Nanodomains in Fe^{+3}-doped lead zirconate titanate ceramics at the morphotropic phase boundary do not correlate with high properties

Li Jin (靳立),[a] Zhanbing He (何战兵), and Dragan Damjanovic
Ceramics Laboratory, Swiss Federal Institute of Technology (EPFL), Lausanne 1015, Switzerland

Configuration of domain walls in undoped and Fe^{+3}-doped lead zirconate titanate (PZT) ceramics at the morphotropic phase boundary has been investigated by the transmission electron microscopy. The distance between domain walls in undoped PZT is on the order of hundreds of nanometers and is drastically reduced to tens of nanometers by acceptor doping. The properties of doped and undoped samples are compared and discussed in terms of domain size, phase mixture, and presence of dopants. It is suggested that the small domain size cannot be a dominant effect in the enhancement of the properties in morphotropic PZT. © 2009 American Institute of Physics.
[DOI: 10.1063/1.3173198]

Pb(Zr,Ti)O$_3$ or PZT is an important ferroelectric material with excellent dielectric and piezoelectric properties in compositions at the morphtropic phase boundary (MPB) region, where tetragonal and rhombohedral phases meet.[1] Origins of the high properties are still being debated. A recent interpretation is based on the discovery of a third, monoclinic phase at the MPB by Noheda *et al.*[2] using high-resolution synchrotron x-ray diffraction (XRD). The high properties were associated to polarization rotation, which is assumed to be facilitated within the monoclinic phase.[3] Observation of the monoclinic phase in XRD experiments has, however, been questioned. As argued by Jin *et al.*,[4] coherently scattering tetragonal nanosize domains would be indexed as a monoclinic phase in XRD patterns. A similar conclusion has been reached more recently in other studies.[5] In addition to the monoclinic phase—nanodomain controversy, it has been proposed that nanodomains at MPB in PZT[5–7] and in other ferroelectrics[4,8–10] are related to the high properties. It has been argued, for example, that the energy of nanodomain walls is inherently low, leading to their easy displacement and consequently to a large contribution to the electromechanical properties.[4] Expression "*nanodomains*" here loosely refers to the structure of ferroelectric domain walls where separation of adjacent domain walls is on the order of tens of nanometers rather than hundreds of nanometers or more.

Understanding of the relationship among MPB, nanodomains, and enhanced properties in PZT is complicated by the fact that small domains (tens to hundreds of nanometers) have been reported in undoped PZT at MPB[6,7,11] and in heavily modified compositions at[12,13] and far[14] from MPB. It is thus difficult to infer from the available data what is the effect of MPB on the domain size and how the domain size influences the properties. On the other hand, the commercial PZT compositions are always doped and at MPB. It is thus of a particular importance to verify whether nanodomains can be correlated with the high properties in doped morphotropic PZT. In an attempt to do this, we conducted a transmission electron microscopy (TEM) study on domain walls structure of undoped and acceptor doped PZT with an MPB composi-

tion. Acceptor doping is known to stabilize domain walls configuration, reduce the properties of PZT (Ref. 1), and in large concentrations, induce nanodomains in rhombohedral PZT.[14,15] We obtain that, together with low properties, acceptor doping of only 1 at. % leads to a homogeneous nanodomain structure. Interestingly, La-doped (soft) PZT with a similar MPB composition was reported to have an increased amount of nanodomains compared to the undoped sample.[7] In soft PZT the properties are higher than in undoped[1] and it is presently not clear whether this is related to the domain size or some other mechanism. Therefore, we draw a conclusion that a presence of nanodomains cannot by itself be a dominant factor responsible for the high properties in the MPB region of PZT.

Undoped and 1 at. % Fe^{+3}-doped PZT ceramics with Zr:Ti ratio of 52:48 were synthesized by a conventional solid state process using standard mixed oxide route, as described in Ref. 16. The nominal formula of the doped samples is Pb(Zr$_{0.52}$Ti$_{0.48}$)$_{0.99}$Fe$_{0.01}$O$_3$. The samples for TEM observation were prepared from sintered ceramic disks (relative density of 96%), using the method similar to the one described in Ref. 6. Before observation by TEM, all specimens were kept at ambient temperature for more than one day to relax the strains probably caused by ion milling. TEM experiments were performed using an FEI CM20 microscope equipped with a double tilt holder and operated at 200 kV. Crystal structure was analyzed with a conventional x-ray diffractometer. The ferroelectric hysteresis loops were generated by a Sawyer–Tower setup. Samples were electroded with silver and some were poled at 100 °C with the field of 20 kV/cm applied for 10 min. The dielectric permittivity was determined from capacitance measured by a bridge. The direct d_{33} piezoelectric coefficient was measured with a homebuilt Berlincourt-type d_{33} meter.

