Influence of Domain Size to the Properties of Domain Engineered Ferroelectric Crystals

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Outline

• Introduction on domain engineering method
• Symmetry analysis on domain patterns
• Experimental work on BaTiO\textsubscript{3}-Domain size influence
• Time Dependent Landau-Ginzburg model
• Simulation of domain size effects for 2-D systems
• Summary and conclusions
Typical ferroelectric and structural phase transition

Cubic $\rightarrow$ Tetragonal Ferroelectric Phase Transition in BaTiO$_3$

High temperature cubic phase

Low temperature tetragonal phase
Multiple structural phase transitions and multiple variants in each ferroelectric phase.

Ti$^{4+}$ ions displace along edge, face diagonal, and body diagonal.

There are three phase transitions in BaTiO$_3$. 
Multivariants and ferroelectric domains in a cubic-tetragonal phase transition

Paraelectric phase

Ferroelectric phase
Domain Engineering and Macroscopic Property Changes

• Applying electric field in a direction different from the polar axes to pole the crystals

• Introduce pre-designed multi-domain state to enhance particular material properties by controlling the size and orientations of domains
Possible domain configuration and associated polarization orientation in a PMN-PT single crystal after being poled in [001].
Domain pattern of $4mm$ Symmetry

Optical micrograph is for a [001] poled PZN-4.5\%PT single crystal

Two sets of intersecting domains
Domain patterns of mm2 symmetry observed in [001] poled PZN-4.5%PT single crystals
Domain patterns observed on different sample surfaces. (a) and (b) twin bands with fairly large domain size. (c) and (d) Charged and uncharged domain walls join together to form "L" or "T" shaped domain walls.
Illustration of possible domain structures that form the patterns in the above figure. (a) front view. (b) top view. (c) top view. (d) front view.
Possible twin sets for PZN-PT and PMN-PT single crystals with rhombohedral symmetry

<table>
<thead>
<tr>
<th></th>
<th>[001]</th>
<th>[110]</th>
<th>[010]</th>
<th>[101]</th>
</tr>
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<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
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<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
<td><img src="image9.png" alt="Diagram" /></td>
<td><img src="image10.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

Where (a) to (h) represent different possible twin sets with specific crystallographic orientations and angles.
Symmetries of Domain Patterns

• Although the average symmetry for [001] poled PMN-PT and PZN-PT is assumed to be tetragonal 4mm, the symmetry of many samples are actually orthorhombic mm2 or even lower. Fortunately, such symmetry difference will not affect $d_{33}$, but will affect off-diagonal components in property matrices.

• Domain pattern formation is critical for the final effective properties. Experience tells us that smaller domains usually give better properties.
Theoretical domain pattern proposed for [001] poled rhombohedral (monoclinic $M_A$ phase has the same domain wall orientation) phase crystal with 4 co-existing domains. (a) 3-D pattern. (b) Projection in [001].
Orientation effects vs domain averaging

Domain state

Single domain deformation

Twin deformation

Field response
Theoretical calculation of material properties of simple twinned crystals
Effect of volume partition in twins

Monoclinic symmetry

Orthorhombic symmetry

FIG. 1. Twin systems and their symmetry in a \(\overline{m}3m \rightarrow 3m\) ferroelectrics. (a) Unequally partitioned twin of \(P^I\) and \(P^{II}\) with a charged DW oriented in [010]. The shaded plane is the mirror plane. (b) Unequally portioned twin of \(P^I\) and \(P^{III}\) with a neutral wall oriented in [001]. Both (a) and (b) have monoclinic \(m\) symmetry. (c) The same as (a) but with equal partition of the two domains. The symmetry is now orthorhombic \(mm2\) because the DW becomes another mirror symmetry plane. The structures shown in (a) and (c) are used to make the calculations of Table IV and \(v^{(1)}\) is the volume ratio of \(P^I = P_N/\sqrt{3}\) [111].

