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Citation: *Appl. Phys. Lett.* **97**, 252904 (2010); doi: 10.1063/1.3530443

View online: <http://dx.doi.org/10.1063/1.3530443>

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Piezoelectric response of single-crystal $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ near morphotropic phase boundary predicted by phase-field simulation

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(Received 7 August 2010; accepted 2 December 2010; published online 23 December 2010)

The piezoelectric property of hypothetical single-crystal $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) is studied using phase-field simulations. The dependence of piezoelectric coefficient (d_{33}) on PbTiO_3 compositions (x) near the morphotropic phase boundary of PZT was obtained. Using the existing thermodynamic description of PZT, it is shown that d_{33} reaches a peak value of 720 pC/N at $x=0.47$ which is more than three times of that for the ceramic counterpart. The relation between the domain structure of the poled PZT single crystals and the enhancement of d_{33} near the MPB composition is discussed.

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Lead zirconate-titanate $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) ceramic is the most widely studied and utilized ferroelectric piezoelectric system in multilayer actuators, sonar and ultrasonic transducers, ultrasonic motors, and Microelectromechanical systems (MEMS) devices.¹⁻⁷ The piezoelectric coefficients d_{33} of PZT as well as many other solid-solution-based relaxor piezoelectric ceramics such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 (PMN-PT) are at the order of a few 10^2 pC/N.^{4,5,8,9} Piezoelectric properties vary with composition and typically exhibit the highest values near the “morphotropic phase boundary” (MPB), which separates two low-temperature ferroelectric phases in the temperature-composition phase diagram. Recently it was discovered that relaxor-based piezoelectric single crystals display much higher piezoelectric coefficients of several 10^3 pC/N, an order of magnitude higher than their polycrystalline counterparts.¹⁰⁻¹⁵ However, despite the widespread use of PZT ceramics, there exist limited fabrication and associated measurements of single-crystal piezoelectric properties due to the difficulty in growing sufficiently large size of PZT single crystals.¹⁶⁻²⁰ Recently it was discovered that a similar system, the solid solution of $x\text{BiScO}_3$ – $(1-x)\text{PbTiO}_3$ single crystals with composition near MPB ($x=0.43$), exhibits good piezoelectric properties that are comparable to the properties of PZN-PT and PMN-PT single crystals.²¹⁻²⁴ The finding raises the question whether the conventional ferroelectric solid solutions of PZT also exhibit large enhancement in piezoelectric responses in the single-crystal form compared to the corresponding ceramic polycrystals. In light of this, the main purpose of this work is to apply phase-field simulations to investigate the piezoelectric responses of PZT single crystals as a function of composition near the MPB and compare them with known experimental data on PZT ceramics at similar compositions.

The phase-field approach has been applied to predicting ferroelectric domain structures and switching of PZT systems.²⁵⁻³⁰ In this method, the spontaneous polarization vector $\mathbf{P}=(P_1, P_2, P_3)$ describes the domain structures in PZT. The total free energy F of a PZT single crystal is expressed as

$$F = \int_V (f_{\text{lan}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{elec}}) dV, \quad (1)$$

where f_{lan} , f_{grad} , f_{elas} , and f_{elec} are stress-free bulk free energy, gradient energy, elastic energy, and electrostatic energy density, respectively. The detailed expressions of f_{lan} , f_{grad} , and f_{elas} can be found in Refs. 26 and 31. The electrostatic energy density is given by

$$f_{\text{elec}} = f(E_i, P_i) = -\frac{1}{2} \epsilon_0 \kappa_{ij} E_i E_j - E_i P_i, \quad (2)$$

where E_i is the electric field component, which includes both the applied electric field and the electric field due to the polarization distribution, ϵ_0 and κ_{ij} are the vacuum permittivity and dielectric constant, respectively. With all the energy contributions to the total free energy F , the temporal evolution of nonequilibrium order parameter \mathbf{P} and the domain structures were obtained by solving the time-dependent Ginzburg–Landau (TDGL) equation

$$\frac{\partial P_i(\mathbf{r}, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(\mathbf{r}, t)}, \quad (i = 1, 2, 3), \quad (3)$$

where L is a kinetic coefficient related to the domain-wall mobility and t is the time.

