

POLAR PHASE INSTABILITY IN THE PARAELECTRIC REGION OF PMN-PT RELAXOR FERROELECTRIC CRYSTALS

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The phase instabilities in the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{PbTiO}_3$ (PMN- x PT) relaxor ferroelectric single crystals with orientations [110] and [111] were investigated as a function of temperature and dc -bias voltage. The composition of crystals was in the range of morphotropic phase boundary (MPB) region with $x \sim 0.33$. Two structural phase transition anomalies were observed in the temperature dependent capacitance of the two crystals related to paraelectric cubic to ferroelectric tetragonal and then to rhombohedral/monoclinic symmetry changes. A remarkable shift in the cubic-tetragonal phase transition boundary towards the higher temperature side was observed with increasing bias voltage. The origin of this dc -bias assisted unusual instability, apparently inside the cubic phase, was associated to the presence and complex dynamics of polar nanoregions (PNRs).

Keywords: Phase instability, Relaxor ferroelectrics, Polar nanoregions, Single crystal

1. Introduction

Single crystals of the solid solutions of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) a prototypical relaxor ferroelectric (RFE), with PbTiO_3 (PT), a pure ferroelectric material, denoted by general formula $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{PbTiO}_3$ (PMN- x PT), have been investigated extensively due to their highly attractive piezoelectric and electromechanical properties [1]. Of special interest, are the compositions near the morphotropic phase boundary (MPB), where the rhombohedral $R(3m)$ and tetragonal $T(4mm)$ phases are separated by a small region exhibiting very high piezoelectric constant ($d_{33} > 2500 \text{ pC.N}^{-1}$), electromechanical coupling coefficient ($k_{33} > 94\%$), and high strain values ($\sim 1.7\%$) and exhibiting an unusually broad frequency dependent dielectric behavior [1, 2]. Compositions near MPB (with monoclinic and/or orthorhombic symmetries) find extremely attractive applications in making large displacement actuators, high sensitivity medical ultrasonic imaging transducers.

Phenomenologically, the nanoscale local ferroelectric active polar entities the so-called polar nanoregions (PNRs) that appear at the Burns temperature (T_B) [3], well above the expected Curie temperature, are crucial to almost all the theoretical models proposed so far to the understanding of the physical mechanism responsible for the extraordinary dynamical properties of RFEs. Formation and thermal evolution of PNRs clearly differentiates RFE state from normal ferroelectric state even in their high temperature paraelectric phase for $T < T_B$. It was demonstrated [4] that interaction of off-centered Pb^{2+} and the soft

phonons is responsible for the appearance of PNRs at much high temperatures, $T \sim T_B$, however; it is still far from clear that what exactly is the origin of PNRs and does T_B exists in reality [5].

In the presence of external bias voltages electromechanical response of the crystal can be altered through symmetry and domain structure modifications [6]. Due to polarization rotation possibility in PMN- x PT crystals around their MPB composition range [7], these crystals are very important from application point view. The field induced phase transitions in relaxor materials have been much studied [8-11] to clarify the relaxor properties. In this study, the investigation of dc -bias influence on the phase transition anomalies in the unpoled [110] and [111] MPB PMN- x PT single crystals is briefly reported.

2. Experimental

$(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{PbTiO}_3$ (PMN- x PT) single crystals of MPB composition ($x \sim 0.33$) having [110] and [111]-orientations were used for present experiments and were grown by the Bridgeman technique [12] and kindly provided by Professor Yao Xi of Xi'an Jiaotong University, China. The crystals were in unpoled state and for capacitance measurements Dotite D-550 silver paste was applied on the larger face of the crystals ($\sim 0.3 \text{ mm}$ thick) and fired at 600°C for 30 minutes to form good electrodes. For temperature variations, the crystal was placed inside a cryostat cell THMSE 600 (M/S Linkam, UK) and frequency dependent capacitance was measured by Agilent 4294A impedance analyzer.

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3. Results and Discussion

In Figure 1 temperature dependence of capacitance of [110]-oriented PMN-*x*PT crystal is plotted without any bias voltage. In this crystal, structural phase transition anomalies from the paraelectric cubic (C) to ferroelectric tetragonal (T) and then to rhombohedral (R) or monoclinic (M) (*Pm/Cm*) symmetries (*C*→*T*→*R*) were clearly observed with a small hysteresis at *C*→*T* transition temperature. As the lower phase transition is actually from tetragonal to rhombohedral symmetry through monoclinic phases by polarization rotation process so it has been denoted by *T*→*R*. A similar phase transition sequence and hysteresis anomalies at *C*→*T* transition temperature were observed for [111] crystal (inset Figure 2). These observations are in good agreement with our previous results for [001] PMN-*x*PT crystal from a different source [13]. The phase transition anomalies in the presence of *dc*-bias voltages for the two crystals are subsequently shown in Figures 2 and 3.

