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Dependence of the Domain Structures of PMN-xPT Single Crystals on Cooling Rates across the Relaxor-Ferroelectric Phase Transition

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Domain structures of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (x=0.27, 0.32 and 0.34, abbreviated as PMN-27%PT, 32%PT and 34%PT, respectively) single crystals were observed at the same area at room temperature after 240°C thermal treatments with various cooling rates. Contact Resonance Piezoresponse Microscope was utilized to observe domain structures for the sake of obtaining microdomain images nondestructively. The average domain size of PMN-34%PT and 32%PT single crystals decreased as cooling rate increased. However, the average domain size of PMN-27%PT was independent of cooling rates.

Key words: PMN-PT, contact resonance piezoresponse force microscopy, cooling rate, phase transition

1. INTRODUCTION

The physical properties of the relaxor ferroelectrics depend on its domain structures strongly. The domain structures of relaxor ferroelectrics, however, are too complicated to clarify as a whole. Principally, the relaxor characteristics are discussed and mostly understood in terms of microdomains (polarized microclusters). Therefore, local polarization information (i.e., real-space microscopic domain structure images) is helpful for understanding the complicated relaxor characteristics.

Recently, Yan *et al.* found that the dielectric constant of relaxor ferroelectric 0.67Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.33$PbTiO_3$ (PMN-33%PT) in the ferroelectric phase increased with decreasing cooling rate across the temperature of the Relaxor-Ferroelectric phase transition (T_{R-F}).[1] They assumed that the average size of domains depended on the cooling rate across T_{R-F} and affected the dielectric properties of PMN-33%PT in the ferroelectric phase. On the basis of the grain-size effect on the properties of ferroelectric ceramics[2], they predicted that the average size of domains increased with decreasing the cooling rate across T_{R-F}.

We have investigated the domain structures of relaxor ferroelectric single crystals by piezoresponse force microscopy (PFM) [3-5] to understand the relationship between real-space domain structures and relaxor characteristics.[6-8] In this study, we investigated relationship between the domain structures and the cooling rate as a function of PT-composition x (x=0.27, 0.32 and 0.34). The domain structures of these single crystals were observed after thermal treatment with various cooling rates. Contact Resonance Piezoresponse Microscope (CR-PFM)[7-9] was utilized to observe domain structures for the sake of obtaining microdomain images nondestructively.

2. EXPERIMENTAL

Piezoelectric force microscopy, which bases on the principle of atomic force microscopy, is the technique for domain structure observation. The domain structures were visualized by detecting inverse piezoelectric oscil-

lations caused by a modulation sinusoidal voltage applied between a conducting tip and an electrode on the back of the sample.[4] These vibrations resulted in the deflection of the cantilever due to the tip being in contact with the ferroelectric sample surface. This modulated cantilever deflection was acquired and amplified using lock-in amplifier. Accordingly, it was possible to determine the projection of the polarization vector onto the vertical direction.

The fundamental difference between PFM and CR-PFM is the frequency of modulation signal. The experimental set-up of CR-PFM was almost the same as conventional PFM set-up. In the contact-resonance mode, the frequency of modulation signal was maintained at the resonance frequency of the cantilever deflection when in contact with a sample surface. Utilizing contact-resonance, we were able to improve the signal-to-noise (S/N) ratio of piezoresponse signal and to operate PFM imaging with a reduced amplitude of the modulation signal. Due to the reduced amplitude of the modulation signal, microdomain structures with a lower coercive field could be observed non-destructively. The details of the CR-PFM imaging principle are described elsewhere.[7,8]

PMN-*x*PT single crystals were grown by the Bridgman method. The obtained PMN-*x*PT ingot was sliced into about 0.4mm thick (100) plates. To observe domain structures, the surface of the PMN-*x*PT plates were polished with diamond paste (0.25μm) and the root-mean-square surface roughness was less than 5nm. Ta/Pt top and bottom electrodes were deposited using rf-sputtering. The diameter of the top electrode was 1.0mm.

In order to approach to the same scanning area after each thermal treatment, checkered pattern Pt/Ta thin films were fabricated by photolithographic technique.

Thermal treatments were performed using electric furnace with the following procedure: (1)heat from room temperature to peak temperature (T_p) at a heating rate of 60°C/h, (2)maintain at T_p for 1hours, (3)cool to room temperature at cooling rates ranging from 30°C/h to quenching (approximately a cooling rate of 1000°C/h). The experimental procedure described above was illustrated in Fig. 1.

