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Pseudolinearity in the inverse dielectric susceptibility of poled Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ – PbTiO$_3$ crystals

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For poled oriented 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ – 0.33PbTiO$_3$ single crystals, dielectric measurements have revealed pseudolinear (Curie–Weiss) behavior for temperatures below a phase transition; however, significant deviations are observed in the paraelectric phase. The value of the Curie constant (C) in the poled polydomain condition was found to be significantly larger than that in a poled monodomain condition. It is believed that polarization heterogeneity exists within the poled polydomain condition. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1483111]

In Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ – PbTiO$_3$ (P–PT) and PMN–PT single crystals, an electromechanical coupling factor of greater than 0.9 has been reported in the rhombohedral ferroelectric (FE$_r$) phase near the morphotropic phase boundary (MPB) for specimens poled along ⟨001⟩.[1–3] Similar enhancements in the electromechanical properties were also reported[4] when crystals were poled at finite angles with respect to the ⟨001⟩, although the coupling factors of these finite miss-oriented crystals were lower (~0.8).[5–7]

Investigations have demonstrated the presence of monoclinic (FE$_m$) and orthorhombic (FE$_o$) ferroelectric states inbetween the FE$_r$ and tetragonal ferroelectric (FE$_t$) phases.[5–7] The result opens an interesting possibility that intermediate states may be responsible for the high electromechanical performance. First principles calculations have indicated that the transformation under electric field between FE$_r$ and FE$_t$ proceeds by a rotation of the polarization between ⟨111⟩ and ⟨001⟩.[8,9] Phenomenological studies have indicated that intermediate FE$_m$ states are only stabilized in the presence of a fourth order self-alloying (random field or rf) term.[10]

Kleeman has previously applied rf theory to PMN–PT relaxor ferroelectrics in the poled condition below the freezing temperature.[11] rf theory has recently been applied to the case of poled MPB PMN–PT.[12,13] Recent dielectric investigations[14] of MPB PMN–PT piezocrystals have revealed the presence of a relaxor ferroelectric state in the thermally depoled condition, and a normal FE transformation in the poled condition. Anisotropy and piezoelectricity are only metastably locked in under applied field.

This investigation reports on phase transitional characteristics in 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ – 0.33PbTiO$_3$ single crystals. The results reveal that the inverse dielectric susceptibility (K^{-1}) obeys Curie–Weiss behavior in the temperature region between the FE$_r$ and FE$_t$ phases, whereas significant deviations are observed for temperatures greater than that of the dielectric maximum T_{max}. The results indicate the importance of polarization heterogeneity within the anisotropic poled condition.

Crystals of 0.67PMN–0.33PT were grown by the Bridgmann method.[15] Various crystals were oriented along the ⟨001⟩, ⟨110⟩, and ⟨111⟩ directions. Typical specimen dimensions were $2\times2\times2$ mm^3. Platinum electrodes were deposited by sputtering. Crystals were poled at room temperature, with monodomain conditions achieved in ⟨111⟩ oriented crystals. Dielectric characterization was carried out using a temperature controlled HP4284A *LCR* meter at 1 kHz.

Previous investigations have shown that the stable phase at 25 °C for 0.67PMN–0.33PT is FE$_r$.[16] The phase transition sequence with increasing temperature is FE$_r$ to FE$_o$ to FE$_t$. In the FE$_r$ state, only the ⟨111⟩ orientation is fully poled and in a monodomain condition. ⟨001⟩ and ⟨111⟩ poled oriented crystals have been shown to be polydomain.[16] In the poled condition, along the ⟨111⟩, the dielectric constant K is $\sim10^3$, whereas along the ⟨001⟩ or ⟨110⟩ it is dramatically higher $\sim10^4$. Also, It has been shown to be possible to trap a metastable FE$_o$ state at 25 °C by poling along the ⟨110⟩.[16]

Figures 1(a)–1(c) show K^{-1} as a function of temperature for poled ⟨111⟩, ⟨011⟩, and ⟨001⟩ oriented 0.67PMN–0.33PT crystals, respectively. In these figures, K^{-1} can be seen to have a pseudolinear relationship with T in the low temperature poled condition for $25<T<75$ °C. The pseudolinear behavior in K^{-1} indicates that the FE$_m$ state may simply be the transformational pathway between FE$_r$ and FE$_t$ phases. Symmetry distortions naturally occur between the low and high temperature phases during FE transformations, which are characterized by linear (Curie–Weiss) behavior.

