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Phase transitional behavior and piezoelectric properties of the orthorhombic phase of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ single crystals

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We report on the observation of an orthorhombic ferroelectric phase in 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ –0.33PbTiO$_3$ single crystals, whose polarization is along $\langle 011 \rangle$ direction and stability can be altered by poling conditions. We studied the piezoelectric properties on poled $\langle 011 \rangle$ crystals, in both monodomain and polydomain states, and found that the piezoelectric d_{32} coefficient, which is the piezoelectric response in perpendicular to the poling direction, is positive in both cases. Based on the phenomenological theory, we show that this is possible in a crystal with the electrostrictive coefficients $Q_{11} > Q_{44} - Q_{12}$. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1372360]

We report in this letter on the phase transition behavior and piezoelectric responses of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ (PMN–PT) single crystals, for compositions close to the morphotropic phase boundary (MPB) between rhombohedral ferroelectric (FE$_r$) and tetragonal ferroelectric (FE$_t$) phases. Recent discoveries in mixed B-site cation ferroelectric perovskites have stimulated significant research activities.[1–4] In Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ (PZN–PT) and PMN–PT single crystals, an electromechanical coupling factor of greater than 0.9 has been reported in the FE$_r$ phase near the MPB for specimens poled along $\langle 001 \rangle$.[1–3] Similar enhancements in the electromechanical properties were also reported when crystals were poled at finite angles with respect to the spontaneous polarization direction, although the coupling factors of these finite miss-oriented crystals were lower (~ 0.8).[5–7]

Naturally, a question to ask is what is unique about the PZN–PT and PMN–PT crystalline solutions and the role of the MPB. In 0.92PZN–0.08PT crystals (which at $T = 25\,^{\circ}$C is in the FE$_r$ phase and near a MPB), recent investigations have demonstrated the presence of monoclinic domains, and orthorhombic ferroelectric (FE$_o$) and monoclinic ferroelectric (FE$_m$) states.[8–10] This opens an interesting possibility that those states, even metastable, may be regarded as intermediate states and responsible for the high piezoelectric and electromechanical responses in PZN–PT and PMN–PT single crystals near the MPB.

In Pb(Zr$_{1-x}$Ti$_x$)O$_3$, which is another related ferroelectric perovskite material, high electromechanical properties have been widely studied over many years for compositions close to the MPB between FE$_r$ and FE$_t$ phases.[11] Much effort has been expended in determining the mechanism responsible for these significant enhancements. Recently, a FE$_m$ state has been reported over a very narrow composition range near MPB. In this FE$_m$ state, the polarization was confined to the

$\langle hhk \rangle$ plane, which is one of the planes that can ''bridge'' the tetragonal $\langle 001 \rangle$ and rhombohedral $\langle 111 \rangle$ directions.[4,12] It was suggested that this ''bridging'' effect, via the FE$_m$ state, is responsible for the enhanced electromechanical properties.[12]

This investigation reports the phase transition behavior and piezoelectric responses in PMN–PT single crystals of approximate compositions of 0.67PMN–0.33PT, which are close to the MPB. Dielectric and piezoelectric methods have been used to study crystals with various poling histories. We have observed, by dielectric and optical microscopy techniques, an intermediate FE$_o$ state whose phase stability depends upon its poling history and mechanical condition. In addition, it was observed that this monodomain FE$_o$ does not exhibit enhanced piezoelectricity and its piezoelectricity can be described quite well by the phenomenological theory.[13,14]

Crystals were grown by the Bridgman method.[15] Various crystals were oriented along the $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. Typical specimen dimensions were $2 \times 2 \times 2$ mm^3. Crystals were poled at room temperature, with monodomain conditions achieved in both $\langle 111 \rangle$ and $\langle 110 \rangle$ oriented crystals. Dielectric characterization (at 1 kHz) was carried out using a standard LCR meter (HP4284A) equipped with a temperature chamber (Delta 9023). Piezoelectric coefficients were measured at 1 kHz using a laser dilatometer.[16] Domain patterns were characterized by a Zeiss Axioskop cross-polarized optical microscope (100× amplification).

