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Domain Structures of $Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$PbTiO_3$ Single Crystals for Various Cooling Rate Observed using Contact Resonance PFM

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The domain structures of (001) plates of $Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT) single crystals were observed at room temperature after 220 °C ($> T_{R-F}$) thermal treatment with various cooling rate. Contact resonance piezoresponse force microscope (CR-PFM) was utilized for domain imaging, because applied modulation voltage was able to be reduced and microdomain images were able to be obtained without domain structure degeneration. The average size of domains was strongly dependent on the cooling rate. If the cooling rate was faster than 30 °C/h, quenched microdomain structure in relaxor phase was observed at room temperature.

Key words: piezoresponse force microscopy; contact resonance; relaxor ferroelectrics; PMN-PT; cooling rate

1 INTRODUCTION

After Smolensky *et al.*[1,2] have found $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), there has been remarkable interest in relaxor ferroelectric materials owing to their peculiar characteristics, so called 'relaxor characteristics': huge permittivity, giant piezoelectric constant, broad dispersion of permittivity and dull variation of spontaneous polarization. Particularly, phase diagrams of the relaxor ferroelectric materials are complicated[3,4] and the relaxor to ferroelectric (R-F) phase transition is the most confusing phenomenon.[5–7] This is because the physical properties depend on the electrical and thermal histories of the specimen at low temperatures, where the polarization fluctuations undergo a freezing into an effectively non-ergodic state.[5] Therefore, local polarization informations (i.e., real-space microscopic domain structure images) are helpful to understand the complicated relaxor characteristics. Practically, the relaxor characteristics are discussed and are mostly understood in terms of microdomains (polarized microclusters).

We investigated domain structures of relaxor ferroelectric single crystals using piezoresponse force microscope (PFM)[8–10] to understand the relationship between real space domain structures and the relaxor characteristics.[11–13] Transmission electron microscopy (TEM) is a representative technique for real-space observations of the microdomains due to its high resolution and capability for investigating dynamic phenomena.[14] However, TEM can hardly visualize 180° domain structures. In spite of lower resolution than TEM, PFM has an ability to visualize 180° domain structures and is easier to operate than TEM.

In our previous work, the domain-structure images of (001) plates of $Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT) single crystals were successfully obtained in a vacuum using a contact-resonance piezoresponse force microscope (CR-PFM).[13] During conventional PFM observations at sufficiently high temperature, the modulation voltages applied between the tip and the counter electrode induced polarization reversals and destroyed local domain structures under the tip. With the help of the contact-resonance mode.[12,13,15,16] (Fig. 1), piezoresponse images could be obtained with a reduced amplitude of the modulation signal, that addressed the issue of the polarization reversals during microdomain observations. Using this CR-PFM, circular domains $30 \sim 100$ nm in diameter were observed at temperatures above 175 °C.

In this article, domain structures of PMN-PT single crystals were observed using CR-PFM after 220 °C ($> T_{R-F}$) thermal treatment with various cooling rate.

2 EXPERIMENTAL

Domain structures were visualized using contact resonance piezoresponse force microscope. In

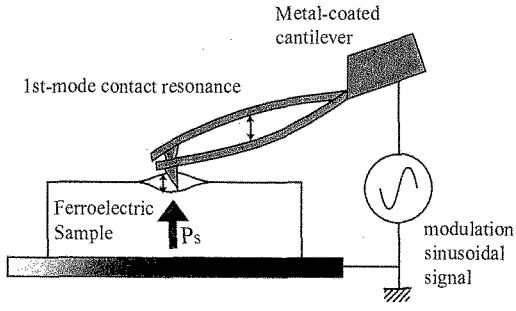

Fig. 1 First mode contact-resonance vibration of a cantilever.

the contact-resonance mode, the frequency of the modulation signal was maintained just below the resonance frequency of the cantilever deflection when in contact with the sample surface. Utilizing contact-resonance, we were able to operate PFM imaging with a reduced amplitude of the modulation signal. The details of CR-PFM imaging principle have been described elsewhere.[13,17]

Figure 2 shows the schematic view of CR-PFM system, which consisted of a commercial scanning probe microscope (Seiko Instruments, SPA300 and SPI3700) connected to a lock-in amplifier (Stanford Research Systems, SR844) and a oscillator (NF Electronic Instruments, WF1945). The experimental setup of CR-PFM was almost the same as conventional PFM setup. Si cantilevers used for domain visualization (Mikro Masch, NSC-12-D,E,F/TI-PT) were coated with Pt/Ti, and had a length of 250 – 350 μm, a thickness of 2.0 μm, a spring constant of 0.25 – 0.65 N/m and a free resonance frequency of 20 – 40 kHz. The amplitude of the applied modulation signal was 0.4 V_{pp}.

