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Analysis of internal-stress-induced phase transition by thermal treatment

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Abstract

The dielectric behavior of PMN–*x*PT single crystals near morphotropic phase boundary has been investigated. A thermal treatment induced dielectric permittivity anomaly, a peak-shoulder below T_m, was found. Internal-stress-induced macrodomain formation has been observed in quenched PMN–*x*PT single crystals. Quenching from different temperatures, the dielectric permittivity spectra of PMN–*x*PT single crystals show different results. The origins of the phenomena are discussed. The correlations among polar regions in quenching samples on zero field-heating process are analyzed using Sherrington–Kirkpatrick relationship. The Ti^{4+} content dependence of quenching effect is also investigated in this paper. A pressure during quenching is found to influence the internal stress significantly.

Keywords: Relaxor ferroelectrics; Internal stress; Stress-induced phase transition

1. Introduction

The relaxor ferroelectric PMN–*x*PT crystals are expected to show properties of both relaxor and normal ferroelectric. They have a morphotropic phase boundary (MPB; tetragonal FE–pseudo-cubic/trigonal FE). For the PMN–*x*PT system, the morphotropic phase boundary exists only in the range from 28 to 36 mol% of PT content [1]. These mixed crystals PMN–*x*PT ($0.36 > x > 0.28$) have a high temperature paraelectric (PE) phase of cubic symmetry and go into a tetragonal FE phase as temperature decreases. In the lower temperature region, the crystals exhibit a trigonal FE phase. PMN–*x*PT single crystals are located between typical relaxor ferroelectrics and normal ones. The characteristic temperature of permittivity maximum decreases with decreasing Ti^{4+} content, whereas the width of the permittivity peak and the degree of relaxor characteristics increase with decreasing Ti^{4+} content. The relative values of Ti^{4+} content in different samples may be compared by analyzing the degrees of their relaxor characteristics.

Studied domain configurations on $\langle 0\,0\,1 \rangle$ cuts in PMN–*x*PT single crystals, Xu et al. [1] thought that unpoled crystals undergo ferroelectric phase transition spontaneously near T_m and form transitional domains consisting of ferroelectric phase in majority and paraelectric microregions in minority. The poled crystals show two special temperature T_d and T_m and are depolarized or undergo ferroelectric-to-paraelectric phase transition in the range of T_d–T_m on heating under zero field. The origins of the occurrence of a small shoulder (a second phase transition below T_m) in poled single crystal are “microdomain to macrodomain” transition [2].

Apparently, the small dielectric permittivity peak-shoulder below T_m indicates a phase transition. The origin of the phase transition is attributed to electric field. However, few attentions have been paid to internal stress. Some phenomena were explained with stress-induced phase transitions [3]. But this prediction seems no enough evidence. An understanding of the mechanism of the stress-induced phase transformation has not yet developed. In this paper, a method that can induce the small peak-shoulder not by electric fields but thermal treatment is presented. The internal-stress-induced macrodomain formation has been observed in quenched PMN–*x*PT single crystals. It is known that relaxor character is suppressed in some annealed samples from high temperatures, whereas the relaxor character is enhanced in quenched samples from high temperatures

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[4]. This phenomenon is caused from the cation order modified in annealing processes. And that has not yet been observed in PMN. In our experiment, at relative low thermal treatment temperature, the result is reversed. The relaxor character of PMN–*x*PT is suppressed in quenched samples, whereas it is enhanced in annealed samples.

2. Experimental procedure

The samples used in this study are typical relaxors, PMN–*x*PT single crystals near morphotropic phase boundary. The crystals are grown by a modified Bridgman method. Processing conditions can be found in a previous publication [5]. It is reported that segregation behavior during crystal growth results in compositional inhomogeneities of the PMN–PT single crystals even in the same boule. The difference of dielectric spectra resulting from change of PT content is distinct. Samples are cut into dimensions of 0.5 cm × 0.5 cm × 0.1 cm and electroded with silver paste. The permittivity is measured as a function of temperature between 20 and 500 °C at heating rate of 2 °C/min using a HP 4284 LCR meter. The measure frequencies used is 1, 10, 10^2 and 10^3 kHz. Only the results of 1 kHz are shown in figures for concise.