Simple Average Formula Given in the Literature Cannot be Satisfied

\[
\begin{align*}
\eta_{ij}^{\text{eff}} &= (1)\eta_{ij}^{(1)} + (2)\eta_{ij}^{(2)} \\
E_i^{\text{eff}} &= (1)E_i^{(1)} + (2)E_i^{(2)} \\
T_{ij}^{\text{eff}} &= (1)T_{ij}^{(1)} + (2)T_{ij}^{(2)} \\
D_i^{\text{eff}} &= (1)D_i^{(1)} + (2)D_i^{(2)}
\end{align*}
\]

Basic Assumptions in Our Model:

- Mechanical compatibility (all surfaces and DW have the same displacements in both domains)
- Mechanical stress \( T_{ij} \), strain \( \eta_{ij} \), electric field \( E_i \), and electric displacement \( D_i \) are uniform in each domain
- Constitutive equations

\[
\begin{pmatrix}
\eta \\
D
\end{pmatrix} =
\begin{pmatrix}
s & d^T \\
d & \varepsilon
\end{pmatrix}
\begin{pmatrix}
T \\
E
\end{pmatrix}
\]

have the same form for each domain and for the combined effective medium.
\[ M^{\text{eff}} = [v^{(1)} M^{(1)} (b^{(1)})^{-1} + v^{(2)} M^{(2)} (b^{(2)})^{-1}] [v^{(1)} (b^{(1)})^{-1} + v^{(2)} (b^{(2)})^{-1}]^{-1} \]

\( v^{(1)} \) and \( v^{(2)} \) are volume ratios of domain 1 and domain 2
\[ \mathbf{b}^{(i)} = \begin{pmatrix}
    s_{11}^{(i)} & s_{12}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & d_{11}^{(i)} & d_{21}^{(i)} & d_{31}^{(i)} \\
    s_{13}^{(i)} & s_{23}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & d_{13}^{(i)} & d_{23}^{(i)} & d_{33}^{(i)} \\
    0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
    s_{14}^{(i)} & s_{24}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & d_{14}^{(i)} & d_{24}^{(i)} & d_{34}^{(i)} \\
    s_{15}^{(i)} & s_{25}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & d_{15}^{(i)} & d_{25}^{(i)} & d_{35}^{(i)} \\
    s_{16}^{(i)} & s_{26}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & d_{16}^{(i)} & d_{26}^{(i)} & d_{36}^{(i)} \\
    0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
    d_{21}^{(i)} & d_{22}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & d_{12}^{(i)} & \epsilon_{22}^{(i)} & \epsilon_{23}^{(i)} \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}, \quad (i = 1, 2) \]
### TABLE V. Calculated effective material constants of twinned BaTiO₃ crystal with a neutral DW[110] (units are the same as in Table IV).

<table>
<thead>
<tr>
<th>(\nu^{(1)})</th>
<th>1.00</th>
<th>0.00</th>
<th>0.50</th>
<th>0.55</th>
<th>0.60</th>
<th>0.65</th>
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<tr>
<td>(S_{11})</td>
<td>7.92</td>
<td>7.92</td>
<td>7.49</td>
<td>7.49</td>
<td>7.51</td>
<td>7.52</td>
<td>7.55</td>
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<tr>
<td>(S_{12})</td>
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<td>-1.28</td>
<td>-1.71</td>
<td>-1.71</td>
<td>-1.69</td>
<td>-1.68</td>
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<tr>
<td>(S_{33})</td>
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<td>-3.88</td>
<td>-3.47</td>
<td>-3.47</td>
<td>-3.48</td>
<td>-3.50</td>
<td>-3.52</td>
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<tr>
<td>(S_{44})</td>
<td>-3.83</td>
<td>-3.83</td>
<td>0.34</td>
<td>0.69</td>
<td>1.04</td>
<td>1.39</td>
<td></td>
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<tr>
<td>(S_{55})</td>
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<td>2.27</td>
<td>7.49</td>
<td>7.49</td>
<td>7.51</td>
<td>7.52</td>
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<td>(S_{66})</td>
<td>-3.83</td>
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<td>1.04</td>
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<tr>
<td>(S_{33})</td>
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<td>7.84</td>
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<td>(S_{44})</td>
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<td>7.49</td>
<td>7.51</td>
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<td>(S_{66})</td>
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<tr>
<td>(d_{11})</td>
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<td>156.66</td>
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<tr>
<td>(\varepsilon_{11})</td>
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<td>(\varepsilon_{23})</td>
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</table>

The two domains are \(F^\prime = P_s / \nu \), \(F^\prime = P_s / \nu \) of Table II. Data blanks represent that the corresponding component is zero and the column of \(\nu^{(1)} = 0.5\) are not available.

