

# High temperature dc field poling effects on the structural phase transformations of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$ single crystal with morphotropic phase boundary composition

Ghulam Shabbir<sup>a)</sup>

*Physics Research Division, PINSTECH, Post Office Nilore, Islamabad 44000, Pakistan*

Seiji Kojima<sup>b)</sup>

*Ultra-Broadband Spectroscopy Laboratory, Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*

Chude Feng

*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China*

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The complex dielectric permittivity of the morphotropic phase boundary [001]-oriented PMN- $x\%$ PT single crystal with  $x=33\%$ , grown by the modified Bridgman technique, has been investigated as a function of both temperature and dc poling field. Structural phase transformation sequence is discussed in the light of polarization rotation process. A remarkable shift in the rhombohedral-tetragonal phase transition temperature is observed with changing of the poling field. It is found that high temperature poled state remained stable even after removal of the field. © 2006 American Institute of Physics. [DOI: [10.1063/1.2337103](https://doi.org/10.1063/1.2337103)]

## I. INTRODUCTION

Relaxors are very interesting materials due to their fascinating characteristics: (i) diffuse phase transition (DPT), (ii) a broad maximum in the real part of dielectric permittivity,  $\epsilon'(\omega, T)$  with a strong relaxation dispersion around and below the dielectric maximum temperature ( $T_m$ ), and (iii) absence of macroscopic polarization and anisotropy at temperatures far below  $T_m$ . It has been shown that in relaxors, the frequency  $\omega$  of the probing ac signal and  $T_m$  are related via the Vögel-Fulcher relation.<sup>1,2</sup> Relaxors also resemble glassy materials, exhibiting glassy characteristics, e.g., aging, memory, and rejuvenation.<sup>3</sup> From the phenomenological point of view it has been established now that relaxor nature is due to fluctuating polar microregions (PMRs) appearing at  $T > T_C$ .<sup>4</sup> While understanding the origin of PMRs is crucial to relaxor phenomena the industrial demand has continuously promoted the search of compositions with attractive properties.  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) is the prototypical relaxor, which exhibits large and weakly temperature dependent dielectric permittivity within a broad so-called Curie range of temperatures around and below room temperature.

The giant piezoelectric response of the [001] poled single crystals of  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$  (PZN- $x\%$ PT) and  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$  (PMN- $x\%$ PT), complex perovskite-type ferroelectrics, is observed near their morphotropic phase boundary (MPB), separating the tetragonal  $P4mm$  and the rhombohedral  $R3m$  polar phases.<sup>5–7</sup> For example, MPB for PMN- $x\%$ PT [001]-oriented single crystal lies at  $x \approx 33\%$ . The electromechanical coupling factor  $k_{33}$  is near 94% for PMN-33%PT single

crystal.<sup>8</sup> The piezoelectric coefficient  $d_{33}$  is about 2820 and 2900 pC/N for PMN-33%PT and PZN-8%PT, respectively. The ultrahigh electromechanical properties are observed in [001] poled crystals in  $R3m$  phase in which the spontaneous polarization ( $\mathbf{P}_s$ ) lies along [111]. Moreover, many recent investigations have been focused on understanding the coexistence of various monoclinic phases ( $M_C/M_A$ ) and their field induced transformational sequence near MPB in PMN- $x\%$ PT and PZN- $x\%$ PT crystals.<sup>9–12</sup> For PMN- $x\%$ PT single crystals the monoclinic phase boundary lies between  $x \approx 31\%$  and 37% with  $R$  and a new  $X$  phase (of an average cubic symmetry) for  $x \leq 31\%$  with different surface and bulk structure.<sup>13</sup>

It has been shown that application of an external bias can lead to symmetry changes and the domain structure can be engineered by polarization switching/rotations, modifying electromechanical response of the crystal.<sup>14</sup> As a result many recent investigations have been concentrated on field-induced changes in PMN- $x\%$ PT and PMN crystals near the MPB composition.<sup>12,15–19</sup> Due to giant piezoelectric response, PMN- $x\%$ PT MPB single crystals poled along [001] or [110] of the cubic directions, different from  $\mathbf{P}_s$  direction, are extremely attractive for applications in large displacement actuators, high sensitivity medical ultrasonic imaging transducers, and many other devices. Here we report dc field poling effects on the dielectric response of [001]-oriented PMN- $x\%$ PT MPB single crystal.

