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## Antiferroelectric–ferroelectric phase boundary enhances polarization extension in rhombohedral $\text{Pb}(\text{Zr,Ti})\text{O}_3$

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The main mechanism of properties enhancement in the morphotropic phase boundary region separating tetragonal and rhombohedral phases of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) is related to polarization rotation. It is shown here that in proximity of the morphotropic phase boundary separating antiferroelectric and rhombohedral phases (near  $x=0.1$ ) and at elevated temperatures the properties are dominated by polarization extension. These results may provide a guideline for developing alternative piezoelectric materials to PZT. © 2011 American Institute of Physics. [doi:10.1063/1.3666233]

The temperature-composition phase diagram of lead-zirconate titanate [ $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  or PZT] exhibits two types of structural instabilities appearing at boundaries separating different crystal phases: temperature-triggered polymorphic and compositionally induced instabilities known as morphotropic phase boundaries (MPB).<sup>1</sup> The structural instabilities are of interest as they may be accompanied by enhanced properties.<sup>2</sup> Several such boundaries may be identified in PZT.<sup>3,4</sup> The morphotropic region around  $x=0.48$  (usually considered as the MPB in PZT) where structure changes from ferroelectric (FE) rhombohedral (R) to tetragonal (T) via a narrow monoclinic (M) region has been of particular interest for applications because it exhibits exceptionally large electromechanical properties and is weakly temperature dependent.<sup>5,6</sup> The structural instabilities in compositions near  $x=0.48$  are associated with composition-dependent “flat” paths in a free energy landscape along which large polarization change can take place at weak electric and mechanical fields.<sup>2,7–9</sup> Consequently, properties related to polarization change, such as dielectric susceptibility  $\chi$  and piezoelectric coefficients  $d$ , are enhanced along directions defined by the “easy” paths in a free energy landscape. Since in a general case the free energy in the MPB region is flattened anisotropically, the properties will also be affected anisotropically; this has been clearly demonstrated by recent experiments in relaxor ferroelectric single crystals by Li *et al.*<sup>10</sup> One such easy path in the free energy profile of PZT compositions close to MPB at room temperature is within monoclinic mirror plane (110) connecting pseudocubic [001] and [111] directions of T and R phases. The corresponding polarization change is between tetragonal polarization  $P_T = (0, 0, P_T)$  and rhombohedral polarization  $P_R = (P_R, P_R, P_R)/\sqrt{3}$ . With  $|P_T| \approx |P_R|$  in the MPB region,<sup>11,12</sup> the dominant change of the polarization vector along  $P_T \leftrightarrow P_R$  path is rotation. The enhanced material coefficients are therefore transverse dielectric susceptibility,  $\chi_{11}$ , and shear piezoelectric coefficients, e.g.,  $d_{15}$ .<sup>13</sup> It is important to remember that the anisotropic flattening of a free energy landscape in one direction will always have some effect on the properties in other directions.<sup>2</sup>

If temperature of a PZT sample with composition near the MPB is increased toward Curie temperature (i.e., toward the region of the cubic (C)–tetragonal–rhombohedral triple point) its structure becomes more cubic-like. The free energy profile now becomes flattened two-dimensionally and becomes globally more isotropic.<sup>14</sup> The new easy paths are along directions linking the C phase exhibiting zero polarization  $P_C = (0, 0, 0)$  with T and R phases. With  $|P_T| \approx |P_R| > |P_C| = 0$ , the two new easy paths near Curie temperature,  $P_C \leftrightarrow P_R$  and  $P_C \leftrightarrow P_T$ , increase propensity of PZT toward polarization extension/contraction; the enhanced properties are now longitudinal dielectric susceptibility  $\chi_{33}$  and piezoelectric coefficients  $d_{33}$  in addition to  $\chi_{11}$ , and  $d_{15}$ .<sup>13</sup>