### TABLE VI. Calculated effective material constants of twinned KNbO₃ crystal (units are the same as in Table IV).

<table>
<thead>
<tr>
<th>(\nu^{(1)})</th>
<th>1.00</th>
<th>0.00</th>
<th>0.50</th>
<th>0.55</th>
<th>0.60</th>
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<tr>
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<td>5133</td>
<td>5133</td>
<td>5133</td>
</tr>
</tbody>
</table>

The two domains in the twin are \(F^\prime = P_s / \nu \), \(F^\prime = P_s / \nu \) of Table III with a charged DW oriented in [010] as shown in Fig. 3(g).
Domain size influence to the macroscopic properties

--- Experimental work on BaTiO$_3$

Engineering domain pattern by applying a poling field along [111] for a tetragonal phase BaTiO$_3$ single crystal whose polarization is along {001}.

Domain size can be controlled by poling temperatures and poling rate.
Domain patterns produced in BaTiO₃ poled along [111]

(a) Domain size > 40 µm  
(b) Domain size = 13.3 µm  
(c) Domain size = 6.5 µm
Table 1  Piezoelectric properties of BaTiO$_3$ single crystals poled along [001]$_c$ and [111]$_c$ directions

<table>
<thead>
<tr>
<th>BaTiO$_3$ single crystal</th>
<th>$\varepsilon^T_{33}$</th>
<th>$s^{E}_{11}$, pm$^2$ N$^{-1}$</th>
<th>$d_{31}$, pC N$^{-1}$</th>
<th>$k_{31}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]$_c$ (single domain)*</td>
<td>129</td>
<td>7.4</td>
<td>-33.4</td>
<td>...</td>
</tr>
<tr>
<td>[111]$_c$ (single domain)$\dagger$</td>
<td>...</td>
<td>...</td>
<td>-62.0</td>
<td>...</td>
</tr>
<tr>
<td>[111]$_c$ (&gt; 40 (\mu)m domain size)$\ddagger$</td>
<td>2185</td>
<td>7.37</td>
<td>-97.8</td>
<td>25.9</td>
</tr>
<tr>
<td>[111]$_c$ (13.3 (\mu)m domain size)</td>
<td>2087</td>
<td>7.68</td>
<td>-134.7</td>
<td>35.7</td>
</tr>
<tr>
<td>[111]$_c$ (6.5 (\mu)m domain size)</td>
<td>2441</td>
<td>8.80</td>
<td>-180.1</td>
<td>41.4</td>
</tr>
<tr>
<td>‘Soft’ PZT ceramic</td>
<td>1700</td>
<td>16.4</td>
<td>-171.0</td>
<td>34.4</td>
</tr>
</tbody>
</table>

* Measured by Zgonik et al.$^{16}$

$\dagger$ Calculated using values measured by Zgonik et al.$^{16}$

$\ddagger$ Measured by Jaffe et al.$^{17}$
Experimental conclusion:

As the size of the domains gets smaller ....

- Dielectric constant increases
- Piezoelectric constant increases

Why?
Time Dependent Ginzburg-Landau model for a 2-D ferroelectric system

Free energy for the polarization:

\[
F_i = \int d\vec{r} \left\{ \alpha_1 (P_x^2 + P_y^2) + \alpha_{11} (P_x^4 + P_y^4) + \alpha_{12} P_x^2 P_y^2 \\
+ \alpha_{111} (P_x^6 + P_y^6) + \alpha_{112} (P_x^2 P_y^4 + P_x^4 P_y^2) - E_x P_x - E_y P_y \\
+ \frac{g_1}{2} (P_{xx}^2 + P_{yy}^2) + \frac{g_2}{2} (P_{x,y}^2 + P_{y,x}^2) + g_3 P_{xx} P_{yy} \right\}, \quad (1)
\]

Elastic energy

\[
F_{el} = \int d\vec{r} \left( \frac{1}{2} c_1 \eta_1^2 + \frac{1}{2} c_2 \eta_2^2 + \frac{1}{2} c_3 \eta_3^2 \right)
\]
2-D GINZBURG-LANDAU MODEL
For a Square-Rectangular Ferroelectric Phase Transition
Electromechanical coupling energy is the mechanical deformation energy from the homogenous state

\[ F_{em} = \lambda \int d\vec{r} \left[ \eta_1 - Q_1 (P_x^2 + P_y^2) \right]^2 + \left[ \eta_2 - Q_2 (P_x^2 - P_y^2) \right]^2 + \left[ \eta_3 - Q_3 P_x P_y \right]^2 \]. \tag{2} \]