Figures 1(a)–1(d) show the dielectric constant and loss as functions of temperature for poled $\langle 111 \rangle$, $\langle 011 \rangle$ ($E_{\text{poling}} > 5$ kV/cm), $\langle 011 \rangle$ ($E_{\text{poling}} = 4$ kV/cm), and $\langle 001 \rangle$ oriented PMN–PT crystals, respectively. It is important to emphasize that the difference between Figs. 1(b) and 1(c) (which are both for $\langle 011 \rangle$ orientations) is only the poling field (E_{poling}). Each figure exhibited a transition at 145 °C which is the FE$_t$ to cubic transformation,[17,18] and a second dielectric anomaly at ~ 80 °C. For $\langle 111 \rangle$ and $\langle 011 \rangle$ ($E_{\text{poling}} < 4$ kV/cm)
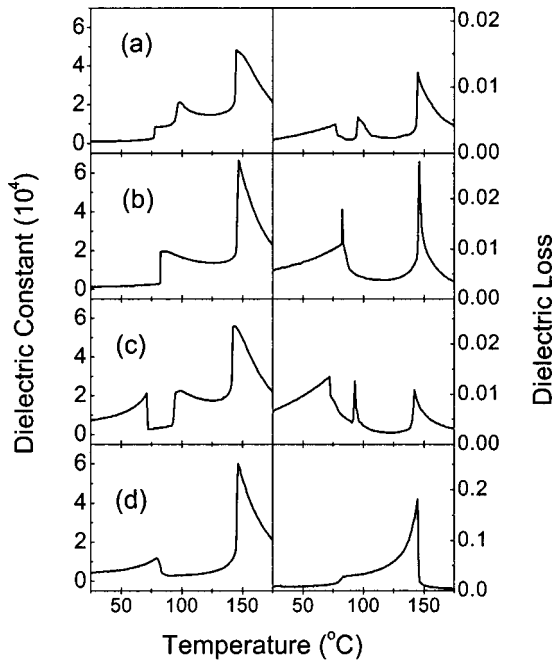
FIG. 1. The dielectric constant and dielectric loss measured at 1 kHz as functions of temperature for 0.67PMN–0.33PT single crystals (a) poled and measured along the [111] direction (monodomain rhombohedral phase); (b) poled and measured along [011] (monodomain orthorhombic phase); (c) poled along [011] direction to form ⟨111⟩ twined crystal and measured along [011]; and (d) poled and measured along [001] (polydomain crystal).

orientations, an additional third anomaly was found at $\sim 100\,°C$.

For ⟨011⟩-oriented crystals poled at $E_{\text{poling}} < 4$ kV/cm, optical microscopy revealed the presence of a polydomain condition with domains oriented along the ⟨111⟩, typical of that of a FE_r state. These domain orientations are schematically illustrated in Fig. 2(a). However, for $E_{\text{poling}} > 5$ kV/cm, ⟨011⟩-oriented crystals were observed under cross-polarized light to be in a monodomain state with the polarization along the ⟨011⟩. This domain orientation is schematically illustrated in Fig. 2(b). It should be mentioned that even small variations in the PT content resulted in deviations from this monodomain condition and the disappearance of the FE_o state at 25 °C, demonstrating that this state only exists over a narrow composition range near the MPB. Accordingly, at room temperature most of the crystals poled along ⟨011⟩ were polydomain and FE_r.

The differences in the dielectric responses of the ⟨011⟩
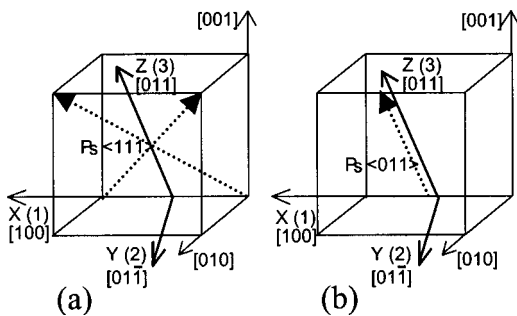

(a)   (b)

FIG. 2. Schematic drawings for [011] poled crystals in (a) twined crystals and (b) monodomain crystals. The dashed arrows indicate the remanent polarization direction and orthorhombic coordinate system used to describe the piezoelectric coefficients is also presented.

TABLE I. Piezoelectric coefficients of 0.67PMN–0.33PT single crystals poled along [011] direction at room temperature.

	d_{33} (pm/V)	d_{32} (pm/V)	d_{31} (pm/V)	$\epsilon_{33}^{(o)}/\epsilon_0$ [a]
Monodomain	250	40	−220	880
Polydomain (experimental)	1780	1100	−2740	
Polydomain (calculated)	1770	980	−2760	

[a] ϵ_0 is the vacuum permittivity.

