

The enhanced and optimal piezoelectric coefficients in single crystalline barium titanate with engineered domain configurations

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In this letter, we report a micromechanical analysis to explain the enhanced piezoelectric coefficients in ferroelectric single crystals poled along a nonpolar axis, where the coexistence of several variants leads to a complicated domain configuration. The engineered domain configuration in the crystal is constructed first using energy minimization approach, and the effective moduli of single crystal with engineered domain configuration is then determined using homogenization theory. Following this procedure, we calculate the effective electromechanical moduli of tetragonal barium titanate poled along [111] direction, where the piezoelectric coefficient d_{33} is found to be 70% higher than those poled along [001], consistent with experimental observation. Piezoelectric coefficient d_{32} is also found to be 114% higher. In addition, we notice that poling along [111] direction does not lead to the optimal domain configuration, since barium titanate poled along [110] direction has much higher d_{32} and d_{33} . The analysis reveals that much higher electromechanical coupling can be obtained in ferroelectric crystals with engineered domain configurations, and offers insight on the design and optimization of ferroelectrics for enhanced functional properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600517]

Ultrahigh strain and piezoelectric behavior have been discovered in relaxor based rhombohedral single crystals $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) poled along [001] direction,^{1,2} though poling along [111] direction, the polar axis, leads to much lower electromechanical coupling. Since then, higher piezoelectric coefficient d_{33} has also been demonstrated in tetragonal single crystal barium titanate poled along the non-polar [111] direction,³ and there is an indication that such phenomena are common in ferroelectric single crystals.⁴ While it is generally believed that the enhanced electromechanical coupling is related to the so-called engineered domain configuration, where two or more crystallographically equivalent ferroelectric variants coexist in the single crystal poled along a nonpolar axis, the exact nature of the enhancement and the optimal domain configuration are not clear, which we intend to address in this letter. We believe that the enhanced piezoelectric coefficient is due to the anisotropy of ferroelectric variants and the interaction between different domains, which will be elaborated here. At higher electric field, polarization rotation⁵⁻⁷ and field-induced phase transition may occur,³ which are beyond the scope of this letter.

The first question we try to answer is how ferroelectric variants accommodate each other within the engineered domain configuration in an energy minimizing fashion. For a tetragonal ferroelectric crystal such as barium titanate, the transformation strains and polarizations are given by

$$\mathbf{e}^{(\pm 1)} = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{bmatrix}, \quad \mathbf{p}^{(\pm 1)} = \pm \begin{bmatrix} p_t \\ 0 \\ 0 \end{bmatrix},$$

$$\mathbf{e}^{(\pm 2)} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{bmatrix}, \quad \mathbf{p}^{(\pm 2)} = \pm \begin{bmatrix} 0 \\ p_t \\ 0 \end{bmatrix},$$

$$\mathbf{e}^{(\pm 3)} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}, \quad \mathbf{p}^{(\pm 3)} = \pm \begin{bmatrix} 0 \\ 0 \\ p_t \end{bmatrix},$$

leading to six ferroelectric variants, all compatible with each other. In another words, they satisfy compatibility equations

$$\mathbf{e}^{(j)} - \mathbf{e}^{(k)} = \frac{1}{2}(\mathbf{a}_{jk} \otimes \mathbf{n}_{jk} + \mathbf{n}_{jk} \otimes \mathbf{a}_{jk}),$$

$$[\mathbf{p}^{(j)} - \mathbf{p}^{(k)}] \cdot \mathbf{n}_{jk} = 0 \quad (1)$$

for $j, k = -3 \dots 3$,⁸ which ensures the existence of a coherent interface of normal \mathbf{n}_{jk} between variants j and k . As a result, each pair of variants can form laminated domain patterns consisting of alternating twins with twin boundary given by \mathbf{n}_{jk} , which is free of stress and electric field.⁹ When the crystal is poled along [111] direction, variants 1, 2, and 3 with positive polarization component coexist in the single crystal, each having an equal volume fraction. Yet, it is still possible for the three variants to form an energy minimizing domain pattern made of alternating bands.⁹⁻¹¹ Band I consists of fine twins of $\{[\mathbf{e}^{(1)}, \mathbf{p}^{(1)}]\}$ and $\{[\mathbf{e}^{(2)}, \mathbf{p}^{(2)}]\}$, with averaging transformation strain and polarization given by

$$\mathbf{e}^{(I)} = \mu \mathbf{e}^{(2)} + (1 - \mu) \mathbf{e}^{(1)}, \quad \mathbf{p}^{(I)} = \mu \mathbf{p}^{(2)} + (1 - \mu) \mathbf{p}^{(1)},$$

and band II consists of fine twins of $\{[\mathbf{e}^{(3)}, \mathbf{p}^{(3)}]\}$ and $\{[\mathbf{e}^{(2)}, \mathbf{p}^{(2)}]\}$ with averaging transformation strain and polarization given by

$$\mathbf{e}^{(II)} = \mu \mathbf{e}^{(2)} + (1 - \mu) \mathbf{e}^{(3)}, \quad \mathbf{p}^{(II)} = \mu \mathbf{p}^{(2)} + (1 - \mu) \mathbf{p}^{(3)},$$

