structure in a nanometer scale resolution. A sharp tip is attached to the end of a flexible cantilever and is in contact with the ferroelectric sample surface while maintains constant force. By applying an ac signal between the conductive tip of the PFM and the bottom electrode of the sample, it results in the surface oscillation of ferroelectric materials with the same frequency as the input ac signal. The cantilever vibrates in response to the oscillation of material surface. This vibration signal can be detected by a laser reflecting off the back of the cantilever, and then impinged on a position-sensitive photodiode array. Finally, the image is revealed by low-pass filter and lock-in amplifier corresponding to topographic and ferroelectric domain images, respectively. Figure 1 shows the schematic diagram of PFM imaging mechanism.

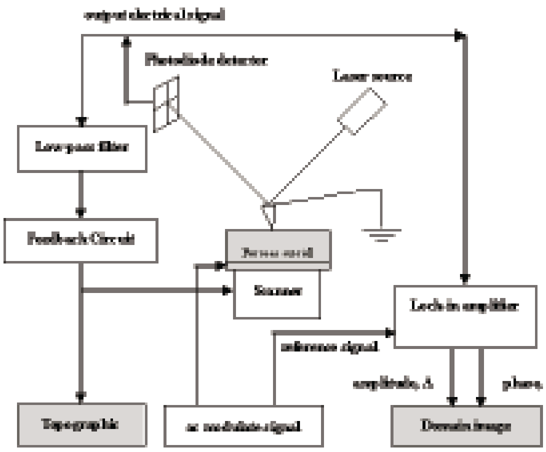

Fig. 1. Schematic diagram of piezoresponse forse microscopy imaging mechanism

The temperature dependence of relative permittivity, x-ray diffraction, and neutron diffraction have been carried out for investigation of relaxor ferroelectric materials. However, the in-situ study of domain evolution in small scale under different temperatures is rare. Shvartsman et al. [11] have reported their investigation on PMN-20%PT single crystal by means of PFM under increasing temperature. In this paper, we report the investigation result of domain structure in the (211)-cut PMN-30%PT single crystals by means of temperature-dependent PFM. The sample temperature can be adjusted by the temperature controller in order to investigate the ferroelectric domain structure at different temperatures.

2. Experimental Details

The PMN-30%PT single crystal was grown by using the modified Bridgman technique [13]. The seed crystals were used along the <111> direction for the growth, and the major faces of sample were cleaved as normal to the <211> direction so it is called (211)-cut PMN-30%PT single crystal. For measurements of the temperature dependence of hysteresis loops and relative permittivity, the samples with area of 6–7 mm^2 and thickness of 0.5 mm coated Cr/Au on both side by using sputtering as electrodes. In order to investigate the domain structure, the sample was poled along the <211> direction by an electric field of 10 kV/cm at 120° for 15 min and of 5 kV/cm in the cooling process. By using Sawyer-Tower circuit, the hysteresis loops of the (211)-cut PMN-30%PT samples with varying temperature from room temperature to 162°, which is higher than the T_m, can be measured. The temperature dependence of relative permittivity of the as-grown and poled samples with different frequency were measured using an impedance analyzer (HP4194A) equipped with a temperature chamber (Delta 9023).

For PFM imaging, the (211)-cut PMN-30%PT single crystals were mechanically polished to optical quality with the thickness of about 30 μm in order to minimize superposition of domains. It has been reported that a skin effect presents in the relaxor-based ferroelectrics material in which the skin layer thickness is around a few microns [14-16]. In order to avoid the skin effect in PFM imaging, we have annealed the sample at 180° ($> T_m$) for 30 min before PFM imaging in order to minimize the skin effect and also release the stress due to polishing. The domain images were obtained by piezoresponse force microscope (Nanoscope IV, Digital Instruments) utilizing a conductive tip coated with Cr/Pt. In the PFM working mechanism, a modulating voltage of 4V (peak-to-peak) with 11 kHz was applied to Cr/Au bottom electrode, while the tip was electrically grounded.

