

# Domain-engineered $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals: Enhanced piezoelectricity and optimal domain configurations

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In this letter, we report a mesoscopic theory of ferroelectrics to explain the dramatically enhanced piezoelectricity in relaxor ferroelectric single crystals poled along a nonpolar axis, where the coexistence of several variants leads to complicated domain configurations. The engineered domain configuration is constructed first using energy minimization approach, and the effective moduli of single crystals with engineered domain configuration are then determined using the lamination theory. Using this approach, we calculate the effective electromechanical moduli of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) crystals poled along [001] and [011] directions, which agree well with experimental observations. In addition, we demonstrate that PMN-PT crystals electromechanically poled by an electric field along [001] direction and an additional positive shear stress  $\sigma_{12}$  possess superior electromechanical coupling factors  $k_{31}$  and  $k_{33}$  simultaneously, while crystals with other domain configurations demonstrate much lower  $k_{31}$ . The analysis reveals that greatly enhanced electromechanical coupling can be obtained in domain-engineered ferroelectric crystals, and offers insight on the design and optimization of ferroelectrics for enhanced functional properties. © 2004 American Institute of Physics. [DOI: 10.1063/1.1745114]

Ultrahigh strain and piezoelectric behavior have been discovered in relaxor based rhombohedral single crystals  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PZN-PT) poled along [001] direction,<sup>1,2</sup> where the electromechanical coupling factor of more than 90% and piezoelectric strain of more than 1.5% were demonstrated. In contrast, PMN-PT and PZN-PT crystals poled along [111] direction, the polar axis, exhibit much lower electromechanical coupling, and the question arises on the mechanism responsible for the dramatic piezoelectric property enhancement in these crystals. While it was suggested that the enhanced electromechanical coupling is related to the so called engineered domain configuration<sup>3-5</sup> as well as the large piezoelectric constant  $d_{15}$  in single-domain crystals,<sup>6-8</sup> the exact nature of the enhancement and the optimal domain configuration are not clear, which we intend to address in this letter. What we present is a mesoscopic theory of ferroelectrics involving numerous domains, which collectively determine the macroscopic behavior of ferroelectrics. At higher electric field, polarization rotation<sup>9-11</sup> and field induced phase transition may occur,<sup>12,13</sup> which we will not consider here. In this letter, we report our main results. A complete description of the theory can be found in a forthcoming article.<sup>14</sup>

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 rhombohedral crystals such as PMN-PT and PZN-PT, the transformation strain and polarization of each variant are given by

$$\begin{aligned} \mathbf{e}^{(\pm 1)} &= \begin{bmatrix} \eta & \delta & \delta \\ \delta & \eta & \delta \\ \delta & \delta & \eta \end{bmatrix}, \quad \mathbf{p}^{(\pm 1)} = \pm \begin{bmatrix} p \\ p \\ p \end{bmatrix}, \\ \mathbf{e}^{(\pm 2)} &= \begin{bmatrix} \eta & -\delta & -\delta \\ -\delta & \eta & \delta \\ -\delta & \delta & \eta \end{bmatrix}, \quad \mathbf{p}^{(\pm 2)} = \pm \begin{bmatrix} -p \\ p \\ p \end{bmatrix}, \\ \mathbf{e}^{(\pm 3)} &= \begin{bmatrix} \eta & \delta & -\delta \\ \delta & \eta & -\delta \\ -\delta & -\delta & \eta \end{bmatrix}, \quad \mathbf{p}^{(\pm 3)} = \pm \begin{bmatrix} -p \\ -p \\ p \end{bmatrix}, \\ \mathbf{e}^{(\pm 4)} &= \begin{bmatrix} \eta & -\delta & \delta \\ -\delta & \eta & -\delta \\ \delta & -\delta & \eta \end{bmatrix}, \quad \mathbf{p}^{(\pm 4)} = \pm \begin{bmatrix} p \\ -p \\ p \end{bmatrix}, \end{aligned} \quad (1)$$