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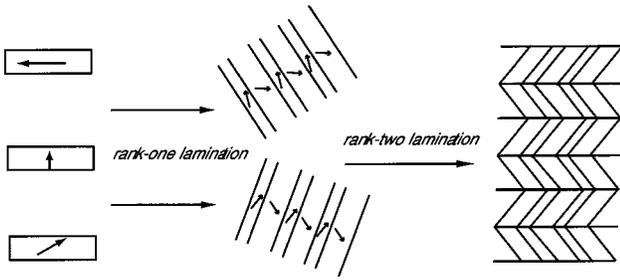


FIG. 1. The construction of energy minimizing domain configuration by rank-two lamination for barium titanate poled along [111] direction.

where μ is the volume fraction of variant 2 within each band, which needs to be identical. Clearly, the two bands satisfy Eq. (1) on average for any $\mu \in [0,1]$,

$$\mathbf{e}^{(I)} - \mathbf{e}^{(II)} = \frac{1-\mu}{2} (\mathbf{a}_{13} \otimes \mathbf{n}_{13} + \mathbf{n}_{13} \otimes \mathbf{a}_{13}),$$

$$(\mathbf{p}^{(I)} - \mathbf{p}^{(II)}) \cdot \mathbf{n}_{13} = [(1-\mu)(\mathbf{p}^{(1)} - \mathbf{p}^{(3)})] \cdot \mathbf{n}_{13} = 0,$$

suggesting that they can form another level of lamination with the interface normal given by \mathbf{n}_{13} . The volume fraction of band II is $\lambda \in [0,1]$, which can be determined from the volume fractions of variants 1, 2, and 3 in the crystal. A schematic representation of this construction is shown in Fig. 1, and such band structure was indeed observed in experiments.^{3,12} When there is separation of scale so that the length scale of the bands is much larger than the length scale of fine twins, no stress and electric field will be induced and the energy of the domain configuration will be minimum,⁹⁻¹¹ leading to a stable domain configuration. As a result, minimum hysteresis was observed in experiments.^{1,3}

Since the energy minimizing domain configuration of barium titanate can be constructed by rank-two lamination with two distinct length scales, the effective electromechanical moduli of ferroelectric single crystal with engineered domain configuration can be determined using lamination theory. To this end we consider the static piezoelectric behavior of ferroelectrics governed by the constitutive equation

$$\begin{bmatrix} \boldsymbol{\epsilon} \\ \mathbf{D} \end{bmatrix} = \begin{bmatrix} \mathbf{S} & \mathbf{d} \\ \mathbf{d}^t & \kappa \end{bmatrix} \begin{bmatrix} \boldsymbol{\sigma} \\ \mathbf{E} \end{bmatrix}, \quad (2)$$

where $\boldsymbol{\epsilon}$ and $\boldsymbol{\sigma}$ are the strain and stress, respectively; \mathbf{D} and \mathbf{E} are the electric displacement and electric field, respectively; \mathbf{S} , \mathbf{d} , and κ are elastic compliance, piezoelectric coefficient, and dielectric constant, respectively; and superscript t is used to denote a matrix transpose. The equation can be rearranged as

$$\begin{bmatrix} \mathbf{Y} \\ \mathbf{Z} \end{bmatrix} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^t & \mathbf{N} \end{bmatrix} \begin{bmatrix} \mathbf{F} \\ \mathbf{G} \end{bmatrix}, \quad (3)$$

where the field variables and the electromechanical moduli are given by

$$\mathbf{Y} = \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_6 \\ D_3 \end{bmatrix}, \quad \mathbf{Z} = \begin{bmatrix} \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ D_1 \\ D_2 \end{bmatrix}, \quad \mathbf{F} = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_6 \\ E_3 \end{bmatrix}, \quad \mathbf{G} = \begin{bmatrix} \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ E_1 \\ E_2 \end{bmatrix},$$

and

$$\mathbf{A} = \begin{bmatrix} S_{11} & S_{12} & S_{16} & d_{31} \\ S_{12} & S_{22} & S_{26} & d_{32} \\ S_{16} & S_{26} & S_{66} & d_{36} \\ d_{31} & d_{32} & d_{36} & \kappa_{33} \end{bmatrix},$$