3. Results

Figure 2 shows the temperature dependence of relative permittivity of the as-grown and poled (211)-cut

PMN-30%PT single crystals upon heating. It can be seen that according to the relative permittivity of as-grown sample as shown in Fig. 2(a), one peak and shoulder can be observed at ~142° and ~92°, respectively, where the peak at 142° represents the transition temperature, T_m, from ferroelectric to paraelectric phase; and the shoulder corresponds to the phase transition from rhombohedral ferroelectric (FE_r) microdomains to tetragonal ferroelectric (FE_t) state. Figure 2(b) shows the comparison of the

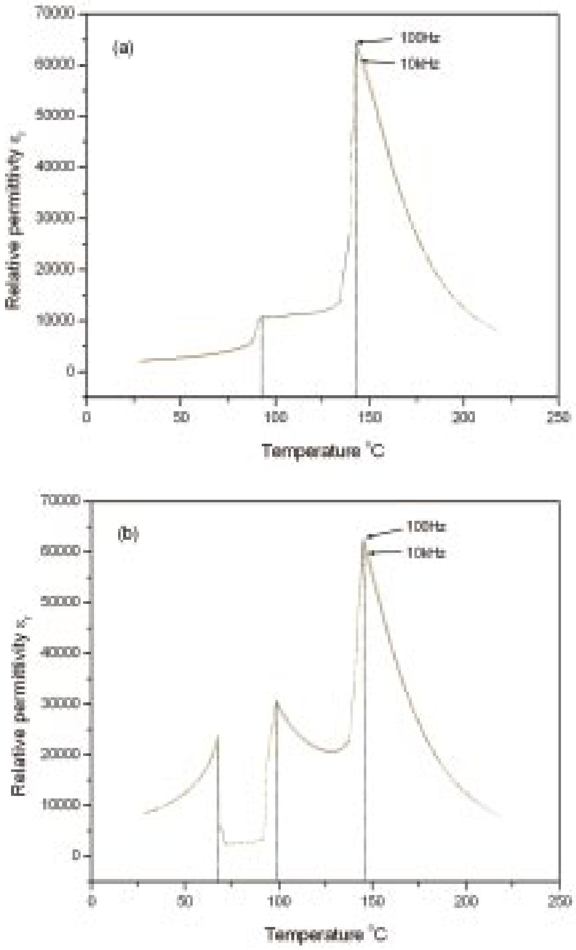

Fig. 2. Temperature dependence of relative permittivity curves for the (211)-cut PMN-30%PT single crystal upon heating of (a) the as-grown and (b) poled samples

relative permittivity curve for poled sample. It can be noticed that three peaks are revealed in the curve, one main peak and two small peaks. The main peak at ~145° represents the T_m temperature which has been shifted to higher temperature compared with the as-grown one due to poling. The other two phase transition peaks are at ~68° and ~99°. The first small peak should coincide with a phase transition from FE_r macrodomains state to orthorhombic ferroelectric (FE_o) or monoclinic ferroelectric (FE_m) state, while the second small peak with the phase transition from FE_o or FE_m to FE_t phase. Therefore, FE_r macrodomains state is dominant in the poled sample at room temperature.