In the high temperature state, significant deviations from linearity were observed, as shown in Fig. 2 for a ⟨001⟩ orientation. Similar deviation was found for ⟨110⟩ and ⟨111⟩ orientations. The value of K^{-1} of PMN–PT relaxors deviates strongly from linear behavior over a wide temperature interval for $T>T_c$,[17–20] similar to that shown in Fig. 2. In this case, the values for the Curie constant C and temperature θ are strongly dependent on the temperature range modeled.[21] The value of C has been reported to be $\sim5\times10^5$ near T_c, however with increasing temperature it decreases to $\sim10^5$.

Normally, the high temperature dielectric susceptibility of ferroelectrics can be modeled using the internal field

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FIG. 2. The 1 kHz K^{-1} as a function of temperature for a $\langle 001 \rangle$ oriented 0.67PMN–0.33PT crystal.

where p is the microscopic dipole, N is the density of dipole moments, γ is the Lorentz factor which reflects the strength of coupling between dipoles, ε_0 is dielectric permitivy of free space, and k is the Boltzman constant. Knowing C and θ, the degree of coupling between dipoles and the magnitude of the dipole moments can be estimated. In the case of oriented piezocrystals, the values of C were determined to be 3.5×10^5 ($\langle 001 \rangle$ FE$_r$ polydomain), 5.5×10^5 ($\langle 011 \rangle$ FE$_r$ polydomain), and 7×10^4 ($\langle 111 \rangle$ FE$_r$ monodomain). These results demonstrate that C is significantly higher in a polydomain condition relative to a monodomain one.

Figure 3 shows the inverse dielectric susceptibility for the $\langle 011 \rangle$ oriented specimen in the FE$_r$ polydomain state, alongside data for a $\langle 011 \rangle$ oriented specimen in a fully poled FE$_o$ monodomain state.[16] Comparisons of these data will confirm that C is significantly higher in the polydomain (5.5×10^5) versus the monodomain condition (1.5×10^5).

Equation (1) is of importance in understanding the Curie–Weiss behavior in oriented piezocrystals. The fact that C is significantly larger for the polydomain condition relative
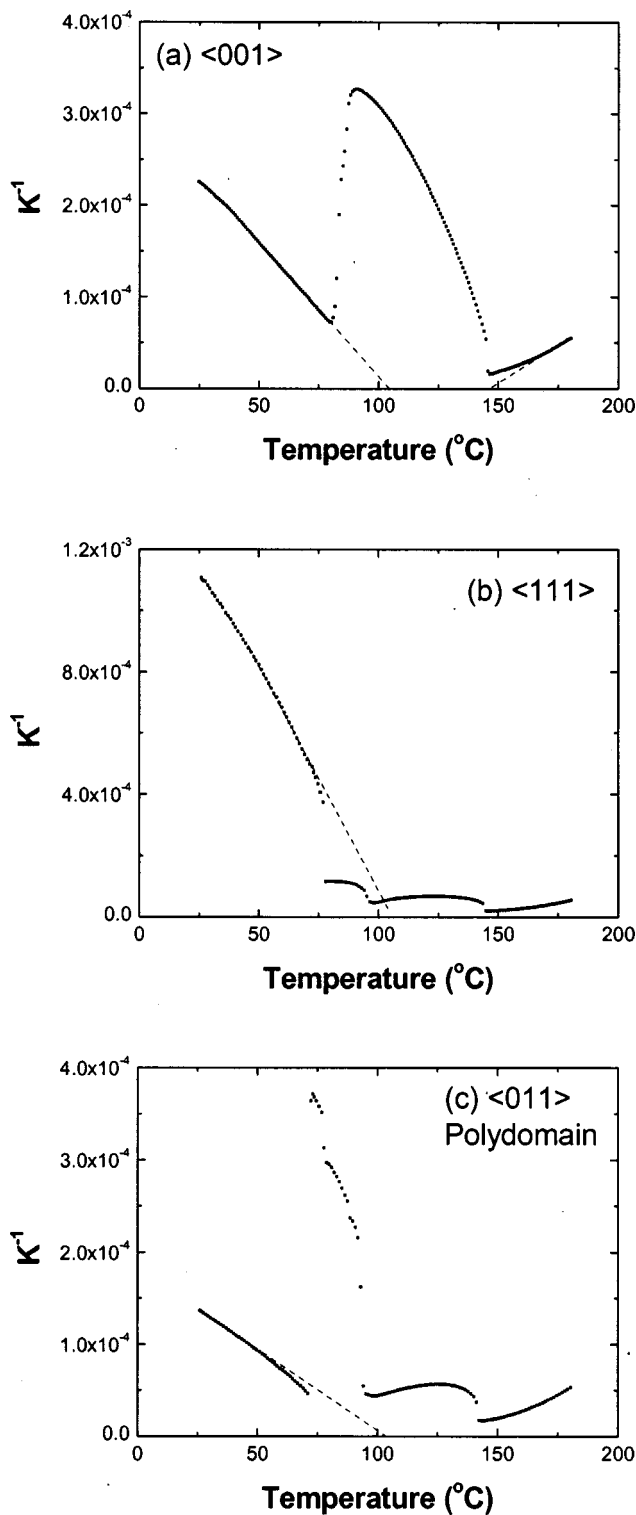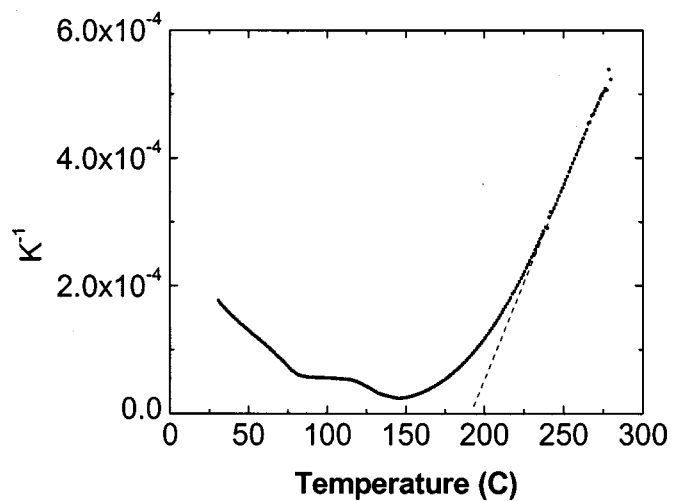