crystals due to the various poling histories can be explained on the basis of these optical microscopy observations. For $E_{\text{poling}} < 4$ kV/cm [Fig. 1(c)], the FE_r state is stable at room temperature. Upon heating to $\sim 80\,°C$, a transition occurs to a FE_o state. On further increase of temperature to $\sim 100\,°C$, a secondary transformation to a FE_t state occurred. In contrast, for $E_{\text{poling}} > 5$ kV/cm [Fig. 1(b)], a monodomain FE_o state can be induced at room temperature. Upon heating to 80 °C, a transition occurs to a FE_t state. Interestingly, the FE_o–FE_t transition temperature in the monodomain condition was significantly lower (80 °C) than in the polydomain condition (100 °C). Clearly, the phase transformational pathway is altered by whether the specimen is elastically constrained (polydomain) or free to deform (monodomain).[9]

The dielectric constant for the poled ⟨111⟩ crystals [Fig. 1(a)] exhibited a similar transition sequence as the polydomain ⟨011⟩ [Fig. 1(c)]. In both cases, the FE_r to FE_t transition proceeded through an intermediate FE_o state, with the FE_o state being present for $\sim 80 < T < 100\,°C$. The dielectric constant for poled ⟨001⟩ crystals was shown in Fig. 1(d). Only one FE–FE transition was observed, which occurred at 80 °C. This transition temperature is close to that of the FE_o–FE_t along the ⟨011⟩ ($E_{\text{poling}} > 5$ kV/cm, monodomain), and with that of the FE_r–FE_o along the ⟨111⟩ and ⟨011⟩ ($E_{\text{poling}} < 4$ kV/cm, polydomain).

The results in Fig. 1 demonstrate a complex transformation sequence that is dependent upon orientation and electrical history. An intermediate FE_o state exists between the FE_r and FE_t ones, whose temperature range of existence varies, suggesting metastability. Furthermore, these results indicate that the margin of stability in the FE_r, FE_o, and FE_t states may all be sufficiently fragile that changes in orientation, electrical history, or mechanical constraints may change the free energy balance. The reason why ceramic specimens have not revealed a FE_o state in the last 20 years[17,18] may then reflect the fact that under all circumstances the polarization is elastically constrained, preventing strain accommodation.

To determine the influence of monodomain versus polydomain conditions upon the electromechanical properties of ⟨011⟩ oriented crystals, the piezoelectric coefficients (d_{33}, d_{31}, and d_{32}) were measured. The results are given in Table I. First, the values of all coefficients were much lower in the monodomain FE_o state than the polydomain FE_r one. The results were a little unusual in that $d_{32} > 0$ for both the mono and polydomain conditions, and also in that $|d_{31}| > |d_{33}|$ for the polydomain condition.

In order to explain the observed piezoelectric properties in poled ⟨011⟩ crystals in both the poly and monodomain states, we derived expressions for the piezoelectric coeffi-

cients from phenomenological theory.[13,14] Along the $\langle 011 \rangle$ in the monodomain condition, the piezoelectric responses were found to be

$$d_{33}^{(o)} = \sqrt{2}(Q_{11} + Q_{12} + Q_{44})\epsilon_{33}^{(o)}P_r^{(o)},$$

$$d_{32}^{(o)} = \sqrt{2}(Q_{11} + Q_{12} - Q_{44})\epsilon_{33}^{(o)}P_r^{(o)}, \qquad (1)$$

$$d_{31}^{(o)} = 2\sqrt{2}Q_{12}\epsilon_{33}^{(o)}P_r^{(o)},$$

where the superscript (o) stands for properties that are referenced with respect to the coordinate system of the FE$_o$ state (see Fig. 2), $\epsilon_{33}^{(o)}$ is the dielectric permittivity of the FE$_o$ state, $P_r^{(o)}$ is the remanent polarization of the FE$_o$ state (0.39 C/m^2),[9] and Q_{11}, Q_{12}, and Q_{44} are the electrostrictive coefficients (in the pseudocubic coordinates) expressed in matrix notation. For ferroelectric perovskites, it is known that $Q_{11} > 0$, $Q_{44} > 0$, $Q_{12} < 0$, and $|Q_{11}| > 2|Q_{12}|$.[13] Therefore, under the condition that $Q_{11} > Q_{44} - Q_{12}$, Eq. (1) predicts that $d_{32}^{(o)}$ is positive. Using Eq. (1) and the data in Table I, the values of the electrostrictive coefficients can be estimated: $Q_{11} = 0.06$ m^4/C^2, $Q_{12} = -0.025$ m^4/C^2, and $Q_{44} = 0.024$ m^4/C^2, respectively.