In our simulation, we chose bulk $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) single crystals with composition (x) near MPB (Ti/Zr = 48/52 for PZT) at $T=25^\circ\text{C}$. The system size of $128\Delta r \times 128\Delta r \times 128\Delta r$ is employed and the periodical boundary condition is applied along r_1 , r_2 , and r_3 directions. The semi-implicit Fourier-spectral method was employed.³² The spacing between any two nearest grid points is chosen to be $\Delta r = \sqrt{G_{110}/\alpha_0}$ and $\alpha_0 = |\alpha_1|_{T=25^\circ\text{C}}$. Furthermore the gradient en-

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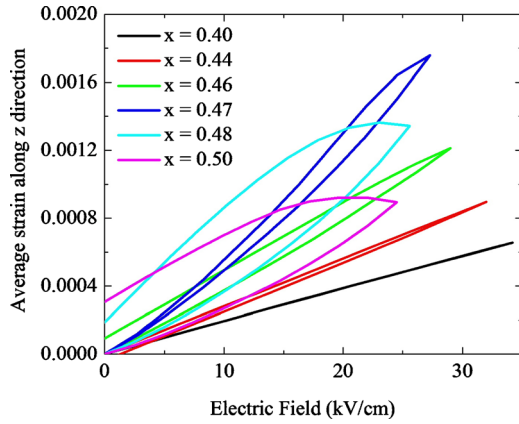


FIG. 1. (Color online) Strain-electric field ($\bar{\epsilon}_{33}-E_3$) behaviors of PZT single crystals with different compositions (x -PbTiO₃).

ergy coefficients are chosen to be $G_{11}/G_{110}=0.6$, $G_{12}/G_{110}=0$, and $G_{44}/G_{110}=G_{44}^*/G_{110}=0.3$. The Landau coefficients, the electrostrictive coefficients (Q_{11} , Q_{12} and Q_{44}), and the elastic compliance tensors (s_{11} , s_{12} , s_{44}) as a function of x are collected from literature.³³

For each PbTiO₃ composition x , an initial domain structure is first generated by assigning a zero value at each cell for each component of polarization with a small random noise, corresponding to the paraelectric state. It is then held at room temperature at which the paraelectric state evolves to a ferroelectric multidomain state following the TDGL equation. We poled the domain by applying a [001] direction electric field, increase to certain magnitude, and remove the field before the rhombohedral to tetragonal phase transition occurs. The piezoelectric coefficient is then measured by applying a [001] electric field again upon the poled domain structure, increase it to a relatively smaller magnitude (~ 30 kV/cm), and reduce back to 0 with strain-electric field loop recorded. The piezoelectric coefficient d_{33} at a given composition is determined using the usual definition, $d_{33} = d\bar{\epsilon}_{33}/dE_3$.

Figure 1 displays the strain-electric field behavior of poled PZT single crystals with composition (x -PbTiO₃) from 0.40 to 0.50. It can be seen that when x is lower than the MPB composition, the overall strain increases linearly with electric field while for compositions close to MPB ($x=0.47$, 0.48, and 0.50), obvious hysteresis loops exist. These loops are attributed to the existence of mixed rhombohedral and tetragonal phases at MPB composition. For $\bar{\epsilon}_{33}-E_3$ loop showing hysteresis, d_{33} is defined by taking the slope of the strain at maximum applied electric field to the origin ($d_{33} = \Delta\bar{\epsilon}_{33}/\Delta E = \bar{\epsilon}_{33}|_{\max}/E_{\max}$). From Fig. 1 the strongest piezoelectric response occurs at $x=0.47$.

Figure 2 gives the dependence of piezoelectric coefficients on PbTiO₃ composition for both PZT single crystals obtained in this work and ceramics from the literature.⁴ In both cases, the piezoelectric responses reach peaks in the region of MPB. For PZT ceramics, the maximum piezoelectric coefficient (d_{33}) is reported to be 223 pC/N at $x=0.48$;⁴ while for PZT single crystals, the d_{33} reaches a peak of 720 pC/N at $x=0.47$ which is more than three times of the ceramic case. Even at other compositions, PZT single crystals exhibit much larger d_{33} than PZT ceramics. Significant enhancement of d_{33} in single crystal form was also observed in PMN-PT relaxors as compared to their ceramic form.^{9,12} Fig-

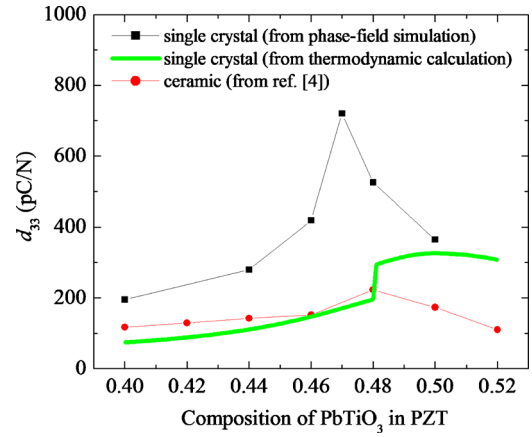


FIG. 2. (Color online) Piezoelectric coefficients (d_{33}) as a function of composition (x -PbTiO₃) for both ceramic and single crystal PZT.

ure 2 also includes the predicted d_{33} values as a function of x for PZT single crystals assuming a single rhombohedral domain for $x < 0.48$ and a single tetragonal domain for $x > 0.48$ based on thermodynamic calculations. It is found that the predicted d_{33} is also lower than the values of single crystal based on phase-field calculation.