Representative domain walls structure of an undoped sample (PZT52/48) is illustrated in Fig. 1(a). We refer to the separation between adjacent domain walls as "domain size" or "domain width." In contrast to the domain morphology of the same composition reported in Ref. 6, our undoped samples exhibit coarser domains. The observed area is mostly composed of domains with the width in the range from 0.1 to 1 μm. Some irregular domains with finer domain walls structure are visible in the upper part of the pic-
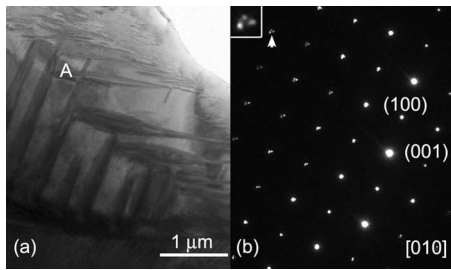
[a]Electronic mail: li.jin@epfl.ch.

FIG. 1. (a) Room temperature bright field TEM image of PZT52/48 taken near [010] direction; (b) Corresponding electronic diffraction pattern from "A" area in (a). Inset in Fig. 1(b) displays the point splitting along two mutually perpendicular directions indicating tetragonal symmetry.

ture. The electronic diffraction pattern in Fig. 1(b) reveals a strong splitting along pseudocubic [100] and [001] directions, which suggests a high lattice distortion along a and c axes. The XRD spectrum (see below) confirms the tetragonal structure.

Typical nanodomains are observed in Fe^{+3}-doped samples (PZT52/48Fe1.0), as shown in Fig. 2. The widths of nanodomains are on the order of 10 nm. These nanodomains do not possess definite crystallographic relationship with respect to each other (Fig. 2). This is qualitatively different from small domains reported by Tan *et al.*[15] in K^+-doped PZT with composition deep in the rhombohedral region, where the domain size was on the order of tens of nm and domain walls had a definite crystallographic orientation. Clearly, MPB has a strong influence on the domain structure of both doped and undoped samples. The extent of the splitting of the electron diffraction spots, shown in the inset of Fig. 2(a), is weaker than in undoped ceramics [Fig. 1(b)], indicating a smaller lattice distortion.

In undoped and donor doped PZT ceramics, the grain size and domain size were reported to be roughly related by a parabolic relation [domain size $\propto$ (grain size)$^{1/2}$] when the grain size ranges from 1 to 10 μm.[17] The grain size of PZT52/48 and PZT52/48Fe1.0 are about 8 and 2 μm, respectively. According to the parabolic scaling, the domain size of PZT52/48Fe1.0 should be around one half of that in the undoped ceramics. However, based on the TEM data, the domain size of PZT52/48Fe1.0 is smaller by a factor of 10–100 than that in PZT52/48. This clearly indicates that the decrease in the domain size in the Fe^{+3}-doped material is not only affected by the grain size and grain boundary conditions, but also by the presence of the acceptor defects.

We next examine the effect of the domain size on the properties of the ceramics. An attempt to make a correlation between the bulk properties and the domain walls structure observed by TEM is a delicate process.[11] Poling, thinning,
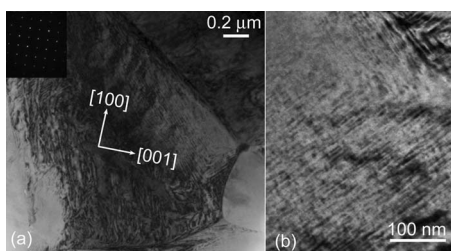

FIG. 2. Room temperature bright field TEM images of high density two dimensional nanodomains in PZT52/48Fe1.0 at large (a) and small (b) scale.
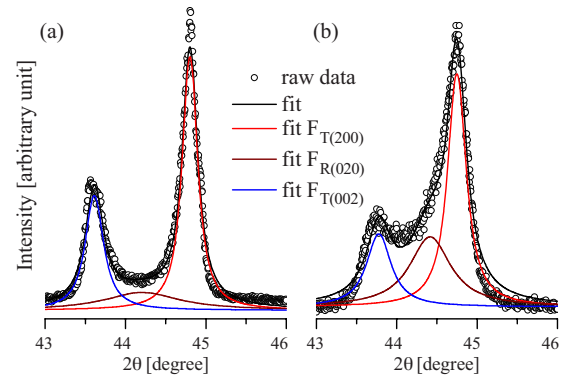