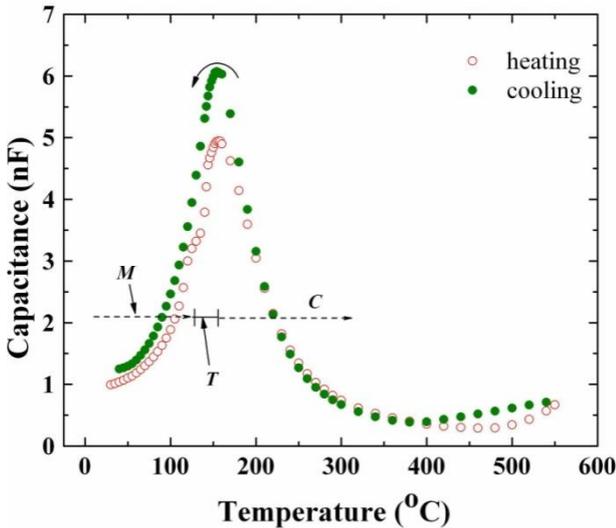


Figure 1. Temperature dependence of capacitance of a PMN-*x*PT [110] crystal in heating and cooling cycles, measured at 1 kHz and zero *dc*-bias.

Both the crystals exhibit two structural phase transition instabilities, cubic to tetragonal and tetragonal to rhombohedral (*C*→*T*→*R*) with and without bias voltage. In [110] crystal an additional anomaly was observed at *T*~90 °C at relatively higher biased voltages (Figure 3) which may be attributed to the phase transition from rhombohedral to orthorhombic symmetry. The polarization vector is along [110] in orthorhombic (O) phase and enhanced *dc*-field facilitates the alignment of polarization vector along the direction of applied field and the additional induced anomaly is observed. Another probable scenario is the rotation of spontaneous polarization (P_s) vector because

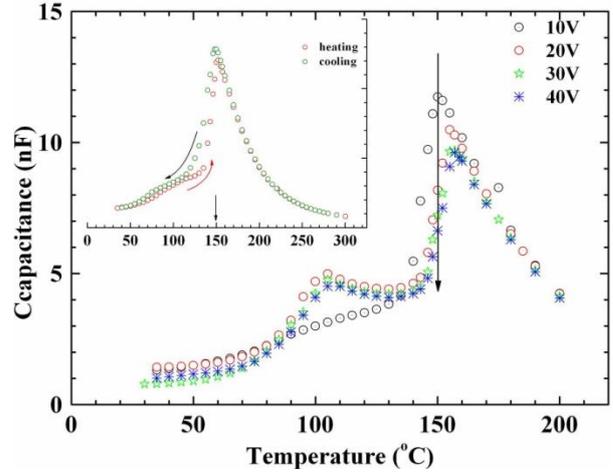


Figure 2. Capacitance-temperature plot of PMN-*x*PT [111] crystal under *dc*-bias measured at 1 kHz. Inset shows heating-cooling curves with no *dc*-bias. Arrow is just a guide to see shift in phase transition point.

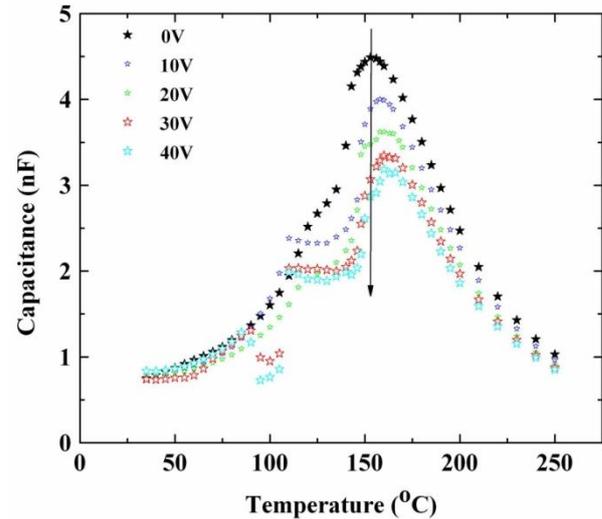


Figure 3. Capacitance versus temperature plot of PMN-*x*PT [110] crystal at some selected bias voltages at a frequency of 1 kHz. Arrow is just a guide to see shift in phase transition point.

for [110] crystal P_s vector is along [111] direction (*Cm*) while biasing is along [110] direction (*Pm*) that may facilitate movement of P_s vector towards the biased direction depending on amplitude of the bias voltage. This observation indirectly suggests that various monoclinic phases, M_A , M_B , and M_C , are present inside the MBP region between *R* and *T* phases, where the polarization vector may be rotated in plane easily [8].