From the practical point of view and the need for temperature stable properties of devices, it is advantageous if the isotropical flattening of a free energy landscape is achieved by compositional instabilities only, without relying on proximity to temperature driven polymorphic phase transitions. A hypothetical temperature-composition phase diagram that could exhibit isotropic free energy profile far from a polymorphic phase transition temperature has been recently proposed.<sup>14</sup> It contains a polar phase situated on composition axis between another polar phase with a different polarization direction and a nonpolar phase. If the intermediary polar phase is narrow on the composition axis (few % wide) its electro-mechanical properties could be enhanced due to increased softness to both polarization extension and rotation. While MPB systems with polarization rotation mechanism (separating two polar phases) are quite common,<sup>6</sup> there are only few known MPBs separating polar and nonpolar phases at which enhancement of electro-mechanical properties has been demonstrated.<sup>15–17</sup> It is not immediately clear whether the nonpolar phase needs to be nonpolar on the scale of crystal unit cell (e.g., a cubic material, as speculated in Ref. 14) or its effects can be achieved if the nonpolar character is present only on a more extended scale [e.g., an antiferroelectric (AFE) material or a macroscopically centrosymmetric material containing randomly oriented nanopolar regions]. The latter possibility would considerably increase the number of materials that could in a solid solution give a phase diagram with an MPB benefiting from both polarization and extension. Recent results suggest that rare- and

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alkaline-earth modified  $\text{BiFeO}_3$  exhibit enhanced properties at a boundary between a polar and an antipolar phase.<sup>15,17–19</sup>

In this study, we choose  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  as the model material and examine using Landau-Ginzburg-Devonshire (LGD) theory how structural instabilities at phase boundaries affect tendency of compositions across the phase diagram (from  $x = 0.1$  to 1) toward polarization rotation and polarization extension. The most important result of this study is that the strong general propensity of the R phase toward polarization rotation<sup>13</sup> changes to “softness” toward polarization extension near the AFE-FE phase boundary. These results may thus open up a possibility for developing piezoelectric materials with alternative type of morphotropic phase boundary. Before presenting the main results, for the sake of self-consistency, we give a brief introduction into the method used to derive results.

Information on lattice properties of PZT and its free energy can be obtained using LGD approach.<sup>11</sup> The presently widely used 6th order LGD function<sup>11</sup> neglects the M phase; however, in many cases, this is acceptable for several reasons, including the following: (i) M region in PZT is compositionally narrow<sup>5</sup> and (ii) increase in properties in vicinity of the MPB region can be qualitatively accounted for by T and R phases alone.<sup>7,8,20</sup> Thus, the 6th order LGD function can be used to describe qualitatively many relevant features of the PZT across the composition-temperature phase diagram without affecting general validity of the results. Porta and Lookman<sup>12</sup> have, for example, recently analysed effects of triple and critical points and temperature dependence of MPB on the piezoelectric properties of PZT using even a more restricted LGD approach. In addition, we calculate only properties for  $x \geq 0.1$ . For  $x < 0.1$ , PZT is antiferroelectric.<sup>6</sup> As our interest here is focused on zero-field piezoelectric properties the discussion is limited to ferroelectric phases (i.e.,  $x \geq 0.1$ ). All coefficients of the LGD function are taken from Haun *et al.*<sup>11</sup> In our approach, we assume that *experimentally* determined LGD coefficients for PZT reflect presence of its AFE end-member,  $\text{PbZrO}_3$ , at  $x$  close to 0.1.

We start with the fact that structural instabilities in ferroelectric materials may favour enhancement of those material coefficients that reflect material’s “softness” toward polarization rotation ( $\chi_{11}$  and piezoelectric shear coefficient, e.g.,  $d_{15}$ ) or polarization extension ( $\chi_{33}$  and  $d_{33}$ ). To quantify their tendency toward polarization rotation or extension, materials are classified as rotators and extenders.<sup>13</sup> Materials which exhibit maximum longitudinal piezoelectric coefficient

$d_{33}^*$  away from the polar axis are defined as rotators ( $d_{15}/d_{33} > \text{critical value}$ ) while those materials in which the  $d_{33}^*$  is maximal along the polar axis ( $d_{15}/d_{33} < \text{critical value}$ ) are defined as extenders.<sup>13</sup> The critical value is determined from the following relations for orientation dependence of  $d_{33}^*$  in, respectively, T and R phases:<sup>13,21</sup>

$$d_{33}^{T,*}(\vartheta) = d_{33}^T \cos^3(\vartheta) + (d_{15}^T + d_{31}^T) \cos(\vartheta) \sin^2(\vartheta) \quad (1)$$

$$d_{33}^{R,*}(\vartheta, \varphi) = d_{33}^R \cos^3(\vartheta) + (d_{15}^R + d_{31}^R) \cos(\vartheta) \sin^2(\vartheta) - d_{22}^R \cos(3\varphi) \sin^3(\vartheta), \quad (2)$$