FIG. 3. (Color online) XRD patterns of PZT52/48 (a) and PZT52/48Fe1.0 (b) at {200} reflections. $F_{T(002)}$ and $F_{T(200)}$ represent the peaks with tetragonal while $F_{R(020)}$ represents the peak with rhombohedral symmetry.

and thinness of the sample, as well as the very observation with TEM may change the domain walls structure. To get as varied conditions as possible, we compare piezoelectric properties of poled and dielectric permittivities of unpoled doped and undoped samples. The relative dielectric permittivities of unpoled PZT52/48 and PZT52/48Fe1.0 ceramics are 1080 and 870, respectively. The piezoelectric coefficients of the undoped and doped samples are 200 and 160 pC/N. These properties are thus decreased in the doped material by about 20%, even though the domain walls structure has become much finer.

The MPB region may contain mixture of phases and properties may depend on the crystal phase content. To verify whether the phase mixture could be responsible for the properties difference, we have examined samples with XRD. These results suggest a coexistence of tetragonal (T) and rhombohedral (R) phases in both doped and undoped samples (Fig. 3). Quantitative evaluation of the phase content was made using the {200} XRD reflections. The tetragonal volume fraction χ_T was estimated using relation $\chi_T = (I_{T200} + I_{T002})/(I_{T200} + I_{R020} + I_{T002})$, where I_T and I_R are the corresponding tetragonal and rhombohedral peaks intensities.[18] Figure 3 shows the fitting results based on the Lorentzian profiles. In PZT52/48, $\chi_T \approx 95\%$ and is decreased to $\approx 82\%$ in PZT52/48Fe1.0. Introduction of Fe^{3+} into PZT52/48 increases the amount of the rhombohedral phase and decreases the lattice distortion. Both lattice and domain wall contributions to the dielectric permittivity are known to be higher in PZT on the rhombohedral side of the MPB.[19] Therefore, a lower χ_T in Fe^{3+}-doped samples would be expected to correspond to higher electromechanical properties than in undoped samples, while the opposite is observed.

Thus, despite the presence of nanodomains and a higher concentration of rhombohedral phase, Fe^{+3}-doped ceramics exhibit lower properties than undoped samples. This suggests that the hardening effect of acceptor dopant is stronger than properties enhancement related to a finer domain walls structure. That doped samples are indeed hardened by Fe^{+3} doping is seen from the polarization-electric field hystereses loops shown in Fig. 4. Strong loop pinching is observed in Fe^{3+}-doped sample, while only slight pinching is seen in undoped samples. The loop pinching in Fe^{3+}-doped PZT is due to oxygen vacancy-acceptor defect dipoles,[20,21] which create a resorting force for domain walls and limit their displacements;[22,23] thus reducing their contribution to the
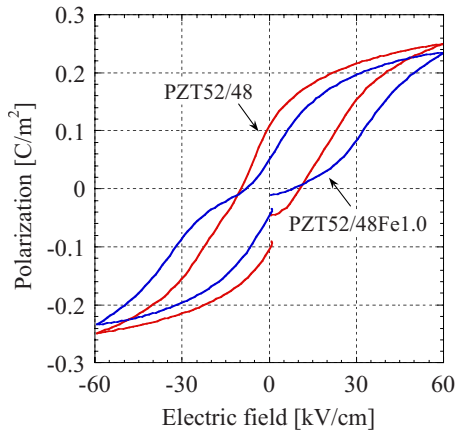
FIG. 4. (Color online) Polarization-electric field loops for PZT52/48 and PZT52/48Fe1.0 at room temperature.

properties. The slight loop pinching observed in undoped sample might originate from naturally present acceptor impurities in the starting powders; it is known that undoped PZT exhibits a *p*-type conductivity.[1]

Note that nanodomains showed in Fig. 2 do not seem to be polar nanoregions (PNRs) as reported in (Pb,La)(Zr,Ti)O$_3$ (Ref. 15) and recently in PZT,[24] although their dimensions are comparable. Ferroelectrics with PNR usually exhibit a dielectric relaxor behavior.[25] This is not the case in PZT52/48Fe1.0 where close inspection of the temperature and frequency dependent dielectric response does not reveal any relaxor characteristics.