$$\mathbf{B}^t = \begin{bmatrix} S_{13} & S_{23} & S_{36} & d_{33} \\ S_{14} & S_{24} & S_{46} & d_{34} \\ S_{15} & S_{25} & S_{56} & d_{35} \\ d_{11} & d_{12} & d_{16} & \kappa_{13} \\ d_{21} & d_{22} & d_{26} & \kappa_{23} \end{bmatrix},$$

$$\mathbf{N} = \begin{bmatrix} S_{33} & S_{34} & S_{35} & d_{13} & d_{23} \\ S_{34} & S_{44} & S_{45} & d_{14} & d_{24} \\ S_{35} & S_{45} & S_{55} & d_{15} & d_{25} \\ d_{13} & d_{14} & d_{15} & \kappa_{11} & \kappa_{12} \\ d_{23} & d_{24} & d_{25} & \kappa_{12} & \kappa_{22} \end{bmatrix}.$$

Within a composite laminate, certain components of electro-mechanical field need to be continuous across the interface, and the reformulated equation simplifies the continuity condition as

$$\mathbf{Y}_1 = \mathbf{Y}_2 = \bar{\mathbf{Y}}, \quad \mathbf{G}_1 = \mathbf{G}_2 = \bar{\mathbf{G}}, \quad (4)$$

for the two-phase laminate we are considering, if the interface normal is chosen as the x_3 axis. Here, each phase represents a variant or a band, and the overhead bar is used to denote the volume averaged field variables in the laminate. As a result, we have

$$\mathbf{F}_r = \mathbf{A}_r^{-1} \bar{\mathbf{Y}} - \mathbf{A}_r^{-1} \mathbf{B}_r \bar{\mathbf{G}},$$

$$\mathbf{Z}_r = \mathbf{B}_r^t \mathbf{A}_r^{-1} \bar{\mathbf{Y}} + (\mathbf{N}_r - \mathbf{B}_r^t \mathbf{A}_r^{-1} \mathbf{B}_r) \bar{\mathbf{G}}, \quad (5)$$

where subscript $r=1,2$ is used to denote a field variable in each phase. This leads to

$$\bar{\mathbf{Y}} = \mathbf{A}^* \bar{\mathbf{F}} + \mathbf{B}^* \bar{\mathbf{G}}, \quad \bar{\mathbf{Z}} = \mathbf{B}^{t*} \bar{\mathbf{F}} + \mathbf{N}^* \bar{\mathbf{G}}, \quad (6)$$

with the effective electromechanical moduli given by

$$\mathbf{A}^* = \langle \mathbf{A}^{-1} \rangle^{-1},$$

$$\mathbf{B}^* = \langle \mathbf{A}^{-1} \rangle^{-1} \langle \mathbf{A}^{-1} \mathbf{B} \rangle,$$

$$\mathbf{B}^{t*} = \langle \mathbf{B}^t \mathbf{A}^{-1} \rangle \langle \mathbf{A}^{-1} \rangle^{-1} \quad (7)$$

$$\mathbf{N}^* = \langle \mathbf{B}^t \mathbf{A}^{-1} \rangle \langle \mathbf{A}^{-1} \rangle^{-1} \langle \mathbf{A}^{-1} \mathbf{B} \rangle + \langle \mathbf{N} \rangle - \langle \mathbf{B}^t \mathbf{A}^{-1} \mathbf{B} \rangle,$$

where $\langle \cdot \rangle$ is used to denote volume averaged physical properties. The effective electromechanical moduli are clearly diagonally symmetric, and are exact for rank-one laminates.

Equation (7) allows us to study the electromechanical behavior of single-crystal barium titanate with engineered domain configurations. The investigation on PZN-PT and PMN-PT is undergoing and will be reported later. The electromechanical moduli of single-domain single crystal barium titanate we used in our calculation are listed in Table I,¹³ which are highly anisotropic. When the crystal is poled along [111] direction, three variants coexist with equal volume fraction, making it necessary that $\mu=1/3$ and $\lambda=1/2$. Since the engineered domain configuration is a rank-two laminate,

TABLE I. Electromechanical moduli of barium titanate.^a $S = 10^{-12} \text{ m}^2/\text{N}$; $d = 10^{-12} \text{ C/N}$; $\kappa: \kappa_0$.

S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}	d_{31}	d_{33}	d_{15}	κ_{11}	κ_{33}
7.38	-1.39	-4.41	13.1	16.4	7.46	-33.72	93.95	560.7	4366	132

^aSee Ref. 13.

