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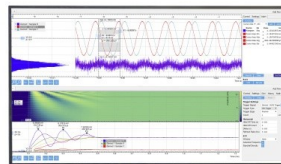
Origin of high piezoelectric response of Pb(Zr$_x$Ti$_{1-x}$)O$_3$ at the morphotropic phase boundary: Role of elastic instability

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Temperature dependent structural changes in a nearly pure monoclinic phase composition ($x=0.525$) of Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) have been investigated using Rietveld analysis of high-resolution synchrotron powder x-ray diffraction data and correlated with changes in the dielectric constant and planar electromechanical coupling coefficient. Our results show that the intrinsic piezoelectric response of the tetragonal phase of PZT is higher than that of the monoclinic phase. It is also shown that the high piezoelectric response of PZT may be linked with an anomalous softening of the elastic modulus $(1/S_{11}^E)$ of the tetragonal compositions closest to the morphotropic phase boundary. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2836269]

A unique feature of the phase diagrams of the technologically important solid solution systems between the ferroelectric PbTiO$_3$ and the antiferroelectric PbZrO$_3$ or relaxor ferroelectrics such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ is the existence of a nearly vertical morphotropic phase boundary (MPB) for which the dielectric and piezoelectric properties show exceptionally high values.[1] There is no satisfactory explanation for this phenomenon. The currently most acceptable model of high piezoelectricity in these materials is based on the premise that the recently discovered intermediate monoclinic phases[2–7] can mediate the rotation of the polarization vector from the [111] polarization direction of the rhombohedral phase to the [001] of the tetragonal phase.[8,9] The results of a high-resolution x-ray powder diffraction study on sintered Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) samples[10] show that the field induced piezoelectric elongations in the tetragonal and rhombohedral compositions occur not along the polar [001] and [111] directions but along the [101] and [001] directions, respectively, corresponding to the atomic displacements in the monoclinic *Cm* phase, which have been taken as evidence for the polarization rotation model. The first-principles calculations by Bellaiche *et al.*[11] suggest that the monoclinic phase possesses intrinsically higher piezoelectric properties, as compared to the tetragonal and rhombohedral phases of the neighboring compositions. However, no attempt has so far been made to compare the piezoelectric properties of the monoclinic phase of PZT with those of the tetragonal and rhombohedral phases for the same composition. In the present work, we have addressed this question experimentally for the tetragonal and monoclinic phases of the PZT system. Much to our surprise, we find that it is the tetragonal phase, and not the monoclinic phase, which has superior piezoelectric properties. The higher piezoelectric response of PZT near MPB is found to be linked with an anomalous elastic softening around the room temperature for the tetragonal compositions close to the MPB.

Chemically homogeneous and highly stoichiometric PZT powders were prepared by the semiwet route developed by Singh *et al.*[12] High-resolution synchrotron x-ray diffraction (XRD) data were recorded using 8C2 HRPD beamline at Pohang Light Source (PLS), Pohang Accelerator Laboratory, Pohang, Korea. For dielectric and piezoelectric characterizations, sintered PZT pellets with densities greater than 98% were electroded with fired-on silver paste. Poling was carried out by applying 20 kV/cm dc field for 50 min at 373 K in silicon oil bath. Dielectric measurements on unpoled and poled samples were carried out at 100 KHz using a Schlumberger (SI 1260) impedance/gain phase analyzer. The planar electromechanical coupling coefficient (k_P) was determined by following the procedure described in Ref. 1. FULLPROF program[13] was used for Rietveld analysis of the XRD data. Anisotropic peak broadening functions due to Stephens[14] were used to model peak profiles. Background was modeled using fifth order polynomial. In agreement with the earlier reports,[2,3] anisotropic thermal parameters were found necessary for the Pb atom in the refinements; for the remaining atoms isotropic thermal parameters were found adequate.