In order to induce the permittivity peak-shoulder below T_m, crystals are soaked at a high temperature for a certain period of time and subsequently put on an iron board for quenching. Another process, the specimens cool slowly in stove, is compared with quenching. The Ti^{4+} content dependence of quenching effect is studied with samples I, II and III. Their Ti^{4+} content gradually increase in turn, which may deduce from their dielectric spectrum. Various quenching temperatures have been chosen in this study.

3. Results and discussion

The dielectric spectrum of quenching sample I from 300 °C is shown in Fig. 1, and that of the slow cooling process is also shown in this figure. This graph shows that the width of dielectric permittivity peak decreases and height of the peak increases in quenching samples. A small peak-shoulder appears at T_d. The dielectric permittivity is suppressed between T_d and T_m, which is similar to the behavior under electric field heating.

It has been found that relaxor-based ferroelectrics exhibit large disparity in spatial microheterogeneity and transition temperatures [6]. Such a fluctuation is believed to result from a quenched unequal occupation of the *B* site by the competitive ions Mg^{2+}, Nb^{5+}, and Ti^{4+}. The composition is locally homogeneous on a nanoscale. This local chemistry is believed to prevent the establishment of normal long-range polar ordering at a Curie transition, instead the system establishes polar moment on the scale of local chemistry. During cooling slowly from high temperature, the system may find the most favorable local configuration and adjust itself to the global equilibrium over time [7]. Whereas, quenching state would correspond to metastable local minima since no sufficient time has been allowed for reaching equilibrium. More electric and elastic free energy may exist in a quenching sample.

The highest electromechanical properties of PMN–PT single crystal specimen at the MPB composition indicate that their sensitive lattice symmetry is easily affected by external perturbations, include electric fields and elastic stresses. There are lots of internal stresses in specimen after quenching. The stresses may play the same role as electric fields. They could induce macrodomain formation, and lead the specimen into a state that is similar to electric field-cooling process. Quenching from higher temperature, the specimen possesses small density of dipole regions and relatively strong strength of internal stresses. The interactions among dipole regions are relatively weak. During fast cooling, the dipole regions have no time to grow in size and merge each other. They freeze into a metastable state. Some characteristics in high temperatures remain. Thus, the distribution of the size of dipole regions is smaller than that of slow cooling. So the degree of dispersion of the size of dipole regions and frozen temperature is relatively small. The width of dielectric permittivity peak decreases, while its height increases. The relaxor character is suppressed. Some microdomains transform into macrodomain between T_d and T_m as the behavior under electric field heating. Consequently, the dielectric permittivity is suppressed in this temperature region.

The correlation among polar regions was analyzed using Sherrington–Kirkpatrick relationship [8]:

$$\chi' = \frac{C(1-q)}{T-\theta(1-q)} \quad (1)$$

where C is the Curie constant, θ is the Curie–Weiss temperature, and q is a local order parameter. The parameters C and θ are determined from high temperature above 350 °C (not shown) where Curie–Weiss behavior is satisfied.

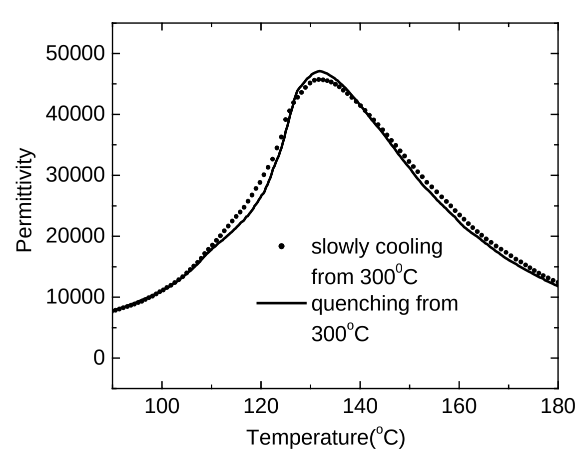

Fig. 1. Temperature dependence of permittivity of sample I.