The area strain, deviatoric strain and shear strain are defined as:

\[ \eta_1 = \eta_{xx} + \eta_{yy}, \quad \eta_2 = \eta_{xx} - \eta_{yy}, \quad \text{and} \quad \eta_3 = \eta_{xy}, \]

where \( \eta_{ij} \) is the linearized strain tensor

\[ \eta_{ij} = (u_{i,j} + u_{j,i})/2 \]
Elastic compatibility relations

\[ \nabla^2 \eta_1 - \left( \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right) \eta_2 - \frac{\partial^2}{\partial x \partial y} \eta_3 = 0. \]

Using this relation to eliminate \( \eta_1 \), then the coupling energy in \( k \)-space can be written as:

\[ F_{em}^{inh} = \lambda \int d\vec{k} |C_2(\vec{k}) \Gamma_2(\vec{k}) + C_3(\vec{k}) \Gamma_3(\vec{k}) - \Gamma_1(\vec{k})|^2 \]

The quantities \( \Gamma_1(\vec{k}), \Gamma_2(\vec{k}), \) and \( \Gamma_3(\vec{k}) \) are respectively the Fourier transforms of \( Q_1(P_x^2 + P_y^2), Q_2(P_x^2 - P_y^2), \) and \( Q_3 P_x P_y \); \( C_2 = (k_x^2 - k_y^2)/(k_x^2 + k_y^2) \) and \( C_3 = k_x k_y/(k_x^2 + k_y^2) \) are the orientation-dependent kernels.
Electrostatic energy due to depolarization field:

$$F_{es} = -\mu \int d\vec{r} \{ \vec{E}_d \cdot \vec{P} + \epsilon_0 (\vec{E}_d \cdot \vec{E}_d / 2) \}.$$  

When there are no free charges, we have the following constraint from Maxwell Equations

$$-\epsilon_0 \nabla^2 \phi + \nabla \cdot \vec{P} = 0 \quad \text{where} \quad E_d = -\nabla \phi$$

This can help to eliminate $E_d$ so that in k-space the electrostatic energy is given by,

$$F_{es} = \frac{\mu}{2\epsilon_0} \int d\vec{k} |\hat{k}_x P_x(\vec{k}) + \hat{k}_y P_y(\vec{k})|^2$$
Master Equation for relaxation process (TDGL)

\[
\frac{\partial P_i}{\partial t} = -\gamma \frac{\delta F}{P_i}
\]

\(\gamma\) is the relaxation coefficient

Using the parameters for BaTiO\textsubscript{3} single crystals (which can be dependent on temperature \(T\)):

\[
\alpha_1 = 3.34 \times 10^5 (T-381) \text{ V m C}^{-1}, \quad \alpha_{11} = 4.69 \times 10^6 (T-393) - 2.02108 \text{ Vm}^5 \text{ C}^{-3},
\]

\[
\alpha_{111} = -5.52 \times 10^7 (T-393) + 2.76 \times 10^9 \text{ Vm}^9 \text{ C}^{-5}, \quad \alpha_{111} = 3.23 \times 10^8 \text{ Vm}^5 \text{ C}^{-3}, \text{ and}
\]

\[
\alpha_{112} = 4.47 \times 10^9 \text{ Vm}^9 \text{ C}^{-5}. \quad \text{The electrostrictive constants are given as}
\]

\[
Q_{11} = 0.11 \text{ m}^4 \text{ C}^{-2}, \quad Q_{12} = -0.045 \text{ m}^4 \text{ C}^{-2}, \quad \text{and} \quad Q_{44} = 0.029 \text{ m}^4 \text{ C}^{-2}.
\]

To calculate the rescaled quantities, we use

\(T_0 = 298 \text{ K} \) and \(P_0 = 0.26 \text{ C m}^{-2}\)
Normalized form of the TDGL equation:

\[ u_{i,t} = u - u^3 - duv + a u_{x,x} + b u_{y,y} + c v_{x,y} + e_x - \mu \int dk^* H(k^*) \Gamma(k^*) \exp(-k^* \cdot r^*) \]

\[ v_{i,t} = v - v^3 - du^2 v + a v_{y,y} + b v_{x,x} + c u_{x,y} + e_y + \nu \int dk^* H(k^*) \Gamma(k^*) \exp(-k^* \cdot r^*) \]

Grid size: 128x128, with the length normalization of \( \delta = 0.5 \) nm, it corresponds to a system of 64x64nm²

Electric field is applied along [11]
Preset size of 90° domains—initial condition

Consider a function

\[ R(x, y) = \cos \left( \frac{N \pi (x + y)}{128 \delta} \right) \]

We set

\[ P_x(x, y) = P_0, \quad P_y(x, y) = 0, \quad R(x, y) > 0, \]

\[ P_x(x, y) = 0, \quad P_y(x, y) = P_0, \quad R(x, y) < 0. \]