leading to eight ferroelectric variants. They satisfy compatibility equations

$$\begin{aligned} \mathbf{e}^{(j)} - \mathbf{e}^{(k)} &= \frac{1}{2}(\mathbf{a}_{jk} \otimes \mathbf{n}_{jk} + \mathbf{n}_{jk} \otimes \mathbf{a}_{jk}), \\ (\mathbf{p}^{(j)} - \mathbf{p}^{(k)}) \cdot \mathbf{n}_{jk} &= 0, \end{aligned} \quad (2)$$

for  $j, k = -4, \dots, 4$ ,<sup>15</sup> thus are compatible with each other, which ensures the existence of a coherent interface of normal  $\mathbf{n}_{jk}$  between variants  $j$  and  $k$ , with  $\mathbf{a}_{jk}$  being the shear across the interface. As a result, each pair of variants can form laminated domain patterns free of stress and electric field, consisting of alternating twins with twin boundary given by  $\mathbf{n}_{jk}$ .<sup>16</sup> When the crystal is poled along [001] direction, variants 1, 2, 3, and 4 with positive polarization component along [001] axis coexist in the single crystal, each having equal volume fraction; see Fig 1. However, it is still possible

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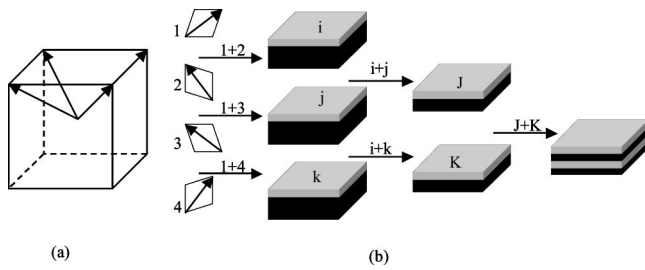


FIG. 1. (a) Coexistence of four ferroelectric variants in rhombohedral crystal poled along [001] axis; (b) the construction of energy minimizing domain configuration by rank-3 laminate.

for the four variants to form an energy minimizing domain pattern made of alternating bands at three different scales:<sup>14,16-18</sup>

- (1) Construct bands *i*, *j*, and *k* using variant 1 with variants 2, 3, and 4, respectively, with domain walls or interface normals given by  $\mathbf{n}_{12} \parallel [011]$ ,  $\mathbf{n}_{13} \parallel [001]$ , and  $\mathbf{n}_{14} \parallel [101]$ ; the volume fraction of variant 1 is  $\mu_1 = 1/4$  within each band.
- (2) Construct rank-2 laminates *J* and *K* using band *i* with bands *j* and *k*, respectively, with interface normals given by  $\mathbf{n}_{23} \parallel [\bar{1}01]$  and  $\mathbf{n}_{24} \parallel [001]$ ; the volume fraction of band *i* within each laminate is  $\mu_2 = 1/3$ .
- (3) Construct a rank-3 laminate using *J* and *K* with interface normal given by  $\mathbf{n}_{34} \parallel [0\bar{1}1]$  and volume fraction of *J* given by  $\mu_3 = 1/2$ .

A schematic representation of this construction is shown in Fig. 1, and such band structure was indeed observed in experiments.<sup>4,19,20</sup> 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

$$\mathbf{e}^{(i)} = \mu_1 \mathbf{e}^{(1)} + (1 - \mu_1) \mathbf{e}^{(2)}, \quad \mathbf{p}^{(i)} = \mu_1 \mathbf{p}^{(1)} + (1 - \mu_1) \mathbf{p}^{(2)},$$

and band *j* consists of fine twins of  $(\mathbf{e}^{(1)}, \mathbf{p}^{(1)})$  and  $(\mathbf{e}^{(3)}, \mathbf{p}^{(3)})$  with averaging transformation strain and polarization given by