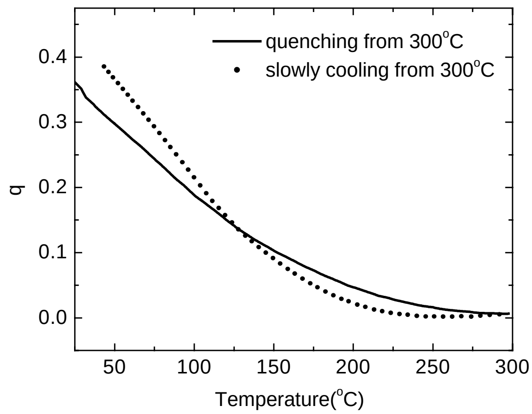

Fig. 2. The order parameter q of sample I determined from Eq. (1).

For sample I, C and θ equal to 1.711×10^5 and 186.9 °C, respectively. The correlation between polar regions may describe by the parameter q, i.e. $q \equiv \langle P_i P_j \rangle^{1/2}$, where P_i and P_j denote neighboring cluster-sized moment. The correlation may have contributions from both local dipolar and electrostrictive strain fields. The parameter q as functions of temperature for quenching sample I and the same sample cooling slowly is shown in Fig. 2. For quenching sample, q increases slowly with decreasing temperature. This indicates the development of correlation between polar regions is slow, the size and density of these polar regions vary smaller than that of slowly cooling sample. The temperature and Ti^{4+} content dependence of quenching effect is illustrated in Fig. 3. In Fig. 3a, sample I was quenched from 250 to 300 °C. In Fig. 3b, sample II with larger Ti^{4+} content was quenched from 200 to 250 °C. It is shown that the quenching effect is enhanced with Ti^{4+} content increasing. The less the Ti^{4+} content, the smaller the electrostrictive strain in the materials, consequently, the smaller scale of the “macrodomain to microdomain” transition in lower Ti^{4+} content specimen.

In Fig. 3, the dielectric permittivity below T_m increases after quenching from lower temperature and decreases after quenched from relatively high temperature. Quenching from lower temperature, the specimen possesses large density of dipole regions and relatively weak strength of internal stresses. During fast cooling, the configurations of dipole regions choose different form from that of slow cooling. The stable equilibrium in slow cooling sample cannot be reached. Thus, activation energy of dipole regions is relatively small. In a heating process, the microdomains transform to polar microregions at low temperature. The internal stress is not enough to induce microdomain-to-macrodomain transition. So the dielectric permittivity is enhanced between T_d and T_m. The height of dielectric permittivity peak is strengthened due to high density of dipole regions.

A crucial temperature seems to exist and this temperature decreases with increasing Ti^{4+} content. When quenching temperature increases above it, the internal stress would be enhanced strong enough to induce microdomains into macrodomains phase transition. In sample II, the Ti^{4+}