<table>
<thead>
<tr>
<th>N</th>
<th>Domain size (nm)</th>
<th>No of domain walls</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22.6</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>11.3</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>6.5</td>
<td>20</td>
</tr>
</tbody>
</table>
Case I  $N=2$, 4 domain walls

The largest domain size simulated.
$E_x = E_y = 0$
\[ E_{[11]} = 8.316 \text{ kV/cm}, \]
\( E_{[11]} = 22.177 \text{ kV/cm}, \)
$E_{[11]} = 23.01 \text{ kV/cm}$,
Field induced phase transition to rhombic phase

$E_{[11]} = 24.025 \text{ kV/cm}$,
• As the field increases, the domain wall width increases but the number of domain walls does not change.

• The field produced deformation strain is the piezoelectric effect

• A field induced phase transition occurs at $E = 24.05$ kV/cm.
Case II  \( N=4, \) 8 domain walls

Domain size is reduced to half of the first case
$E_x = E_y = 0$
$E_{[11]} = 8.316 \text{ kV/cm}$,
$E_{[11]} = 12.936 \text{ kV/cm},$
$E_{[11]} = 17.557 \text{ kV/cm}$,
$E_{[11]} = 18.481 \, \text{kV/cm,}$
$E_{[11]} = 19.404 \text{ kV/cm}$,
• As the field increases, the domain wall width increases but the number of domain walls do not change.

• The field produced deformation is causes effective piezoelectric effect

• A field induced phase transition occurs at 
E = 19.404 kV/cm.
Case III  N=10, 20 domain walls

Smallest domain size case simulated
$E_{[1]} = 0.924 \text{ kV/cm},$
$E_{[11]} = 1.848 \text{ kV/cm}$,
\[ E_{[11]} = 2.772 \text{ kV/cm}, \]
$E_{[11]} = 3.696 \text{ kV/cm}$,
$E_{[11]} = 4.620 \text{ kV/cm}$,
• More dipoles tilt away from the [01] and [10] directions

• Relatively large elastic deformation observed

• The field induced phase transition occurs at a much reduced field level of only

E = 4.620 kV/cm
Evolution of average polarizations $P_{[10]}$ (a) and $P_{[01]}$ (b) with the applied field $E_{[11]}$. Solid lines correspond to the single-domain state with initial polarization along [01]. One can see that the average polarization are not zero in both [10] and [01] directions, which reflects the tilt of the polarization vectors in the domain wall regions. Smaller domains have more such titled dipoles, hence have larger non-zero components along the two principal directions.
Evolution of average field induced longitudinal strains (a) and (b) and the shear strain (c) by the applied field $E_{11}$. Solid lines correspond to the single-domain state with initial polarization along [01].
Calculation of the piezoelectric coefficient

Longitudinal strain along [01] and [10]

\[ <\eta_{xx}(E_{11})> - <\eta_{xx}(0)> \quad <\eta_{yy}(E_{11})> - <\eta_{yy}(0)> \]

Shear strain

\[ <\eta_{xy}(E_{11})> - <\eta_{xy}(0)> \]

Induced strain by an electric field along [11]

\[ \eta_{11} = \frac{1}{2}(\eta_{xx} + \eta_{yy} + \eta_{xy}) \]

Effective piezoelectric coefficient along [11]

\[ d_{33}^{[11]} = \frac{d\eta_{11}}{dE_{11}} \]
Variation of $d_{33}$ (the longitudinal piezoelectric constant along [11] with $E/[11]$). The lines with circles correspond to the multidomain state with domain size $L_0 \sim 22.6$ nm, lines with crosses correspond to the multidomain state of with domain size $L_0 \sim 11.3$ nm, and lines with squares correspond to the multidomain state with domain size $L_0 \sim 4.5$ nm. Solid lines correspond to the single domain state.
Summary and conclusions

- Domain engineering is a new way to enhance certain material properties. There are two factors contributing to the enhancement. One is the orientation effect and the other is the lattice distortion in domain wall regions.
- Domain pattern symmetry determines the macroscopic properties of materials. Domain pattern symmetry can be higher or lower than the crystal symmetry.
- There is a strong domain size dependence of physical properties of domain engineered crystals. Smaller domain systems can produce large piezoelectric effect due to the dipole title in the domain wall regions.
- The electric field induced structural phase transition occurs at smaller field level in smaller domain size systems, which can be used to interpret the enhancement due to domain size reduction.