To understand the peak piezoelectric response at MPB composition, as well as the enhancement of d_{33} in multidomain single crystals than those in ceramics and single-domain single crystals, we further investigate the poled domain structure of PZT single crystal at MPB composition as shown in Fig. 3. For three-dimensional PZT single crystal at MPB composition without electric field, the initial domain structure consists of eight equivalent [111] rhombohedral variants and six [100] tetragonal variants. After the domain is poled along [001] direction, four of the total eight rhombohedral variants with polarization component $P_3 > 0$ and $(0, 0, +P_3)$ tetragonal domain are favored. It has been pointed out that a multidomain state is easier to switch than a single domain case since a large number of possible directions are

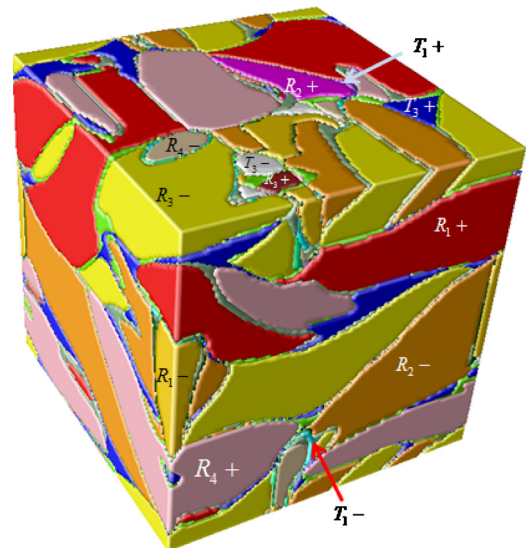


FIG. 3. (Color online) A snapshot of the multidomain structure of a PZT single crystal after poling: $R_{1+}:(+P_1,+P_2,+P_3)$; $R_{1-}:(-P_1,-P_2,-P_3)$; $R_{2+}:(+P_1,+P_2,-P_3)$; $R_{2-}:(-P_1,-P_2,+P_3)$; $R_{3+}:(+P_1,-P_2,-P_3)$; $R_{3-}:(-P_1,+P_2,+P_3)$; $R_{4+}:(+P_1,-P_2,+P_3)$; $R_{4-}:(-P_1,+P_2,-P_3)$; $T_{1+}:(+P_1,0,0)$; $T_{1-}:(-P_1,0,0)$; $T_{2+}:(0,+P_2,0)$; $T_{2-}:(0,-P_2,0)$; $T_{3+}:(0,0,+P_3)$; $T_{3-}:(0,0,-P_3)$.

available along which the polarization can be reoriented.^{34,35} Therefore, it helps to increase the piezoelectric coefficients at MPB. PZT single crystals with $x < \text{MPB}$ composition is composed of rhombohedral phase only, while PZT single crystals with $x > \text{MPB}$ composition is dominated by tetragonal phase. In either case, the number of domain variants is less than that of MPB composition and the piezoelectric response is inhibited. This also explains why the piezoelectric coefficients are much smaller in PZT single-domain single crystals.

The significant increase of piezoelectric coefficients in multidomain PZT single crystals compared to PZT ceramics is due to the random distribution of grain orientation in ceramics. The piezoelectric coefficient d_{33} of polycrystals is calculated as the average of different grain orientations, rather than the maximum d_{33} in polycrystals. On the other hand, it has been reported that the grain boundaries severely inhibit the domain wall motion due to the elastic coupling between domain wall and grain boundary.³⁶ Thus the domain evolution becomes more difficult and the piezoelectric response is significantly inhibited.

It should be pointed out that the above results were obtained using a dielectric constant of 100.0. There have been a number of recent discussions on the use of dielectric constants in conjunction with the Landau thermodynamic description of ferroelectrics.^{37–42} These include the use of vacuum dielectric constant 1.0,^{37,38} or so-called the background dielectric constant, and the dielectric permittivity of a ferroelectric crystal far away from the ferroelectric instability temperature.^{39–41} Background dielectric constant values from 7.0–10.0 (Ref. 41) to 50.0–100.0 (Ref. 39) have been suggested. We have used the high end for the range of background dielectric constant values considering the fact that we ignore the presence of charged defects that may compensate polarization changes, which effectively decrease the electrostatic field and thus an apparent increase in the dielectric constant.

In summary, we studied the piezoelectric response to the [001] electric field in bulk $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ single crystals $x=0.40\text{--}0.50$ near the MPB. The peak piezoelectric coefficient d_{33} around 720 pC/N is observed at $x=0.47$. As it has been suggested previously, this large increase is attributed to the largest number of possible domain variants present at MPB composition. Similar to PMN-PT, bulk PZT single crystal exhibits large increase of d_{33} with respect to its ceramic counterpart.

The authors are grateful to the financial support for NSF-IUCRC Center for Dielectric Studies at Penn State and the National Science Foundation under Grant Nos. ECCS-0708759 and DMR-1006541.

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