For the $\langle 011 \rangle$-oriented FE$_r$ polydomain state, assuming that there are [111] and [$\bar{1}$11] domains only, the piezoelectric coefficients were derived as

$$d_{33}^{(o)} = \sqrt{2}/3[(Q_{11} + Q_{44})(\epsilon_{11}^{(R)} + 2\epsilon_{33}^{(R)})$$

$$+ Q_{12}(4\epsilon_{33}^{(R)} - \epsilon_{11}^{(R)})]P_r^{(R)},$$

$$\approx \sqrt{2}/3(Q_{11} + Q_{44} - Q_{12})\epsilon_{11}^{(R)}P_r^{(R)},$$

$$d_{32}^{(o)} = \sqrt{2}/3[(Q_{11} - Q_{44})(\epsilon_{11}^{(R)} + 2\epsilon_{33}^{(R)}) \qquad (2)$$

$$+ Q_{12}(4\epsilon_{33}^{(R)} - \epsilon_{11}^{(R)})]P_r^{(R)},$$

$$\approx \sqrt{2}/3(Q_{11} - Q_{44} - Q_{12})\epsilon_{11}^{(R)}P_r^{(R)},$$

$$d_{31}^{(o)} = 2\sqrt{2}/3[Q_{11}(\epsilon_{33}^{(R)} - \epsilon_{11}^{(R)}) + Q_{12}(2\epsilon_{33}^{(R)} + \epsilon_{11}^{(R)})]P_r^{(R)},$$

$$\approx 2\sqrt{2}/3(-Q_{11} + Q_{12})\epsilon_{11}^{(R)}P_r^{(R)},$$

where $\epsilon_{33}^{(R)}$ and $\epsilon_{11}^{(R)}$ are the dielectric permittivity measured in the FE$_r$ state along and perpendicular to the [111] polar-

ization direction, respectively, and $P_r^{(R)}$ is the remanent polarization of the rhombohedral phase (~ 0.39 C/m^2).[9] In the second part of each relationship in Eq. (2), we have made use of the fact that $\epsilon_{11}^{(R)} \gg \epsilon_{33}^{(R)}$. The values of $d_{33}^{(o)}$, $d_{33}^{(o)}$, and $d_{33}^{(o)}$ for the FE$_r$ polydomain condition can be estimated by placing the values of the electrostriction coefficients estimated in the proceeding paragraph into Eq. (2). These calculated values for the piezoelectric coefficients are given in Table I where $\epsilon_{11}^{(R)}/\epsilon_0 = 10\,000$ is used. Inspection of the data in the table reveals remarkable agreement, in particular in consideration of the use of a single crystalline single domain phenomenological approach to the properties of polydomain conditions.

[1] J. Kuwata, K. Uchino, and S. Nomura, Jpn. J. Appl. Phys., Part 1 **21**, 1298 (1982).

[2] S. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).

[3] S. Park and T. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **44**, 1140 (1997).

[4] B. Noheda, D. E. Cox, G. Shirane, J. Gonzalo, L. Cross, and S. Park, Appl. Phys. Lett. **74**, 2059 (1999).

[5] K. Nakamura and Y. Kawamura, in *1999 IEEE Ultrasonics Symposium Proceedings*, edited by S. C. Schneider, M. Levy, and B. R. McAvoy (IEEE, New York, 1999), pp. 1013–1018.

[6] S. Park, S. Wada, L. Cross, and T. Shrout, J. Appl. Phys. **86**, 2746 (1999).

[7] X.-H. Du, J. Zheng, U. Belegundu, and K. Uchino, Appl. Phys. Lett. **72**, 2421 (1998).

[8] M. K. Durbin, J. C. Hicks, S. Park, and T. Shrout, J. Appl. Phys. **87**, 8159 (2000).

[9] D. Viehland, J. Appl. Phys. **88**, 4794 (2000).

[10] B. Noheda, D. Cox, G. Shirane, S. Park, L. E. Cross, and Z. Zhong (unpublished).

[11] B. Jaffe, W. Cook, Jr., and H. Jaffe, *Piezoelectric Ceramics* (Academic, New York, 1971), Chap. 7.

[12] R. Guo, L. Cross, S. Park, B. Noheda, D. Cox, and G. Shirane, Phys. Rev. Lett. **84**, 5423 (2000).

[13] A. F. Devonshire, Philos. Mag. **3**, 85 (1954).

[14] F. Jona and G. Shirane, *Ferroelectric Crystals* (Dover, New York, 1993), Chap. IV.

[15] Z. Yin, H. Luo, P. Wang, and G. Xu, Ferroelectrics **229**, 207 (1999).

[16] Q. M. Zhang, W. Pan, and L. Cross, J. Appl. Phys. **63**, 2492 (1988).

[17] S. W. Choi, T. Shrout, S. Jang, and A. Bhalla, Ferroelectrics **100**, 29 (1989).

[18] O. Noblanc, P. Gaucher, and G. Calvarin, J. Appl. Phys. **79**, 4291 (1996).