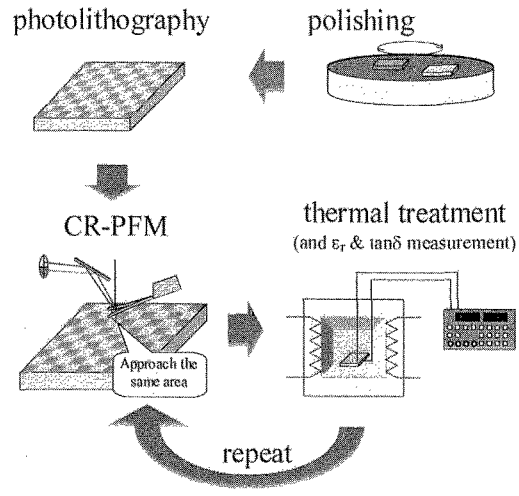

Figure 1 A schematic diagram of experimental procedure.

3. RESULTS AND DISCUSSION

Figure 2-4 shows CR-PFM images of (001) plate PMN-*x*PT single crystals obtained after 240°C thermal treatment at various cooling rates. Figure 2 shows CR-PFM images of PMN-34%PT. All images were obtained at the same area. It was found that average size of domains decreased as cooling rate increased. Note that smaller circular domains were observed in quenched sample. The diameter of these domains was less than 100nm, which agrees with the diameter of circular domains observed at temperatures above the Curie temperature in our previous work[8].

Figure 3 shows CR-PFM images of PMN-32%PT. It was found that average size of domains also decreased as cooling rate increased. Smaller circular domains were observed in quenched sample too, but the number of these domains was less than observed in quenched sample of PMN-34%PT.

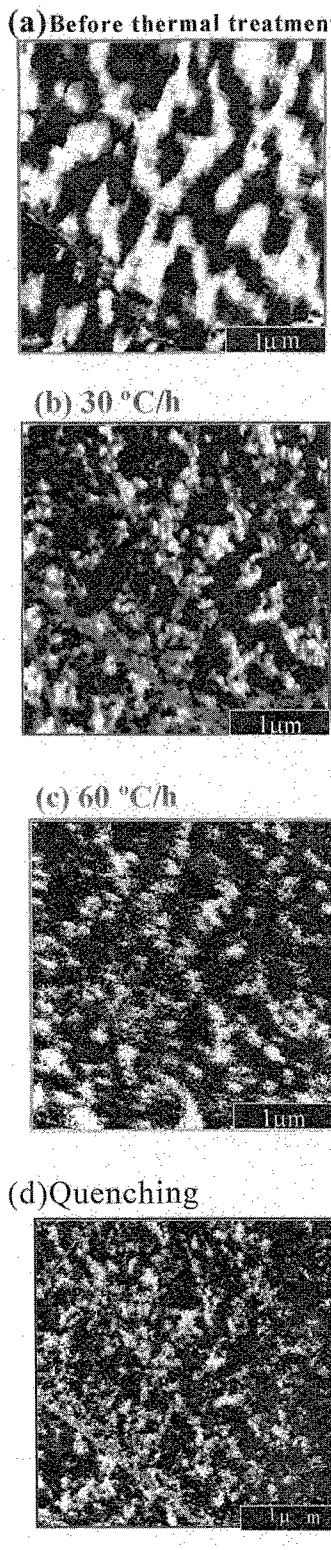

Figure 2 CR-PFM images of PMN-34%PT (3μm x 3μm). Cooling rate is (a)before thermal treatment, (b)30°C/h, (c)60°C/h and (d)quenching.