We have recently shown that the structure of PZT is tetragonal (space group *P4mm*) and monoclinic (space group *Cm*) for $x \le 0.515$ and $x \ge 0.525$ while the two phases coexist for $x=0.520$.[15] The monoclinic structure of $x=0.525$ transforms to the tetragonal structure upon heating above room temperature due to the tilted nature of the MPB toward the Zr-rich region.[1] Figure 1 depicts the XRD profiles of the pseudocubic 110, 111, and 200 reflections along with the Rietveld fits obtained from full pattern refinements in the two-theta range of 18°–130° at three representative temperatures. The observed and calculated profiles match extremely well using monoclinic (*Cm*) and tetragonal (*P4mm*) phase models at 300 and 570 K [see Figs. 1(a) and 1(c)]. For the
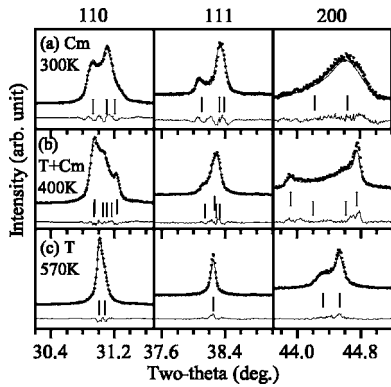
FIG. 1. Temperature evolution of the 110, 111, and 200 pseudocubic powder synchrotron x-ray diffraction profiles of Pb(Zr$_{0.525}$Ti$_{0.475}$)O$_3$. The solid dots show the observed diffraction profiles, while the continuous line shows the calculated patterns obtained by the Rietveld analysis of the data for different structures. The vertical tick marks show the positions of various Bragg reflections.

FIG. 3. Temperature variation of the real part of the dielectric constant (ε') for Pb(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x=0.525$: (a) Poled and (b) unpoled sample.

temperature range (350–550 K) across the monoclinic to tetragonal phase transition temperature, the monoclinic and the tetragonal phases coexist, as can be seen from the excellent Rietveld fits to the observed XRD data for a representative temperature (400 K) in Fig. 1(b). The evolution of the unit cell parameters as a function of temperature, as obtained by Rietveld analysis of the XRD data at each temperature, is shown in Fig. 2, which reveals monoclinic to tetragonal phase transition around 490 K and tetragonal to cubic transition around 650 K. Both transitions are found to be of first order, as inferred from the coexistence of the low and high temperature phases across the phase transition temperature.

The monoclinic to tetragonal phase transition is accompanied with an anomaly in the dielectric constant, which is found to occur at the same transition temperature ($\sim$493 K) for both unpoled and the poled samples [see Figs. 3(a) and 3(b) for $x=0.525$]. Thus, poling does not affect the monoclinic to tetragonal phase transition temperature. The monoclinic to tetragonal phase transition temperature obtained by dielectric measurements is in close agreement with the transition temperature ($\sim$490 K) obtained from the XRD studies (see Fig. 2). The temperature variation of the planar electromechanical coupling coefficient (k_P) and piezoelectric strain coefficient (d_{31}) for $x=0.525$ is shown in Fig. 4(a). The d_{31} values were obtained using Eq. (6) on page 293 of Ref. 1. It is evident from this figure that upon heating above the room temperature ($\sim$300 K), the values of k_P and d_{31} gradually increase and peak at the monoclinic to tetragonal phase

transition temperature of $\sim$490 K. Above the transition temperature, k_P and d_{31} finally stabilize to nearly temperature independent values of $\sim$0.44 and $\sim$125 pC/N, respectively, in the tetragonal phase. These values are significantly higher than the room temperature values of $k_P \sim 0.35$ and $d_{31} \sim 55$ pC/N for the monoclinic phase. This shows that the piezoelectric response of the tetragonal phase is distinctly higher than that of the monoclinic phase. The intrinsic difference between the k_P and d_{31} values of the tetragonal and monoclinic phases may be higher than $\sim$0.1 and 70, respectively, since at high temperatures (above the tetragonal to monoclinic transition temperature), partial depoling can lead to the deterioration of the piezoelectric response of the tetragonal phase. Figure 4(a) shows one more peak in k_P versus temperature plot below room temperature, which is linked with the phase transition from the monoclinic Cm phase to a superlattice monoclinic phase with Cc space group.[4,5] We find that higher piezoelectric response of the tetragonal phase vis-à-vis the monoclinic phase is a common feature of other tetragonal compositions as well, as can be seen from Figs. 4(b) and 4(c) for $x=0.520$ and 0.515. The k_P for all the three compositions shown in Fig. 4 is nearly temperature independent above the monoclinic Cm to tetragonal phase transition temperature, and its value is significantly higher than that of the Cm phase.