PMN-PT single crystals with practically morphotropic phase boundary composition were grown by the Bridgman method. The obtained PMN-PT ingot was sliced into 0.5 mm thick (001) plates. Pt/Ta electrodes were deposited onto the back of the samples by rf sputtering. The Curie temperature of the specimens was approximately 135 °C, which was estimated from the permittivity measurements. The surface of the PMN-PT plates were polished and the root mean square of surface roughness was less than 5 nm.

After samples were polished, thermal treatment was performed using electric furnace. The values of parameters for the thermal treatment are shown in table 1. Domain structures of the samples were observed in the air at room temperature.

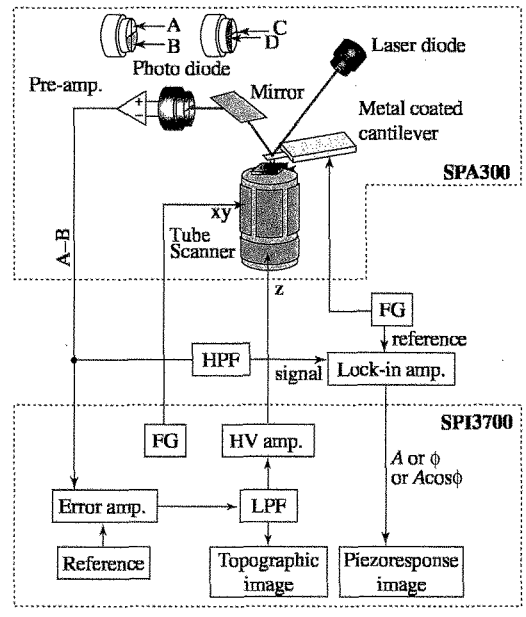

Fig. 2 Schematic view of contact resonance piezoresponse force microscope (CR-PFM). The setup of CR-PFM was almost the same as conventional PFM setup.

3 RESULTS AND DISCUSSION

The average size of domains depended on the cooling rate. Figure 3 shows CR-PFM images obtained before and after 220 °C thermal treatment with various cooling rate. Before the thermal treatment, clear finger print pattern[11,18] was observed with typical size of 500 nm to 1 μm (Fig. 3(a)). After the thermal treatment with a cooling rate 15 °C (Fig. 3(b)), finger print pattern was also obtained, but was slightly modified with some smaller domains. After the thermal treatment with a cooling rate 30 °C (Fig. 3(c)), the finger print pattern was fragmented by circular domains. The diameter of these circular domains was ranging from 50 nm to 300 nm and the average diameter was approximately 150 nm. In addition, after the thermal treatment with a cooling rate 60 °C (Fig. 3(d)), still smaller circular domains were observed. The diameter of the circular domains was ranging from 20 nm to 100 nm and the average diameter was approximately 40 nm, which coincided with the size of circular domains observed at temperatures above 175 °C in our previous work.[13] Recently, Yan *et al.*[7] found that dielectric constant of PMN-33%PT in ferroelectric phase increased with decreasing cooling rate at the relaxor-ferroelectric phase transition temperature T_{R-F}. They assumed that the average size of domains depended on the cooling rate across T_{R-F} and affected the dielectric properties. On the basis

Table 1 Values of parameters for thermal treatment.