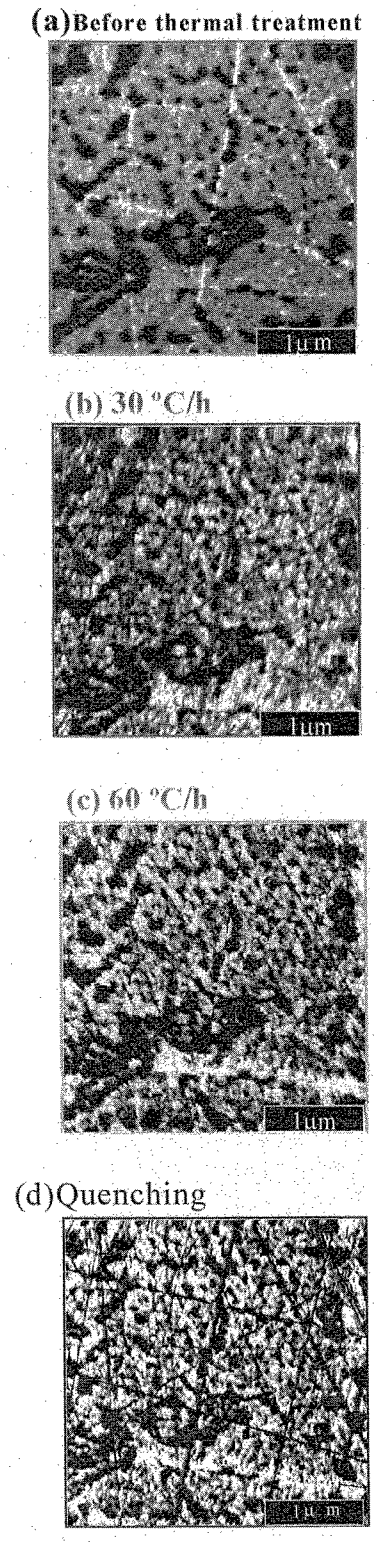

Figure 3 CR-PFM images of PMN-32%PT (3μm x 3μm). Cooling rate is (a)before thermal treatment, (b)30°C/h, (c)60°C/h and (d)quenching.

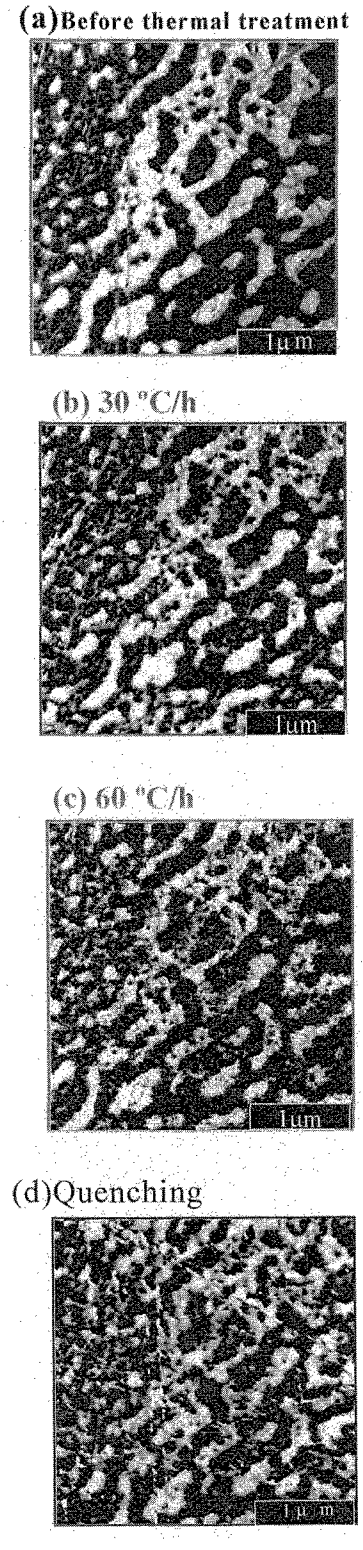

Figure 4 CR-PFM images of PMN-27%PT (3μm x 3μm). Cooling rate is (a)before thermal treatment, (b)30°C/h, (c)60°C/h and (d)quenching.

Figure 4 shows CR-PFM images of PMN-27%PT. It was clearly observed that the average size of domains was independent of the cooling rates for PMN-27%PT.

PMN-32%PT and PMN-34%PT single crystals undergoes a relaxor-ferroelectric phase transition from the Tetragonal phase to the Cubic phase. On the other hand, PMN-27%PT single crystals undergoes a relaxor-ferroelectric phase transition from the Rhombohedral phase to the Cubic phase.[10] We assume that this difference of the relaxor-ferroelectric phase transition behaviour affected the cooling-rate dependence of the domain structures of PMN-xPT.

4. CONCLUSIONS

Domain structures of PMN-27%PT, 32%PT and 34%PT single crystals were observed at room temperature after 240°C thermal treatment with various cooling rate using Contact Resonance Piezoresponse Microscope. The average domain size of PMN-34%PT and 32%PT single crystals decreased as the cooling rate increased. However, the average domain size of PMN-27%PT was independent of cooling rates. We assume that difference of relaxor-ferroelectric phase transition form affected cooling rate-dependent domain structures.

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