## II. EXPERIMENTAL PROCEDURE

PMN- $x\%$ PT MPB single crystal with  $x \approx 33\%$  was grown by the modified Bridgman technique. A crystal of an approximate size of  $5 \times 5 \times 1 \text{ mm}^3$  with large face normal to [001] was polished and silver paste electrodes were coated

<sup>a)</sup>Electronic mail: gshabbir@pinstech.org.pk

<sup>b)</sup>Electronic mail: kojima@bk.tsukuba.ac.jp

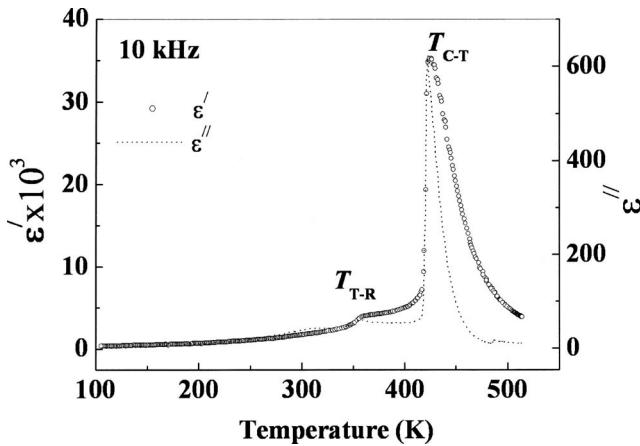


FIG. 1. Real  $\epsilon'(\omega, T)$  and imaginary  $\epsilon''(\omega, T)$  parts of the complex permittivity along [001] axis of the unpoled PMN- $x\%$ PT MPB single crystal measured in a broad temperature range.

on two  $5 \times 5 \text{ mm}^2$  faces. The crystal was then annealed at  $\sim 600 \text{ K}$  in air for 1 h to ensure good Ohmic contact. Complex dielectric permittivity of the crystal was measured along [001] direction by using a Solartron impedance analyzer (SI 1260) at a heating/cooling rate of  $\pm 1 \text{ K/min}$ . A closed cycle helium refrigerator (RMC LTS-22) was used for low temperature experiments whereas a homemade furnace was employed for measurements above room temperature. The amplitude of probing ac signal was 1 V for all measurements. For poling experiments the crystal was placed in silicon oil at a temperature of  $\sim 450 \text{ K}$  (above  $T_C$ ) and then a dc field in the range of 0–500 kV/m was applied for  $\sim 20 \text{ min}$  along the pseudocubic [001] direction. The crystal was then slowly cooled down to room temperature with applied field [Field cooling (FC)] and measurements were done under zero-field heating (ZFH) conditions. Before each measurement, the crystal was thermally depoled at a temperature of  $\sim 500 \text{ K}$ .

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the real,  $\epsilon'(\omega, T)$ , and imaginary,  $\epsilon''(\omega, T)$ , parts of the complex permittivity,  $\epsilon^*(\omega, T) = \epsilon'(\omega, T) + i\epsilon''(\omega, T)$ , of the unpoled [001]-oriented MPB PMN- $x\%$ PT single crystal measured at a frequency of 10 kHz in a broad temperature range. In Fig. 2 we plot temperature and frequency dependence of  $\epsilon'(\omega, T)$  and loss factor,  $\tan(\delta) = \epsilon''(\omega, T)/\epsilon'(\omega, T)$ , for the same crystal measured along [001] direction. These data sets were obtained during heating cycle. In the investigated temperature range the complex permittivity showed two clear phase transition anomalies at temperatures of  $\sim 424$  and  $\sim 355 \text{ K}$ . These temperatures correspond to (i) cubic-tetragonal ( $T_{C-T}$ ) and (ii) tetragonal-rhombohedral ( $T_{T-R}$ ) structural phase transformations, respectively, as expected from PMN- $x\%$ PT MPB single crystal's phase diagram.<sup>13</sup> MPB is actually an intermediate monoclinic/orthorhombic phase region between the tetragonal and rhombohedral phases. Because its symmetry  $m$  is related to both  $4mm$  and  $3m$  phases (being their subgroup) and macroscopically averages to  $4mm$ , we take lower phase transition anomaly as  $T_{T-R}$  throughout the text. The relatively sharp phase transition anomaly with symmetry change from

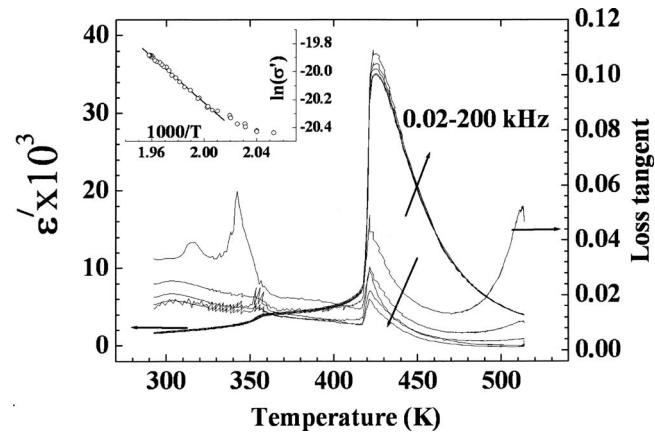


FIG. 2. Temperature and frequency dependence of the dielectric constant ( $\epsilon'$ ) and loss tangent of the unpoled [001]-oriented MPB PMN- $x\%$ PT crystal. Inset shows Arrhenius plot of ac conductivity.