$$\mathbf{e}^{(j)} = \mu_1 \mathbf{e}^{(1)} + (1 - \mu_1) \mathbf{e}^{(3)}, \quad \mathbf{p}^{(j)} = \mu_1 \mathbf{p}^{(1)} + (1 - \mu_1) \mathbf{p}^{(3)},$$

where  $\mu_1$  is the volume fraction of variant 1 within each band. Clearly the two bands satisfy compatibility condition on average for any  $\mu_1 \in [0, 1]$ , suggesting that they can form laminate *J* with the interface normal given by  $\mathbf{n}_{23}$ . The laminate *K* can be constructed in a similar manner, which would again be compatible with laminate *J* on average. As a result, the crystal can be constructed by alternating laminates *J* and *K* with interface normal given by  $\mathbf{n}_{34}$ . When there is separation of scale so that the length scale of the bands is much larger than the length scale of twins, yet much smaller than the length scale of the laminates, no stress and electric field will be induced and the energy of the domain configuration will be minimum,<sup>14,16-18</sup> leading to a stable domain configuration and minimum hysteresis.<sup>1,4</sup>

The rank-3 laminates follow from a general procedure for constructing the energy-minimizing microstructure with *N* pair-wise compatible variants.<sup>17,18</sup> A detailed examination of four variants available here, however, suggests that sim-

pler rank-2 laminates are also possible. For example, we can use variants 1 and 3 with equal volume fraction to construct a band *I* of orthorhombic symmetry:

$$\mathbf{e}^I = \begin{bmatrix} \eta & \delta & 0 \\ \delta & \eta & 0 \\ 0 & 0 & \eta \end{bmatrix}, \quad \mathbf{p}^I = \begin{bmatrix} 0 \\ 0 \\ p \end{bmatrix}.$$

Similarly, we can construct a band *J* using variants 2 and 4:

$$\mathbf{e}^J = \begin{bmatrix} \eta & -\delta & 0 \\ -\delta & \eta & 0 \\ 0 & 0 & \eta \end{bmatrix}, \quad \mathbf{p}^J = \begin{bmatrix} 0 \\ 0 \\ p \end{bmatrix}.$$

In each band, only 109° domain wall is present. Clearly, bands *I* and *J* are compatible with each other with interface normal given by [010], thus they can form another level of laminate to represent crystals poled along [001] direction. In a similar fashion, bands *I* and *J* can also be constructed to contain only 71° domain walls using variants 1 and 4, and variants 2 and 3, so that

$$\mathbf{e}^I = \begin{bmatrix} \eta & 0 & \delta \\ 0 & \eta & 0 \\ \delta & 0 & \eta \end{bmatrix}, \quad \mathbf{p}^I = \begin{bmatrix} p \\ 0 \\ p \end{bmatrix},$$

and

$$\mathbf{e}^J = \begin{bmatrix} \eta & 0 & -\delta \\ 0 & \eta & 0 \\ -\delta & 0 & \eta \end{bmatrix}, \quad \mathbf{p}^J = \begin{bmatrix} -p \\ 0 \\ p \end{bmatrix}.$$

In this case, the interface normal between bands *I* and *J* is [001]. Since there are less interfaces involved in rank-2 laminates, it is more likely to occur in crystals. Indeed, interweaving domain configurations containing either 109° or 71° domain wall have been observed in PMN-PT crystals poled along [001] direction.<sup>20</sup>