Finally, it is tempting to speculate about the origin of the fine domain walls structure in Fe^{+3}-doped PZT. With 1 at. % concentration, one Fe^{+3} cation and associated oxygen vacancy would be placed in average in a cube of $5 \times 5 \times 5$ unit cells, which is every 2 nm[1] and less than the size of the observed nanodomains (10 nm). Oxygen vacancies are expected to disrupt the continuity of the oxygen octahedral network and spontaneous polarization. The homogeneous regions of polarization which define ferroelectric domains should be of the same scale as the regions undisturbed by the defects. This may suggest that the oxygen vacancies are concentrated within the walls region, which would be consistent with *ab initio* predictions[26] but inconsistent with the bulk model of defect dipoles in perovskite ferroelectrics.[27] This conjecture thus potentially raises an important question of the placement of defect dipoles in hard ferroelectrics.

In conclusion, our results suggest that the fine domain walls structure cannot by itself explain enhancement of the properties in morphotropic PZT. The mobility of the domain walls should be taken into account to explain the enhanced properties and as shown here, the high mobility is not strictly correlated with the fine domain walls structure. In addition, the results show that the parabolic scaling between grain and domain size is broken in Fe^{+3}-doped PZT.

[1]B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, New York, 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]L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000).
[4]Y. M. Jin, Y. U. Wang, A. G. Khachaturyan, J. F. Li, and D. Viehland, J. Appl. Phys. **94**, 3629 (2003).
[5]K. A. Schönau, L. A. Schmitt, M. Knapp, H. Fuess, R. A. Eichel, H. Kungl, and M. J. Hoffmann, Phys. Rev. B **75**, 184117 (2007).
[6]L. A. Schmitt, K. A. Schönau, R. Theissmann, H. Fuess, H. Kungl, and M. J. Hoffmann, J. Appl. Phys. **101**, 074107 (2007).
[7]R. Theissmann, L. A. Schmitt, J. Kling, R. Schierholz, K. A. Schönau, H. Fuess, M. Knapp, H. Kungl, and M. J. Hoffmann, J. Appl. Phys. **102**, 024111 (2007).
[8]S. Wada, K. Yako, H. Kakemoto, T. Tsurimi, and T. Kiguchi, J. Appl. Phys. **98**, 014109 (2005).
[9]J. Hlinka, P. Ondrejkovic, and P. Marton, Nanotechnology **20**, 105709 (2009).
[10]R. Ahluwalia, T. Lookman, A. Saxena, and W. W. Cao, Phys. Rev. B **72**, 014112 (2005).
[11]D. I. Woodward, J. Knudsen, and I. M. Reaney, Phys. Rev. B **72**, 104110 (2005).
[12]H. Zheng, I. M. Reaney, W. E. Lee, N. Jones, and H. Thomas, J. Am. Ceram. Soc. **85**, 2337 (2002).
[13]C. A. Randall, D. J. Barber, and R. W. Whatmore, J. Mater. Sci. **22**, 925 (1987).
[14]Q. Tan, J. F. Li, and D. Viehland, Philos. Mag. A **76**, 59 (1997).
[15]Q. Tan, Z. Xu, J. F. Li, and D. Viehland, Appl. Phys. Lett. **71**, 1062 (1997).
[16]M. I. Morozov and D. Damjanovic, J. Appl. Phys. **104**, 034107 (2008).
[17]W. W. Cao and C. A. Randall, J. Phys. Chem. Solids **57**, 1499 (1996).
[18]M. J. Hoffmann, H. Kungl, R. Theissmann, and S. Wagner, *Piezoelectricity: Evolution and Future of a Technology*, edited by W. Heywang, K. Lubitz, and W. Wersing (Springer, Berlin, 2008), pp. 403–421.
[19]D. Damjanovic and M. Demartin, J. Phys.: Condens. Matter **9**, 4943 (1997).
[20]K. Carl and K. H. Härdtl, Ferroelectrics **17**, 473 (1978).
[21]R. A. Eichel, J. Electroceram. **19**, 11 (2007).
[22]U. Robels and G. Arlt, J. Appl. Phys. **73**, 3454 (1993).
[23]L. X. Zhang and X. B. Ren, Phys. Rev. B **71**, 174108 (2005).
[24]K. A. Schönau, M. Knapp, M. Maglione, and H. Fuess, Appl. Phys. Lett. **94**, 122902 (2009).
[25]L. E. Cross, Ferroelectrics **76**, 241 (1987).
[26]C. H. Park and D. J. Chadi, Phys. Rev. B **57**, R13961 (1998).
[27]L. X. Zhang and X. B. Ren, Phys. Rev. B **73**, 094121 (2006).