$m3m$  to  $4mm$ , exhibiting characteristics similar to those of normal ferroelectrics, is weakly frequency dependent only in the sense that  $\epsilon'(\omega, T)$  peak shows minor decrease in its magnitude with frequency. Thermodynamically, both the transition anomalies are of first order nature due to the presence of a clear thermal hysteresis.<sup>20</sup> The dielectric loss with increasing temperature above  $T_{C-T}$  shows a significant rising trend beyond  $\sim 475 \text{ K}$  with decreasing frequency, as can be observed from Fig. 2. This low frequency dielectric dispersion at higher temperature may be associated with the thermally activated complex ac electrical conductivity,  $\sigma^*(\omega, T)$ , superimposed on the dielectric loss factor in the respective temperature range ( $\sim 475$ – $512 \text{ K}$ ).

In disordered solids, complex ac conductivity is closely related to the frequency dependent complex permittivity,  $\epsilon^*(\omega, T)$ , and can be expressed as

$$\sigma^*(\omega, T) = \sigma'(\omega, T) - i\sigma''(\omega, T) = i\omega\epsilon_0[\epsilon^*(\omega, T) - 1],$$

where  $\sigma'(\omega, T)$ ,  $\sigma''(\omega, T)$ , and  $\epsilon_0$ , are the real and imaginary parts of the complex ac conductivity, and permittivity of the free space ( $8.85 \times 10^{-12} \text{ F/m}$ ), respectively.

By plotting the  $\ln[\sigma'(\omega, T)]$  vs  $1000/T$  (Fig. 2 inset), it could be modeled by the Arrhenius law:

$$\sigma'(\omega, T) = \sigma_0 \exp(-E_a/kT),$$

where  $\sigma_0$  is the preexponential coefficient,  $k$  is the Boltzmann factor,  $E_a$  is the activation energy, and  $T$  is the temperature. Arrhenius fit of the data measured at the lowest frequency of 20 Hz in the temperature range from 475 to 512 K gave activation energy  $E_a = 0.704 \text{ eV}$  and pre-exponential coefficient  $\sigma_0 = 0.021 \text{ S/cm}$ . These results are in good agreement with those of [001] PMN-42%PT ( $E_a = 0.79 \text{ eV}$ ) single crystal.<sup>21</sup> The observed  $E_a$  is lower than that for diffusion of oxygen ions (0.9–1.1 eV) but is comparable to that observed for SrTiO<sub>3</sub> perovskite single crystal<sup>22</sup> (0.6–1.0 eV) and provides a clear evidence that the thermally activated oxygen vacancy transport in the bulk can be accounted for by the observed low frequency dispersion in the loss factor. It should be remembered that  $E_a$  in other words is related to the relaxation time which is affected by hopping of vacancy related defects and/or structural disorder.

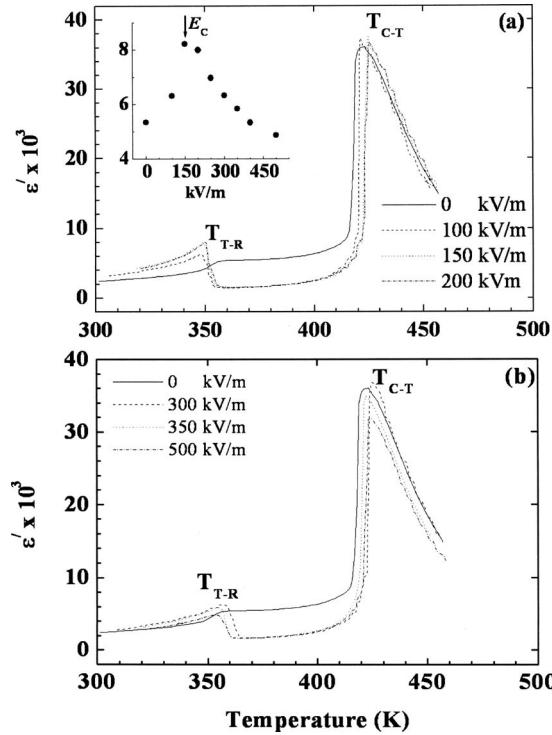


FIG. 3. Temperature dependence of dielectric constant of MPB PMN- $x\%$ PT [001]-oriented single crystal measured at 10 kHz and poled at different dc fields. These data were measured in heating run. Inset in (a) shows the variation of  $\epsilon'(\omega, T)$  maximum vs  $E_p$ , around  $T_{T-R}$  phase boundary.