The clue to this higher piezoelectric response of the tetragonal phase, as compared to the monoclinic Cm phase, lies in the softening of some elastic modulii on approaching the tetragonal to monoclinic phase transition temperature. The elastic modulus ($1/S_{11}^E$) of the poled PZT ceramics can be estimated from the piezoelectric resonance frequency (f_r) using the relationship, $1/S_{11}^E = \pi^2 d^2 f_r^2 (1 - \sigma^{E2}) \rho / \eta_1^2$, where d is the diameter of the pellet, ρ is the density, and σ^E ($=0.31$) and η_1 ($=2.05$) are the constants.[1] The variation of
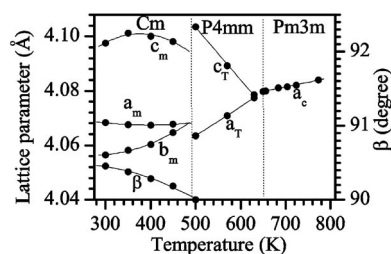

FIG. 2. Evolution of the lattice parameters with temperature obtained after Rietveld analysis of the synchrotron XRD data for Pb(Zr$_{0.525}$Ti$_{0.475}$)O$_3$. For easy comparison, the equivalent perovskite cell parameters a_m and b_m calculated from the monoclinic cell parameters A_m and B_m, are plotted in the monoclinic region ($a_m = A_m/\sqrt{2}$, $b_m = B_m/\sqrt{2}$).
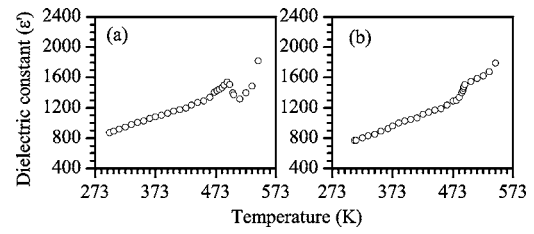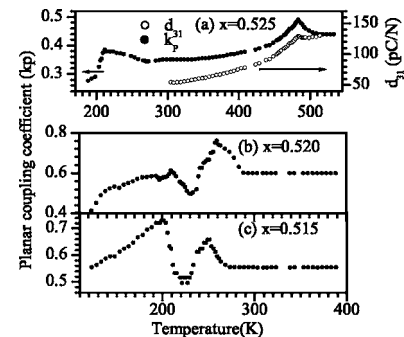

FIG. 4. Temperature variation of the planar electromechanical coupling coefficient (k_P) of Pb(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics: (a) $x=0.525$, (b) $x=0.520$, and (c) $x=0.515$. For $x=0.525$, the temperature dependence of d_{31} is also shown in (a).
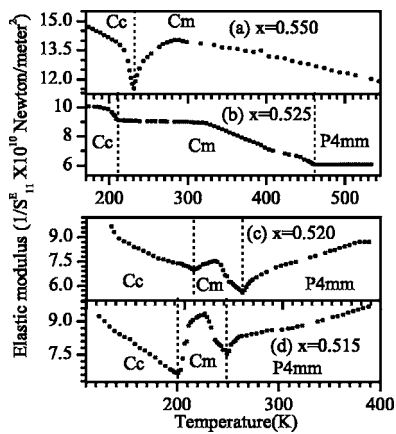
FIG. 5. Temperature variation of the elastic modulus $(1/S_{11}^E)$ of $Pb(Zr_xTi_{1-x})O_3$ ceramics: (a) $x=0.550$, (b) $x=0.525$, (c) $x=0.520$, and (d) $x=0.515$.

$1/S_{11}^E$ with temperature is shown in Fig. 5 for $x=0.515$, 0.520, and 0.525 and also for a pseudorhombohedral composition $x=0.550$ [whose correct space group is Cm (Ref. 15)], which transforms to the cubic phase without any intermediate tetragonal phase. It is evident from Figs. 5(c) and 5(d) that the $1/S_{11}^E$ of the tetragonal phase decreases with decreasing temperature up to the tetragonal to monoclinic (Cm) phase transition temperature, as expected for a soft mode system. After the transformation to the monoclinic phase, the elastic modulus hardens in the Cm phase region until another instability corresponding to the Cm to the superlattice Cc phase transition sets in when the elastic modulus again starts decreasing with decreasing temperature. In the Cc phase, the normal hardening of the elastic modulus is restored. For the composition $x=0.525$ also, the $1/S_{11}^E$ above the tetragonal to monoclinic phase transition temperature of ~490 K is anomalous, as it does not increase with decreasing temperature. Since the tetragonal-monoclinic phase transition of PZT is closest to room temperature for $x=0.520$, the elastic softening effects shall also be most pronounced for this composition at room temperature. We believe that the highest piezoelectric response of PZT for $x=0.520$ is linked with this anomalous elastic softening. A small electric field applied to such an elastically soft solid can produce large piezoelectric strain through the electromechanical coupling. In contrast to the tetragonal compositions at room temperature, the monoclinic and pseudorhombohedral compositions do not exhibit elastic softening in the vicinity of the room temperature [see Figs. 5(a) and 5(b) for $x=0.550$ and 0.525] as a result of which their piezoelectric properties are inferior to those of the tetragonal compositions near the MPB. In addition to the piezoelectric properties, the composition (x) dependence of the dielectric constant also shows a peak at $x \approx 0.52$, which may be linked with the softening of the zone center E(TO) mode frequency $\omega(x)$ on approaching the MPB from the tetragonal side, as has been pointed out earlier on the basis of Raman scattering studies.[16]