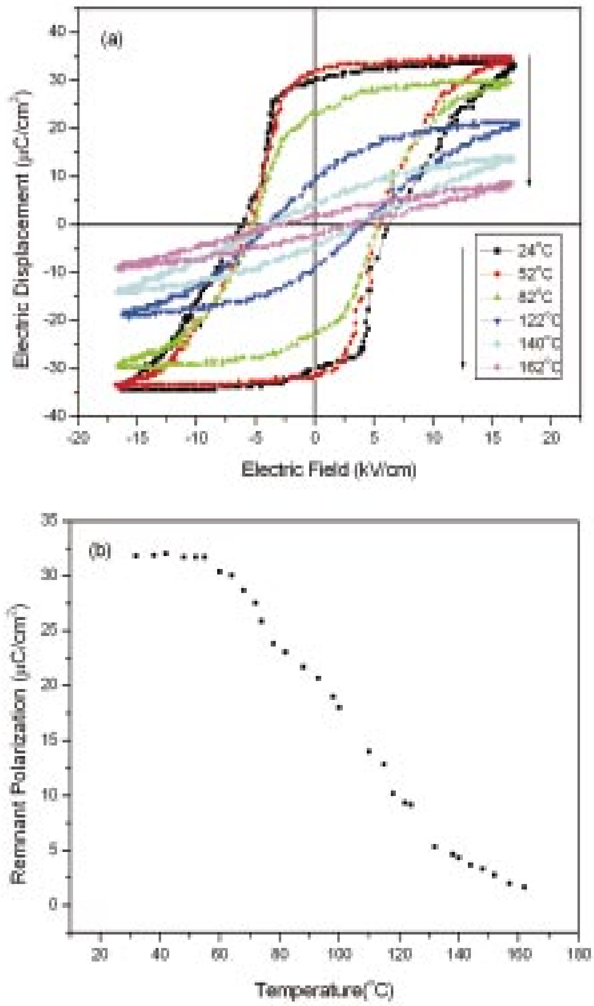

Fig. 3. Temperature dependence of (a) hysteresis loops, and (b) remnant polarization

Typical hysteresis characteristic for the (211)-cut PMN-30%PT single crystal varying temperatures are shown in Fig. 3(a). From the hysteresis loop at 32°, the value of the saturation polarization (P_s) is nearly the same as the remnant polarization (P_r), which is determined to be 31.8 μC/cm^2; and also the coercive electric field (E_c) is determined to be 6.4 kV/cm. The remnant polarization at different temperatures can be revealed from the temperature dependence of hysteresis loop, as shown in Fig. 3(b), in which P_r undergoes a continuous second order phase transition. At temperature higher than T_m, the hysteresis loop can still be observed because of the existence of polar nanosized regions (PNRs) in the PMN-xPT single crystal. It is generally accepted that the properties of relaxor ferroelectric material are closely related to the formation of PNRs.