It is important to see that *dc*-bias has a substantial effect on the both structural phase transition instabilities of both crystals as is clearly demonstrated in presented data (Figures 2 and 3). With increasing *dc*-bias there is a decrease in magnitude of capacitance at cubic-tetragonal

phase transition temperature (T_{C-T}) with a marked shift in T_{C-T} phase transition boundary towards the higher temperature side. This easy shifting of $C \rightarrow T$ phase transition boundary in presence of a small bias voltage towards the paraelectric phase region depicts that PNRs are indeed present in the cubic phase facilitating field induced ferroelectric phase transition at higher temperatures. The increased bias voltage tries to force the crystal towards the mono domain state. This would result a decrease in number of domains in the crystal and hence capacitance will be lowered markedly as is observed for two crystals (Figures 2&3). As to the role of PNRs it is well established that they appear at $T \leq T_B$ and grow in size and density with further decreasing temperature until they permeate the paraelectric lattice and a transformation from paraelectric to ferroelectric state occurs or a typical relaxor behavior is observed. Our results are also indicative of the presence of an inherent structural instability inside the cubic paraelectric phase of relaxors assisted by the PNRs. The boundary of this instability is expected to strictly depend on the applied bias and critical density of the PNRs that may respond to external field perturbation. High resolution x -ray diffraction studies on PMN-0.32PT [001] crystal [14] also showed the presence of a similar external field induced phase instability inside the cubic region. It is therefore anticipated that this may be a common feature of relaxor ferroelectrics at least in the MPB composition range. Further work is in progress to confirm this statement for compositions above and below the MPB range.

4. Summary

In summary, capacitance measurements of the MPB PMN- x PT single crystals ($x \sim 0.33$) with [110] and [111] orientations were carried out as a function of temperature and difference dc -bias voltages to examine their structural phase transition behavior. These investigations clearly demonstrated marked shifts in the cubic to tetragonal and then to rhombohedral phase transition boundaries towards the high temperature side with increasing bias voltages. This instability in the phase transition boundary was attributed to the

temperature dependent growth and dynamics of PNRs in the paraelectric cubic phase. The additional low temperature anomaly observed in [110] crystal was from rhombohedral to orthorhombic phase induced by the applied dc -bias and temperature variations.

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References

- [1] S.-E. Park and T.R. Shrout, *J. Appl. Phys.* **82** (1997) 1804.
- [2] J. Kuwata, K. Uchino and S. Nomura, *Jpn. J. Appl. Phys.* **21** (1982) 1298.
- [3] G. Burns and B.A. Scott, *Solid State Commun.* **13** (1973) 417.
- [4] W. Dmowski, S.B. Vakhrushev, I.-K. Jeong, M.P. Hehlen, F. Trouw and T. Egami, *Phys. Rev. Lett.* **100** (2008) 137602.
- [5] V. Bobnar and Z. Kutnjak, *Ferroelectrics* **415** (2011) 14.
- [6] D. Viehland, J.F. Li and A. Amin, *J. Appl. Phys.* **92** (2002) 3985.
- [7] G. Shabbir, S. Kojima and C. Feng, *J. Appl. Phys.* **100** (2006) 064107.
- [8] D. Lin, Z. Li, S. Zhang, Z. Xu and X. Yao, *J. Appl. Phys.* **108** (2010) 034112.
- [9] S.G. Lushnikov, J.-H. Ko and S. Kojima, *Appl. Phys. Lett.* **84** (2004) 4798.
- [10] E. Dulkan, M. Roth, B. Dkhil and J.M. Kiat, *J. Appl. Phys.* **98** (2005) 023520.
- [11] M. Iwata, K. Tanaka, M. Maeda and Y. Ishibashi, *Ferroelectrics* **440** (2012) 67.
- [12] Z.R. Li, Z.Z. Xi, Z. Xu and X. Yao, *J. Mater. Sci. Lett.* **21** (2002) 1325.
- [13] G. Shabbir, C. Feng and S. Kojima, *Trans. Mat. Res. Soc. Jpn.* **29** (2004) 1131.
- [14] H. Cao, C. Stock, G. Xu, P.M. Gehring, J. Li and D. Viehland, *Phys. Rev. B* **78** (2008) 104103.