where  $\vartheta$  and  $\varphi$  are Euler angles,  $\vartheta$  indicating rotation from the polar axis. Note that all coefficients are expressed in crystallographic coordinate system. The piezoelectric anisotropy ratios depend on the value of the electrostrictive coefficients and can also be expressed in terms of ratios of dielectric permittivities,  $\chi_{11}/\chi_{33}$ .<sup>13,21</sup> A tetragonal phase with symmetry 4mm will behave as an extender if  $d_{15}^T < 3d_{33}^T/2 - d_{31}^T$  and  $\chi_{11}^T/\chi_{33}^T < 3(Q_{11}^C - Q_{12}^C)/Q_{44}^C$ , where  $Q$ ’s are electrostrictive coefficients in the cubic phase.<sup>13</sup> In the R phase,  $d_{33}^*$  exhibits threefold symmetry with maxima in  $d_{33}^*$  appearing at  $\varphi = 0, 2\pi/3$  and  $4\pi/3$ . Taking the case for  $\varphi = 0$  (which does not affect the general nature of the results), one obtains the following condition for the maximum in  $d_{33}^*$  appearing along the polar axis:  $d_{15}^R < 3d_{33}^R/2 - d_{31}^R$  and  $\chi_{11}^R/\chi_{33}^R < (3c/2 - b)/a$ , where  $a = (1/\sqrt{3})(4Q_{11}^C - 4Q_{12}^C + Q_{44}^C)$ ,  $b = (1/\sqrt{3})(2Q_{11}^C + 4Q_{12}^C - Q_{44}^C)$ , and  $c = (1/\sqrt{3})(2Q_{11}^C + 4Q_{12}^C + 2Q_{44}^C)$ .

We next analyse  $d_{33}^*(\vartheta)$  for rhombohedral compositions ( $x = 0.1$  to 0.4) at 25 °C and at a normalized temperature equal to 0.78 $T_C(x)$ , Fig. 1. The results do not change qualitatively if another normalization factor is used, as indicated in Fig. 2. A maximum of  $d_{33}^*(\vartheta)$  away from  $\vartheta = 0$  (near  $\vartheta = \pi/3$ ) in R phases with  $x = 0.2$ –0.4 indicates dominant rotator character.<sup>13</sup> Significantly higher  $d_{33}^*(\vartheta = 0)$  at 0.78 $T_C$  than at 25 °C indicates that tendency toward polarization extension is nevertheless promoted in all compositions as the Curie temperature (cubic phase) is approached. The most interesting is behavior of the R composition with  $x = 0.1$ : it changes its character from a weak rotator at 25 °C to a strong extender at elevated temperatures. Such change in character of the R phase from rotator to extender happens only near the AFE-FE(R) boundary, i.e., it appears to reflect more properties of this AFE-FE(R) morphotropic phase boundary than proximity to the polymorphic R-C transition. This behaviour may thus indicate difference between two triple points in the PZT phase diagram: one at the MPB among R, T, and C phases, and one at  $x = 0$  formed by C, R, and AFE phases. The triple point at the R-T MPB strongly favours polarization rotation, while the one at  $x = 0$  favours polarization extension. Since C phase is implied in both triple points, the extender/rotator character seems to be dominated by the nature of (anti)ferroelectric phases. This point is further illustrated below in Fig. 2. It is important to mention that most rhombohedral ferroelectrics based on oxygen octahedra exhibit rotator rather than extender character.<sup>13</sup>

To further verify this important observation and get global information on behaviour of PZT, we calculated

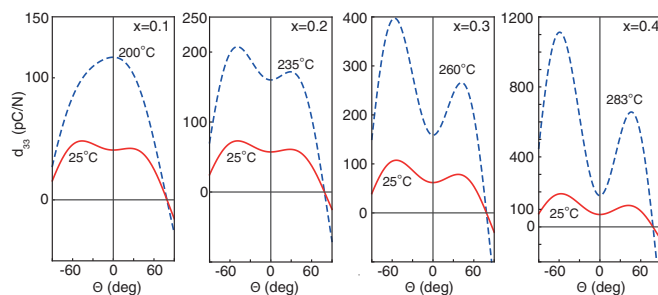


FIG. 1. (Color online) The orientation dependence of  $d_{33}^*(\vartheta)$  for rhombohedral ( $x = 0.1$  to 0.4)  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  at 25 °C and normalized temperature 0.78 $T_C(x)$ .  $\varphi$  is taken to be 0°.