Above  $T_{C-T}$ , temperature dependent fluctuations/flippings of the PMRs may also be another source of enhanced  $\sigma'(\omega, T)$ .

Figure 3 shows the real part of the complex dielectric permittivity of MPB PMN- $x\%$ PT [001]-oriented single crystal as a function of temperature at some selected poling dc field strengths (measured under FC-ZFH conditions). The data for low and high poling fields ( $E_p$ ) have been plotted separately for the sake of clarity. It can be seen from Fig. 3(a) that when  $E_p$  is increased from 0 to 100 kV/m,  $T_{T-R}$  phase transition boundary slightly shifts towards lower temperature and the anomaly becomes sharp, and  $\epsilon'(\omega, T)$  is increased markedly. With further increasing  $E_p$  up to 250 kV/m,  $\epsilon'(\omega, T)$  enhances further (with maximum at  $E_p \sim E_c$ ) and  $T_{T-R}$  peak becomes sharper, while  $T_{T-R}$  slightly moves to the higher temperature side. These changes in  $T_{T-R}$  and  $\epsilon'(\omega, T)$  are similar to those observed for [001]-oriented PMN-33%PT crystal, taken under bias field heating conditions.<sup>23</sup> At  $E_p = 300$  kV/m [Fig. 3(b)],  $\epsilon'(\omega, T)$  decreases slightly and  $T_{T-R}$  significantly shifts towards the higher temperature side, however,  $\epsilon'(\omega, T)$  and  $T_{T-R}$  show decreasing trend with further increasing  $E_p$  strength. As to the  $T_{C-T}$  phase transition temperature, it sharpens at first and exhibits a shift to higher temperature with increase in  $E_p$  from 0 to 300 kV/m, but the magnitudes of  $\epsilon'(\omega, T)$  and  $T_{C-T}$  boundaries both decrease for further increase in  $E_p$ . Another interesting observation is that the magnitude of  $\epsilon'(\omega, T)$  is lowered significantly in the poled state in the tetragonal phase regime, even for very low  $E_p$ , in the investigated poling field range. These variations in  $T_{T-R}$  boundary and  $\epsilon'(\omega, T)$  in 4mm symmetry are similar to several other

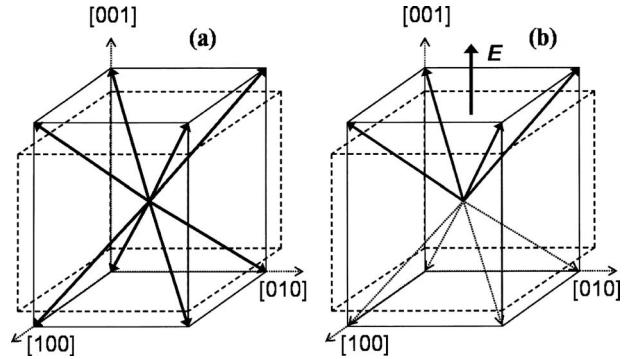


FIG. 4. Schematic view of the polarization behavior, (a) unpoled state and (b) under poling field, along the [001] cube direction, in the rhombohedral phase.

recent investigations (e.g., Refs. 16, 17, and 19. Figure 3 also demonstrates that high temperature poling field effects prevail even after removal of the field until the crystal is heated well above  $T_{C-T}$ . This observation resembles x-ray diffraction studies on the rhombohedral Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)TiO<sub>3</sub> PZT,<sup>24</sup> and high-resolution synchrotron experiments on PMN- $x\%$ PT,<sup>12</sup> where a monoclinic (*m*) phase is induced by poling at high temperatures and remains stable even after the field is removed.

In order to understand the nature of phase transitions in relaxors and/or ferroelectric (FE) materials, importance of the dynamics of the so-called PMRs with randomly oriented local polarization, intrinsic to the relaxor phenomena, cannot be over-ruled. It seems appropriate to state that the behavior of relaxors is governed by the persistence of PMRs appearing at/above the Burns temperature ( $T_B$ ) and existing up to very low temperatures. With decreasing temperature the PMRs grow in size and/or density and ultimately percolate the whole crystal, and a sharp cooperative FE phase transformation occurs at  $T_{C-T}$ . It was noticed that the weak  $E_p$  (<100 kV/m) does not produce any detectable change in randomly oriented PMRs, in agreement with several other reports on PMN- $x\%$ PT crystals (e.g., Refs. 23 and 25).