FIG. 1. The 1 kHz K^{-1} as a function of temperature for 0.67PMN–0.33PT single crystals: (a) $\langle 001 \rangle$ oriented crystal poled to a polydomain FE$_r$ condition; (b) $\langle 111 \rangle$ oriented crystal poled to a monodomain FE$_r$ condition; and (c) $\langle 110 \rangle$ oriented crystal poled to a polydomain FE$_r$ condition.

model.[22] The values of C and θ can be obtained as given in Eq. (1)

$$C = Np^2/3\varepsilon_0 k, \tag{1a}$$
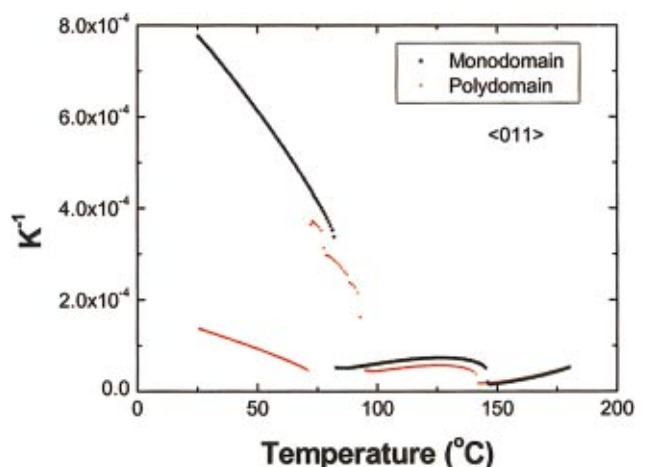
$$\theta = \gamma C, \tag{1b}$$

FIG. 3. (Color) The 1 kHz K^{-1} as a function of temperature for a $\langle 110 \rangle$ oriented 0.67PMN–0.33PT single crystal. Data are shown for both a polydomain FE$_r$ state and a fully poled monodomain FE$_o$ state.

to the monodomain one demonstrates that the product of Np^2 is higher in the polydomain condition. In fact, the values of C in the polydomain states were nearly equal to those observed in the relaxor condition ($C \sim 5 \times 10^5$).[17,20] However, the value of C was independent of temperature in the poled piezocrystal condition, unlike the strong temperature dependence found in relaxors (and above T_c in piezocrystals). For $T > T_c$, the product of Np^2 varies with temperature, as the density of polar clusters changes.[23,24] However, in the poled piezocrystal state, the product of Np^2 is high, but temperature invariant. Piezocrystals may be poled and anisotropic, but polarization nonuniformities play a significant role in the polydomain condition.

The results of this investigation demonstrate: (i) that the inverse dielectric susceptibility exhibits pseudolinear behavior over a moderate temperature range below T_c, whereas significant deviations are observed above T_c, and (ii) that the value of C is significantly higher in the polydomain condition relative to a monodomain. The results indicate that polarization nonuniformity exists within the poled anisotropic state of 0.67PMN–0.33PT crystals.

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