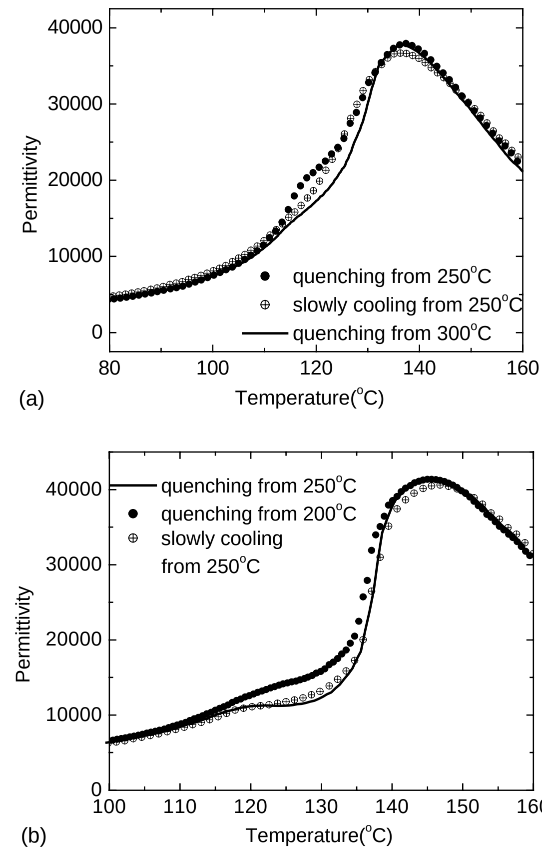

Fig. 3. Temperature dependence of permittivity of: (a) sample I and (b) sample II.

content and electrostrictive strain are larger than those of sample I. So the crucial temperature of sample II is lower than that of sample I. Fig. 3a indicates the crucial temperature of sample I is in the region between 250 and 300 °C. Fig. 3b shows the crucial temperature of sample II is in the region between 200 and 250 °C.

A uniaxial press pressure was put on the sample along orientation $\langle 0\,0\,1 \rangle$ during quenching. Fig. 4 shows the result

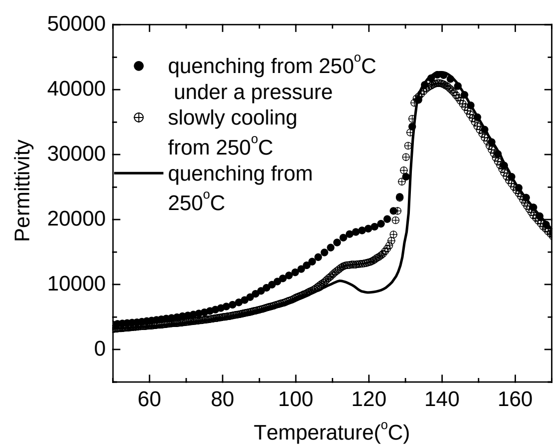

Fig. 4. Temperature dependence of permittivity of sample III.

of sample III quenching under a pressure about 10^6 N/m^2. The result of sample III quenching from the same temperature under free condition is also shown in the same figure for comparison. The dielectric permittivity below T_m becomes enhancing, whereas it is suppressed in free condition quenching sample. In quenching process, pressure restrains growing and merging of dipolar microdomains because the dipolar regions elongate along $\langle 0\,0\,1\rangle$. This means the average size of microdomain becomes smaller. When the external press is taken out after quenching, some internal stress releases and the mechanical conditions of assembling configurations of microdomains change. The internal stress reduces and is not strong enough to transform the microdomains into macrodomains. Some assembling configurations of microdomains become unstable due to the changing of mechanical conditions. These unstable and small microdomains may easily be agitated at low temperature. So the dielectric permittivity enhances below T_m distinctly.

$\langle 1\,1\,1\rangle$ cut specimens were studied for comparison. The quenching effect seems not as distinct as that of $\langle 0\,0\,1\rangle$ cuts (not shown here).

4. Conclusions

By studying with PMN–*x*PT single crystals, we have found a method that can induce dielectric permittivity peak-shoulder by thermal treatment. Internal-stress-induced macrodomain formation has been observed in quenched PMN–*x*PT single crystals. Quenching from higher temperature, the relaxor character is suppressed and the correlation among polar regions increases more slowly with decreasing temperature. Under zero-field heating, strong internal stresses induce a second phase transition at $T_d < T_m$, which is similar to electric-field-induced transition. The quenching effect is enhanced with Ti^{4+} content increasing. Quenching from lower temperature, the specimen possesses large density of dipole regions and relatively weak strength of internal stresses. So the dielectric permittivity is enhanced between T_d and T_m. A pressure during quenching may reduce internal stress and frustrate the macrodomains formation.

Acknowledgements

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