To summarize, we have correlated the structural changes associated with the monoclinic Cm to tetragonal phase transition in PZT with the change in the electromechanical response. We have presented unambiguous evidence for higher electromechanical response of the tetragonal phase than that of the monoclinic which contradicts the predictions of the first-principles calculations about higher piezoelectric response of the monoclinic phase.[8,11] The high piezoelectric response of PZT at the MPB is shown to be linked with the elastic instability of the tetragonal compositions and the proximity of the tetragonal to monoclinic phase transition temperature to room temperature for $x=0.520$.

[1]B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971).
[2]B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S.-E. Park, Appl. Phys. Lett. **74**, 2059 (1999).
[3]Ragini, R. Ranjan, S. K. Mishra, and D. Pandey, J. Appl. Phys. **92**, 3266 (2002).
[4]Ragini, S. K. Mishra, D. Pandey, H. Lemmens, and G. Van Tendeloo, Phys. Rev. B **64**, 054101 (2001).
[5]D. M. Hatch, H. T. Stokes, R. Ranjan, Ragini, S. K. Mishra, D. Pandey, and B. J. Kennedy, Phys. Rev. B **65**, 212101 (2002); R. Ranjan, A. K. Singh, Ragini, and D. Pandey, *ibid.* **71**, 092101 (2005).
[6]A. K. Singh and D. Pandey, J. Phys.: Condens. Matter **13**, L931 (2001); A. K. Singh, D. Pandey, Phys. Rev. B **67**, 064102 (2003); A. K. Singh, D. Pandey, and O. Zaharko, *ibid.* **74**, 024101 (2006); J. M. Kiat, Y. Yesu, B. Dkhil, M. Matsuda, C. Malibert, and G. Calvarin, *ibid.* **65**, 064106 (2002).
[7]R. Haumont, A. Al-Barakaty, B. Dkhil, J. M. Kiat, and L. Bellaiche, Phys. Rev. B **71**, 104106 (2005); D. La-Orauttapong, B. Noheda, Z.-G. Ye, P. M. Gehring, J. Toulouse, D. E. Cox, and G. Shirane, *ibid.* **65**, 144101 (2002).
[8]H. Fu and R. E. Cohen, Nature (London) **403**, 281 (2000).
[9]D. Vanderbilt and M. H. Cohen, Phys. Rev. B **63**, 094108 (2001).
[10]R. Guo, L. E. Cross, S. E. Park, B. Noheda, D. E. Cox, and G. Shirane, Phys. Rev. Lett. **84**, 5423 (2000).
[11]L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000).
[12]A. P. Singh, S. K. Mishra, D. Pandey, Ch. D. Prasad, and R. Lal, J. Mater. Sci. **28**, 5050 (1993).
[13]J. Rodriguez-Carvajal, FULLPROF, Laboratoire Leon Brillouin (CEA-CNRS), France, 2001.
[14]P. W. Stephens, J. Appl. Crystallogr. **32**, 281 (1999).
[15]A. K. Singh, D. Pandey, S. Yoon, S. G. Baik, and N. Shin, Appl. Phys. Lett. **91**, 192904 (2007).
[16]A. Pinczuk, Solid State Commun. **12**, 1035 (1973); D. Bauerle, Y. Yacoby, and W. Richter, *ibid.* **14**, 1137 (1974); G. Burns and B. A. Scott, Phys. Rev. Lett. **25**, 1191 (1970).