Eq. (7) need to be applied repeatedly to determine the effective moduli of the single crystal. The effective moduli of bands I and II were calculated first using Eq. (7), with the electromechanical moduli of single-domain single crystal as input. The effective moduli of bands I and II were then used as input to calculate the effective moduli of a single crystal, which needs to be transformed into a new coordinate system with $x_1 \parallel [\bar{1}2\bar{1}]$, $x_2 \parallel [\bar{1}01]$, $x_3 \parallel [111]$. When there is separation of scales between bands and twins, so that the bands I and II can be regarded as homogeneous as far as the macroscopic behavior of single crystal is concerned, the procedure leads to exact effective moduli of a single crystal with an engineered domain configuration.

It is not obvious, however, that the three-variant system is optimal as far as the piezoelectric coefficients are concerned. As such, we also consider a two-variant system with $\mu=1/2$ and $\lambda=1$, so that only variants 2 and 3 coexist. Such an engineered domain configuration can be obtained, for example, if the single crystal is poled along $[011]$ combined with a compressive stress along $[100]$ direction. This is a rank-one laminate, which requires the application of Eq. (7) only once, with $x_1 \parallel [100]$, $x_2 \parallel [01\bar{1}]$, $x_3 \parallel [011]$. The predicted piezoelectric coefficients for both systems are summarized in Table II.

From Table II, it is confirmed that the three-variant domain configuration indeed leads to enhanced piezoelectricity, where piezoelectric coefficient d_{33} is found to be 70% higher than that of the single-domain single crystal, consistent with 62% enhancement observed in experiment.³ The single-domain piezoelectric coefficient d_{33} was reported to be 125 pC/N in,³ slightly higher than 93.95 pC/N reported in Ref. 13. Most likely this is an extrinsic effect due to some 180° domain wall movement. In addition, piezoelectric coeffi-

TABLE II. Piezoelectric coefficients of barium titanate crystals with engineered domain configuration; $d = 10^{-12} \text{ C/N}$.

d_{ij}	d_{31}	d_{32}	d_{33}
Single crystal	-33.72	-33.72	93.95
Two-variant	-23.85	-176.9	219.5
Three-variant	-72.03	-72.01	159.3

icients d_{31} and d_{32} is about 114% higher than those of the single-domain single crystal. As such, we are able to explain the enhanced piezoelectric coefficient in barium titanate poled along $[111]$ direction from the engineered domain configuration, which takes into account the energy minimizing domain configuration, the anisotropy of ferroelectric variants, and the interaction between ferroelectric domains. We not only demonstrate the enhancement in the longitudinal direction, which is consistent with experiment observation, but also predict the enhancement in the transverse direction. This is certainly worth investigating experimentally.

Even more interestingly, this three-variant system is by no means optimal. As a matter of fact, for the two-variant system poled along $[011]$ direction, the piezoelectric coefficient d_{32} is more than 400% higher than that of the single-domain single crystal, and the piezoelectric coefficient d_{33} is more than 100% higher, suggesting much larger property enhancement than the three-variant systems. To the best of our knowledge, such a two-variant engineered domain configuration has yet to be explored in experiment, and is also worth investigating.

In summary, we developed a theory to determine the effective electromechanical moduli of ferroelectric single crystals with engineered domain configurations. The enhanced piezoelectric coefficient d_{33} in single-crystal barium titanate poled along $[111]$ direction has been explained, the enhanced piezoelectric coefficient d_{32} has been predicted, and the optimal domain configuration has been identified. It demonstrates that much greater electromechanical coupling can indeed be obtained by engineering domain configurations in ferroelectric single crystals.

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¹S. E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).²J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys.* **21**, 1298 (1982).³S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S. E. Park, L. E. Cross, and T. Shrout, *Jpn. J. Appl. Phys.* **38**, 5505 (1999).⁴S. E. Park, S. Wada, L. E. Cross, and T. R. Shrout, *J. Appl. Phys.* **86**, 2746 (1999).⁵H. X. Fu and R. E. Cohen, *Nature (London)* **403**, 281 (2000).⁶L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).⁷B. Noheda, D. E. Cox, G. Shirane, S. E. Park, L. E. Cross, and Z. Zhong, *Phys. Rev. Lett.* **86**, 3891 (2001).⁸Y. C. Shu and K. Bhattacharya, *Philos. Mag. B* **81**, 2021 (2001).⁹J. Y. Li and K. Bhattacharya, *AIP Conf. Proc.* **626**, 224 (2002).¹⁰K. Bhattacharya, *Continuum Mech. Thermodyn.* **5**, 205 (1993).¹¹A. DeSimone and R. D. James, *J. Mech. Phys. Solids* **50**, 283 (2002).¹²G. Arlt and P. Sasko, *J. Appl. Phys.* **51**, 4956 (1980).¹³M. Zgonik, P. Bernasconi, M. Duelli, R. Schlessler, P. Gunter, M. H. Garrett, D. Rytz, Y. Zhu, and X. Wu, *Phys. Rev. B* **50**, 5941 (1994).