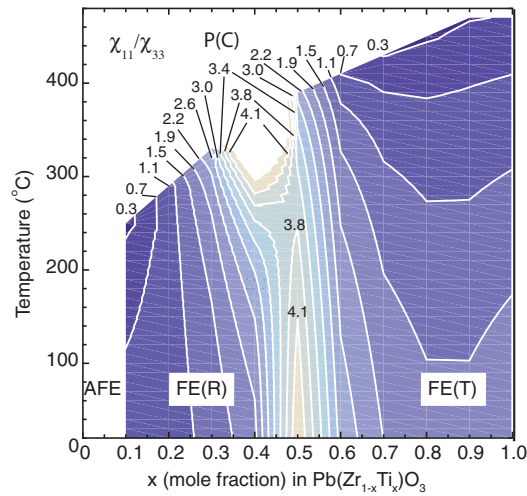


FIG. 2. (Color online) Contour plot of the dielectric anisotropy ratio  $\chi_{11}/\chi_{33}$  across the  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  phase diagram, for  $0.1 \leq x \leq 1$ , in steps of  $x = 0.1$ , and from  $0^\circ\text{C}$  to Curie temperature for each composition. The graph is cut-off at  $\chi_{11}/\chi_{33} = 4.4$  to avoid large values near the C-R-T triple point. The darker fields in the plot indicate tendency toward polarization extension (condition for R phase is  $\chi_{11}/\chi_{33} < 0.7$  and  $\chi_{11}/\chi_{33} < 2.7$  for the T phase), the lighter toward polarization rotation. LGD coefficients for the high temperature rhombohedral phase were taken for all temperatures (see Ref. 23).

dielectric anisotropy ratio  $\chi_{11}/\chi_{33}$  across the phase diagram and up to Curie temperature. Such calculation is simpler than calculating  $d_{15}/d_{33}$  and leads to the similar conclusions. The calculations were made for  $0.1 \leq x \leq 1$  in the crystallographic coordinate system of each phase and are shown as a contour plot in Fig. 2 for  $\chi_{11}/\chi_{33} < 4.4$ . For R phase of PZT  $\chi_{11}/\chi_{33} < 0.7$  and for T phase  $\chi_{11}/\chi_{33} < 7.5$  indicate extender character of the material. As expected, T phase behaves as an extender (global maximum of  $d_{33}^*(\vartheta)$  at  $\vartheta = 0$ ) at all temperatures and compositions, with exception of points lying in the close proximity of the triple C-R-T point (not shown). Proximity to the MPB increases also tendency of the T phase toward polarization rotation while the dominant extender character is preserved (see that  $\chi_{11}/\chi_{33} < 7.5$ ). Parallel contour lines to the composition axis in the T phase away from the MPB indicate that in this region C-T polymorphic phase transition instability has a larger influence on the properties than distance from the MPB. The opposite is observed in the R phase. It exhibits a strong rotator character for all  $x$  except for  $x$  close to 0.1 (see also Fig. 1). The properties are influenced more by the distance from the MPB between T and R phases than by the distance from the C-R polymorphic instability. This is seen in the contour lines being parallel to the temperature axis. Interestingly, near T-R MPB, both polymorphic and compositional instabilities increase the tendency of the R phase toward polarization rotation. The C-R instability strongly increases the softness of the R phase toward polarization extension but the rotator character dominates (i.e.,  $\chi_{11}$  increases more rapidly with increasing temperature than  $\chi_{33}$ ). Most significantly, however, the rotator character of the R phase becomes weaker as the AFE-FE(R) boundary is approached. Nearing the C-R-AFE triple point, the R phases with  $x \approx 0.1$  become

extenders ( $\chi_{11}/\chi_{33} < 0.7$ ) in agreement with the piezoelectric data shown in Figure 1. The dominant effect of the AFE rather than the C phase in the transformation of the R phase from rotator into extender is also seen in Fig. 2 in the nearly vertical  $\chi_{11}/\chi_{33}$  contour lines.