The observed phase transformation sequence of the poled crystal may be explained as follows. In the 3*m* unpoled symmetry state ( $T < T_{T-R}$ ),  $P_s$  has eight possible orientations [Fig. 4(a)], because  $P_s \parallel [111]$  in the virgin state. For  $E_p \parallel [001]$ , only four ([111], [1̄1̄1], [11̄1], and [1̄11]) out of eight polarization vectors survive with equivalent probability to be oriented along [001] [Fig. 4(b)]. The poling field can cause stretching and/or shearing of the domains. This will result in a higher dielectric/piezoelectric constant. In the 4*mm* symmetry range, i.e.,  $T_{T-R} \leq T \leq T_{C-T}$ , only stretching of the [001] domains can occur by poling along [001] because already  $P_s \parallel [001]$ . In the absence of shearing (no induced strain) in 4*mm* symmetry the effective piezoelectric coefficient (*d*) becomes small. In other words  $\epsilon'(\omega, T)$  will decrease because  $d \propto \epsilon$ . On the basis of the above stated polarization response, it seems appropriate to argue that the single domain state can be attained at relatively lower  $E_p$  in the tetragonal symmetry as compared in the rhombohedral symmetry. This is the most probable reason that  $\epsilon'(\omega, T)$  attains its stable value in the tetragonal phase at lower poling

field ( $\sim 100$  kV/m) as compared in the rhombohedral phase, where it is still decreasing even at 500 kV/m.  $E_p > E_c$ , may cause polarization vector to tilt and align domains in the monoclinic symmetry. But macroscopically, monoclinic symmetry averages to  $4mm$  phase with similar micro- and macrosymmetries. Fluctuations in  $T_{T-R}$  boundary with changing of the poling field ( $E_p > 300$  kV/m) is an evidence of polarization rotation and coexistence of different symmetries. Moreover, it shows that increasing external poling field can drive the system into a global  $4mm$  symmetry that is stabilized finally at higher poling fields and not the metastable monoclinic phase.

The behavior of  $T_{C-T}$  (of the poled crystal) elucidates that the external poling field can stabilize the FE phase at higher temperature by forcing the PMRs to align along [001] at a relatively higher temperature that results in higher  $T_{C-T}$ . But shifting back of  $T_{C-T}$  boundary to the unpoled transition point for  $E_p > 300$  kV/m cannot be explained at present. It is worth mentioning here that under ZFC (after FH) conditions, both the  $T_{C-T}$  and  $T_{T-R}$  were suppressed with increasing  $E_p$  with overall lowering  $\epsilon'(\omega, T)$  throughout the  $E_p$  and temperature range, in good agreement with the FC measurements.<sup>23</sup> Shift in  $T_{C-T}$  with  $E_p$  is a signature of the coexistence of cubic and tetragonal phases, that seems to be a common feature of crystals with MPB composition as have been shown by recent (x)-ray diffraction studies of [001]-oriented PMN-32%PT crystal under field cooled conditions.<sup>16</sup>

#### IV. SUMMARY AND CONCLUSION

The complex dielectric permittivity studies of the [001]-oriented PMN- $x\%$ PT single crystal with the MPB composition were carried out as a function of temperature and poling field along [001]. The dielectric permittivity of the unpoled crystal exhibited two phase transition anomalies at  $T_{T-R} \sim 355$  K and  $T_{C-T} \sim 424$  K. No other anomaly could be observed down to  $\sim 110$  K. The low frequency ac electrical conductivity followed the Arrhenius-type behavior with an activation energy of  $E_a = 0.704$  eV, in good agreement with reported value for PMN-42%PT and SrTiO<sub>3</sub> perovskite single crystals, and was associated with the oxygen vacancy transport in the bulk and defect related mechanism. The permittivity measurements on previously poled (along [001]) crystal showed considerable fluctuations in the  $T_{C-T}$  phase boundary associated with the coexistence of two phases. The poling field dependence of  $T_{T-R}$  was attributed to the field assisted polarization rotation and coexistence of  $3m$  and  $4mm$  symmetries with a possible  $m$  phase. The increasing

poling field may drive the system to tetragonal phase. A more detailed study of rotating polarization behavior under unpoled, poled, and with applied field conditions in a broad temperature range is planned in the future by using Brillouin scattering technique.

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