Since the energy minimizing domain configuration of PMN-PT and PZN-PT can be constructed by multi-rank laminates with distinct length scales, the effective electromechanical moduli of ferroelectric single crystal with engineered domain configuration can be calculated using lamination theory.<sup>5</sup> In particular, within a composite laminate, certain components of electromechanical field need to be continuous across the interface, which allows us to determine its effective electromechanical moduli. For a rank-3 laminate, we repeat the calculation three times: (1) the effective moduli of bands *i*, *j*, and *k* were calculated first with the electromechanical moduli of single-domain single crystal as input, obtained from Ref. 21, which is given in coordinate system  $x_1 \parallel [\bar{1}10]$ ,  $x_2 \parallel [\bar{1}\bar{1}2]$ , and  $x_3 \parallel [111]$ ; (2) the effective moduli of laminate *J* and *K* were then calculated using the effective moduli of bands *i*, *j*, and *k* as input; (3) they were then used as input to calculate the effective moduli of single crystal, which are transformed into a new coordinate system with  $x_1 \parallel [100]$ ,  $x_2 \parallel [010]$ , and  $x_3 \parallel [001]$ . The calculations for the rank-2 laminates follow similar procedures. The calculated piezoelectric coefficients  $d_{31}$  and  $d_{33}$  and electromechanical coupling factor  $k_{31}$  and  $k_{33}$  of four-variant PMN-PT with various kinds of engineered domain configurations are given in Table I, compared with measured values for

TABLE I. Piezoelectric coefficients and electromechanical coupling factors of single crystalline PMN-PT poled along [001] direction;  $d$ :  $10^{-12}$  C/N.

	$d_{31}$	$d_{33}$	$k_{31}$	$k_{33}$
Rank-3	-1100	2210	46%	93%
Rank-2 (109°)	-1152	2309	46%	93%
Rank-2 (71°)	-1038	2196	44%	93%
Experiment	-1330	2820	59%	94%

PMN-PT poled along [001] axis.<sup>22</sup> It is observed that the effective piezoelectric coefficients calculated for rank-3 and rank-2 laminates are one order higher in magnitude than those of single-domain single crystal, agreeing well with experimental measurement. The electromechanical coupling factors, much higher than those of single-domain single crystal, also show excellent agreement with the experiment, especially for  $k_{33}$ . Among all three domain configurations, rank-2 laminate with 109° domain wall agrees with measurement best. This suggests that the engineered domain configurations can indeed lead to the enhanced piezoelectricity in ferroelectric crystals.

It is not clear, however, that whether the four-variant system is optimal as far as the electromechanical couplings are concerned. In particular,  $k_{31}$  for this four-variant system is modest. As such, we also consider a two-variant system where only variants 1 and 3 coexist by 109° domain wall. Such engineered domain configuration can be obtained, for example, if the single crystal is electromechanically poled by an electric field along [001] direction and a positive shear stress  $\sigma_{12}$ . Similarly, we can also construct a two-variant system with only variants 1 and 2 coexisting by 71° domain wall, obtained by poling along [011] direction. In such case, the final coordinate is chosen to be  $x_1 \parallel [0\bar{1}1]$ ,  $x_2 \parallel [100]$ , and  $x_3 \parallel [011]$ . The calculation, along with measured piezoelectric coefficients of a similar crystal PZN-PT poled along [110],<sup>8</sup> is listed in Table II. Again, we observe good agreement between our calculation and experimental measurement for crystal poled along  $\langle 110 \rangle$  direction. In addition, crystal electromechanically poled along [001] direction with two variants coexisting has superior electromechanical coupling coefficients  $k_{31}$ ,  $k_{32}$ , and  $k_{33}$  simultaneously.  $k_{33}$  is comparable to that of four-variant system, while  $k_{31}$  is much higher. This suggests that the two-variant system poled along [001]

TABLE II. Piezoelectric coefficients and electromechanical coupling factors of single crystal with two variants coexisting, poled along [001] or  $\langle 011 \rangle$  direction;  $d$ :  $10^{-12}$  C/N.

	$d_{31}$	$d_{32}$	$d_{33}$	$k_{31}$	$k_{32}$	$k_{33}$
[001] poling + $\sigma_{12}$	-1146	-1158	2309	92%	86%	93%
$\langle 011 \rangle$ poling	700.2	-1629	936.9	71%	84%	89%
$\langle 011 \rangle$ poling, measured	690	-1670	980			

direction with appropriate shear stress applied is optimal for electromechanical coupling.

In summary, we have calculated the effective electromechanical moduli of ferroelectric single crystals with engineered domain configurations, agreeing well with experimental observation. The optimal engineered domain configurations are also identified.

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