In summary, the analysis shows that AFE-FE(R) boundary in PZT promotes extension of polarization in the R phase. This result is in agreement with recent experimental results reported for  $\text{BiFeO}_3$ -rare earths solid solutions<sup>15,18</sup> although data for La-modified  $\text{BiFeO}_3$  are not conclusive.<sup>19,22</sup> Our results suggest that in the search for new piezoelectric materials (e.g., lead-free) it may be worth looking at solid solutions forming MPBs between nonpolar (including AFE) and polar phases in addition to the boundaries separating polar phases only. Recent experimental studies seem to suggest that such MPBs in at least some solid solutions may be associated with enhancement of electro-mechanical properties.<sup>15,17-19</sup>

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- <sup>1</sup>V. M. Goldschmidt, *Naturwiss.* **14**(21), 477 (1926).
- <sup>2</sup>D. Damjanovic, *J. Am. Ceram. Soc.* **88**(10), 2663 (2005).
- <sup>3</sup>B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S.-E. Park, *Appl. Phys. Lett.* **74**(14), 2059 (1999).
- <sup>4</sup>D. I. Woodward, J. Knudsen and I. M. Reaney, *Phys. Rev. B* **72**, 104110 (2005).
- <sup>5</sup>B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, *Phys. Rev. B* **63**, 014103 (2000).
- <sup>6</sup>B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, New York, 1971).
- <sup>7</sup>Y. Ishibashi and M. Iwata, *Jpn. J. Appl. Phys.*, Part 1 **38**(2A), 800 (1999).
- <sup>8</sup>M. Iwata and Y. Ishibashi, *Jpn. J. Appl. Phys.*, Part 1 **44**(5A), 3095 (2005).
- <sup>9</sup>L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**(23), 5427 (2000).
- <sup>10</sup>F. Li, S. Zhang, Z. Xu, X. Wei, and T. R. Shrout, *Adv. Funct. Mater.* **21**, 2118 (2011).
- <sup>11</sup>M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, *Ferroelectrics* **99**, 63 (1989).
- <sup>12</sup>M. Porta and T. Lookman, *Phys. Rev. B* **83**(17), 174108 (2011).
- <sup>13</sup>M. Davis, M. Budimir, D. Damjanovic, and N. Setter, *J. Appl. Phys.* **101**(5), 054112 (2007).
- <sup>14</sup>D. Damjanovic, *Appl. Phys. Lett.* **97**, 062906 (2010).
- <sup>15</sup>I. Troyanchuk, D. Karpinsky, M. Bushinsky, V. Khomchenko, G. Kakazei, J. Araujo, M. Tovar, V. Sikolenko, V. Efimov, and A. Kholkin, *Phys. Rev. B* **83**(5), 054109 (2011).
- <sup>16</sup>M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, Y. Takeuchi, and N. Kawahara, *Adv. Mater.* **21**, 593 (2009).
- <sup>17</sup>D. V. Karpinsky, I. O. Troyanchuk, J. V. Vidal, N. A. Sobolev, and A. L. Kholkin, *Solid State Commun.* **151**(7), 536 (2011).
- <sup>18</sup>I. O. Troyanchuk, D. V. Karpinsky, M. V. Bushinsky, O. S. Mantyskaya, N. V. Tereshko, V. N. Shut, and D. D. Viehland, "Phase Transitions, Magnetic and Piezoelectric Properties of Rare-Earth-Substituted  $\text{BiFeO}_3$  Ceramics," *J. Am. Ceram. Soc.* (in press) DOI: 10.1111/j.1551-2916.2011.04780.x.
- <sup>19</sup>S. Fujino, M. Murakami, V. Anbusathaiah, S. H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, *Appl. Phys. Lett.* **92**(20), 202904 (2008).
- <sup>20</sup>K. Carl and K. H. Härdtl, *Phys. Status Solidi A* **8**, 87 (1971).
- <sup>21</sup>D. Damjanovic, F. Brem, and N. Setter, *Appl. Phys. Lett.* **80**(4), 652 (2002).
- <sup>22</sup>C.-J. Cheng, D. Kan, V. Anbusathaiah, I. Takeuchi, and V. Nagarajan, *Appl. Phys. Lett.* **97**(21), 212905 (2010).
- <sup>23</sup>M. J. Haun, E. Furman, S. J. Jang, H. A. McKinstry, and L. E. Cross, *J. Appl. Phys.* **62**(8), 3331 (1987).