No.	heating rate (°C/h)	maximum temperature (°C)	hold time (h)	cooling rate (°C/h)
(0)		— (before thermal treatment) —		
(1)	60	220	6	15
(2)	60	220	6	30
(3)	60	220	6	60

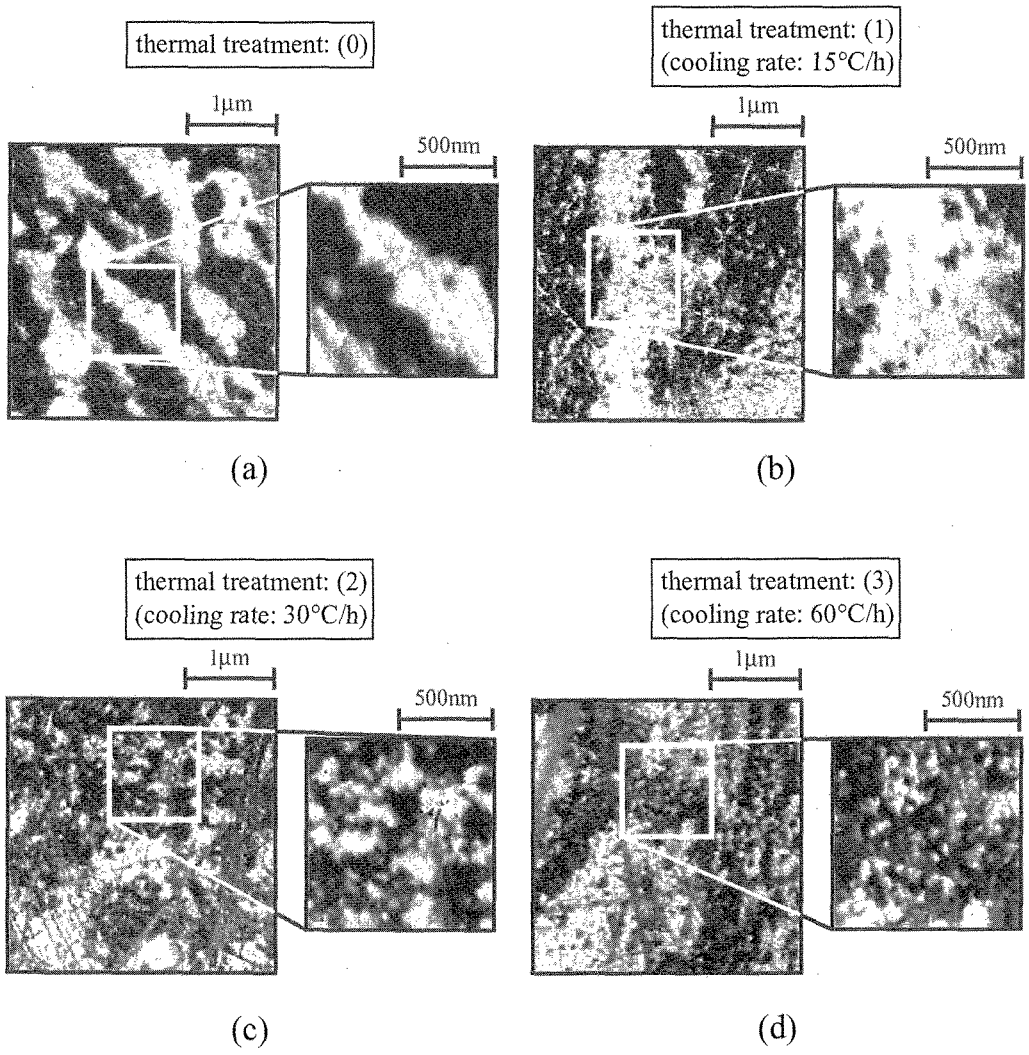

Fig. 3 CR-PFM images obtained (a) before and (b)-(d) after thermal treatment with various cooling rate ((b) 15 °C/h, (c) 30 °C/h and (d) 60 °C/h).

of the grain size effect of ferroelectric ceramics,[19] they predicted that the average size of domains increased with cooling rate across T_{R-F} decreased. Our result were qualitatively consistent with their prospect.

4 CONCLUSIONS

The domain structures of PMN-PT single crystals were observed using CR-PFM after 220 °C ($> T_{R-F}$) thermal treatment with various cooling rate. The average size of domains was found

to be strongly affected by the cooling rate. This size effect of domain structures could be the reason for the dependence of dielectric constant on the cooling rate.

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