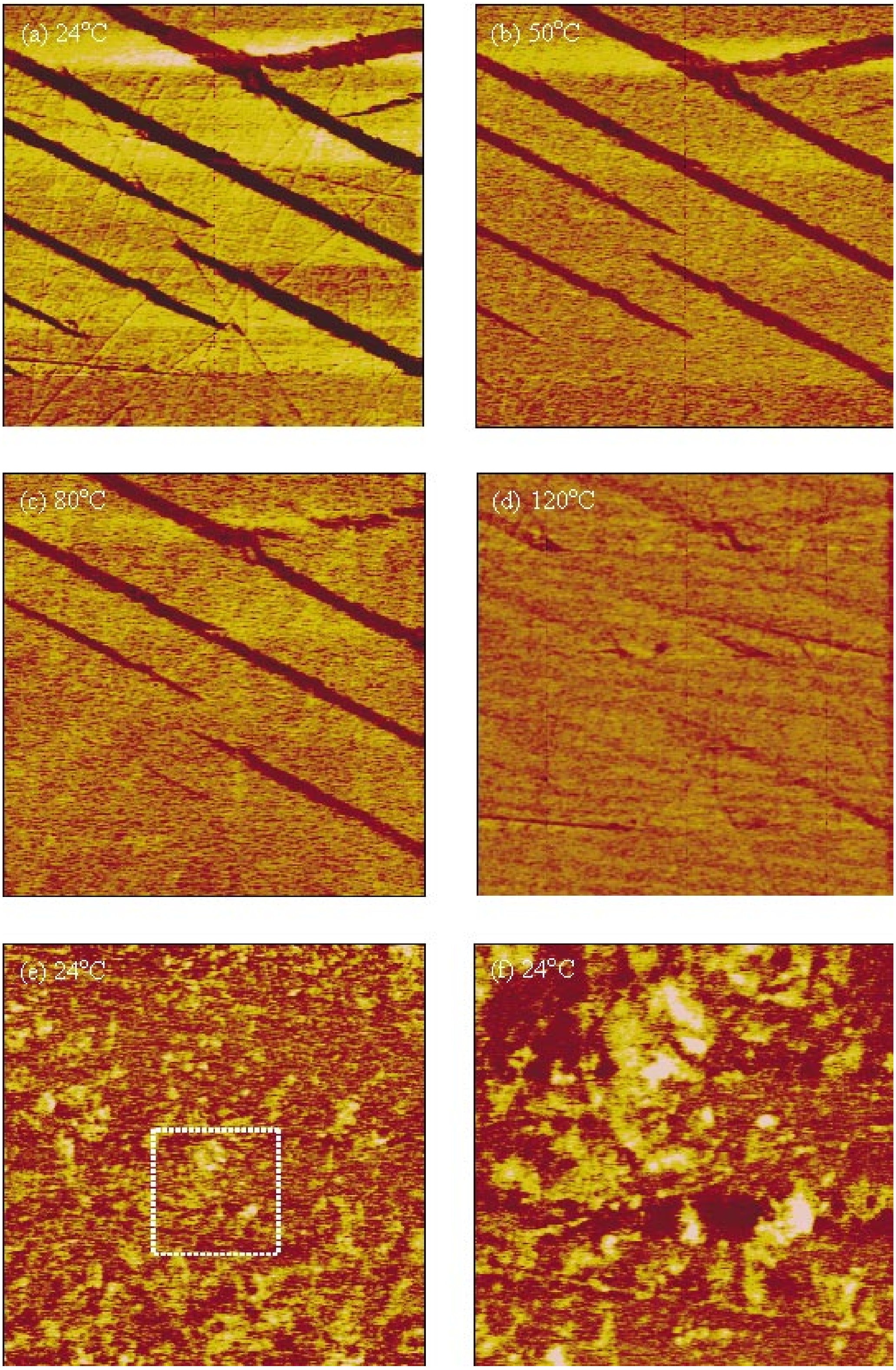

Fig. 4. The domain evolution of temperature-dependent piezoresponse phase images of the poled (211)-cut PMN-30%PT single crystal with scan size 30 μm upon heating: (a) 24°C, (b) 50°C, (c) 80°C, and (d) 120°C. (e) Piezoresponse phase image with scan size 10 μm after the sample cool down to room temperature; (f) The magnified image of the outlined region in (e) in the size of 3 μm

Figure 4 shows the temperature-dependent piezoresponse force microscopy of the poled (211)-cut PMN-30%PT single crystal, where (a)-(d) correspond to the phase images at 24°C, 50°C, 80°C, and 120°C, respectively. All of the PFM images in Fig. 4 are observed in the same region. It can be seen that at room temperature the contrast of the lamellar domains in the sample are sharp, and an angle of 140° between the two "dark" domains can be observed as shown in Fig. 4(a). When temperature reaches 80°C, the size of the "dark" lamellar domain becomes smaller, and some "dark" lamellar domains disappear and blur as shown in Fig 4(c). This change is due to the temperature induced depolarization, and the phase transition from the macrodomain state of FE_r to FE_o or FE_m phase. The domain evolution of poled (211)-cut sample observed under PFM is found to be consistent with the study of temperature-dependent remnant polarization and relative permittivity. However, PFM cannot distinguish the phases of FE_r, FE_o, FE_m, and FE_t. At 120°C, the contrast of lamellar domain becomes very weak. Finally, no obvious domain structure can be observed in the PFM image at the temperature higher than T_m. When the sample was cooled down to room temperature, the speckle-shaped microdomains can be revealed in PFM image instead of the lamellar domains. It is interesting to notice that in the magnified phase image of the outlined region as shown in Fig. 4(f), some PNRs with the size around 20-60 nm can be observed.

4. Conclusion

The ferroelectric domain structure and evolution of (211)-cut PMN-30%PT single crystal has been studied by means of piezoresponse force microscopy and a macrodomain to micro- and nanodomain transition has been revealed by heating and cooling thermal cycle. The domain observation results are consistent with temperature dependence of relative permittivity measurement.

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