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Low-temperature superlattice in monoclinic $PbZr_{0.52}Ti_{0.48}O_3$

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Transmission-electron microscopy has shown that the strongly piezoelectric material $PbZr_{0.52}Ti_{0.48}O_3$ separates into two phases at low temperatures. The majority phase is the monoclinic phase previously found by x-ray diffraction. The minority phase, with a nanoscale coherence length, is a slightly distorted variant of the first resulting from the antiphase rotation of the oxygen octahedra about [111]. This work clears up a recent controversy about the origin of superlattice peaks in these materials, and supports recent theoretical results predicting the coexistence of ferroelectric and rotational instabilities.

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Ferroelectric ceramics of $PbZr_{1-x}Ti_xO_3$ (PZT) with compositions around $x=0.50$ display anomalously high dielectric and piezoelectric responses, which are related to the ''morphotropic phase boundary'' (MPB), the steep boundary separating the rhombohedral (zirconium-rich) and tetragonal (titanium-rich) phases of the phase diagram.[1] The technological relevance of PZT as the active element in electromechanical transducers has motivated a large amount of fundamental research in the last fifty years, aimed at revealing the nature of the MPB and the origin of the outstanding physical properties of these materials, which to this date are still not well understood.

Recently, a monoclinic (M) phase with space group (sg) Cm, has been discovered by *x*-ray powder diffraction at the MPB of PZT,[2–4] in between the rhombohedral (R) and tetragonal (T) phases, as shown in Fig. 1. The importance of this new phase (called M_A, after Ref. 5) is remarkable because, due to the lack of a symmetry axis, it allows for the rotation of the ferroelectric polarization between the polar axes of the R and T phases.[3,6] The remaining symmetry element is a mirror plane, the pseudocubic $(\bar{1}10)$ plane, which is also common to T and R (with sg's $P4mm$ and $R3m$, respectively). Due to the near degeneracy of the different phases at the MPB, the polarization rotation can also be easily achieved by applying an electric field, which induces the monoclinic phase, and thus explains the high electromechanical response observed in PZT.[7,8]

First-principles calculations have been able to reproduce the intermediate monoclinic phase observed in PZT in excellent agreement with the experiments, provided that the atomic disorder in the Zr/Ti site is taken into account.[6] Furthermore, they have shown that this phase is directly related to the very high electromechanical response of the ceramic material (single crystals of PZT are not available) mainly due to the d_{15} component of the piezoelectric tensor, which indicates the easy rotation of the polarization in the monoclinic plane.[6] From a phenomenological point of view, it has recently been shown that the monoclinic phase can be derived from the Devonshire expansion of the free energy to eighth order, while a twelfth-order expansion would be needed to derive the lowest-symmetry triclinic perovskites.[5] All the above is a clear indication of the very high anharmonicity of the energy potentials in PZT, which is also present in other related systems.[9]

With decreasing temperatures $PbZr_{0.52}Ti_{0.48}O_3$ (PZT48) transforms from a cubic to a tetragonal phase at about 660 K, and from a tetragonal to a monoclinic phase at about 300 K.[3,4] X-ray diffraction reveals no further phase transformation down to 20 K.[3] The reported M_A cell is rotated 45° about the *c* axis with respect to the tetragonal one and is double in volume, with $a_m \simeq b_m \simeq a_p\sqrt{2}$ and $c_m \simeq a_p$, with $a_p \simeq 4$ Å being the length of the cubic cell. However, recently, Ragini *et al.*[10] have observed superlattice (sl) reflections at low temperatures by transmission-electron microscopy (TEM) that are not consistent with the M_A phase. These sl reflections are also observed by neutron diffraction,[4,11,12] but are not seen in the x-ray-diffraction patterns.[3,10]

The appearance of a superlattice is a common phenomenon in perovskites, related in most cases to the softening of one or more Γ_{25} zone-corner (R-point) phonons,[13] which involves rotations of the oxygen octahedra.[14] In ferroelectric perovskites, the octahedra tilts occur independently of the cation displacements (associated with the softening of the Γ_{15} zone-center mode) and therefore do not essentially affect the ferroelectric properties. In PZT, such rotations have been observed in the rhombohedral region of the phase diagram (see Fig. 1).[15] At low temperatures, in the R_{LT} phase, in addition to the cation displacements along the pseudocubic [111] direction, there is a tilt of the oxygen octahedra about

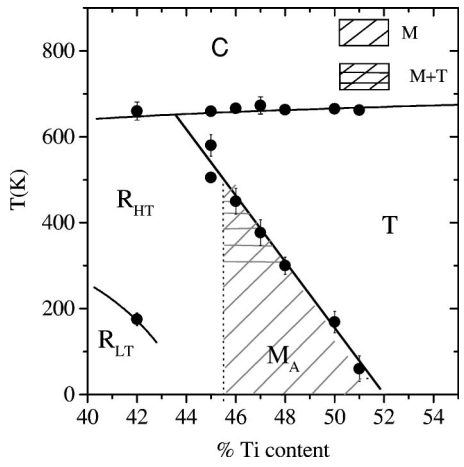

FIG. 1. Phase diagram of $PbZr_{1-x}Ti_xO_3$ (PZT) around the morphotropic phase boundary adapted from Ref. 4.

the [111] axis. This rotation doubles the unit cell[14,15] and produces sl reflections of the 1/2{hkl} type (h,k,l all odd),[18] with an intensity approximately proportional to the tilt angle.

To explain the sl reflections recently observed in monoclinic PZT, Ranjan *et al.*,[12] based on a Rietveld analysis of neutron powder-diffraction data, have proposed that the M_A phase transforms, at low temperatures, into a different monoclinic phase, with space group Pc, in which the M_A unit cell is doubled along the c direction due to an antiphase octahedral tilt about the c axis. However, Rietveld analysis of disordered systems with low symmetry is not unambiguous due to the number of constraints that need to be included. For example, similar neutron patterns have also been successfully modeled by Frantii *et al.*[11] in terms of the coexistence of monoclinic M_A and rhombohedral R_{LT} phases. In this paper we clarify this controversy by means of TEM measurements on a PZT48 sample at low temperatures. We show that the M_A phase persists at low temperatures and that the observed superlattice originates from nanoregions of the sample that undergo rotations of the oxygen octahedra about the [111] direction, without altering the cation distortion.

TEM experiments were carried out using a JEOL 300-kV field-emission microscope equipped with an energy filter and low-temperature stages. Diffraction and image data were recorded using a parallel beam on either imaging plates or charge coupled device cameras. The same ceramic pellets of Ref. 3 were used in these experiments. The excellent quality of the samples was established in previous x-ray-diffraction work[3] that showed very narrow Bragg peaks and very sharp and well-defined phase transitions. TEM samples were prepared using a standard thinning procedure, i.e., first mechanically polishing down to less than 10 μm, then ion-milling to perforation with low-energy ion guns. The thickness of the samples usually ranged from 50 to 100 nm. To minimize multiple scattering, thinner regions (5–10 nm) were also used. Electron diffraction presents the advantage of simultaneously acquiring dozens of reflections from a local area and reaching far out in reciprocal space due to the high energy of the incident electrons. In the presence of domain variants and twins, formed due to the reduction of crystal symmetry, electron diffraction can unambiguously reveal the change of the crystal symmetry, including those caused even by an extremely small lattice distortion, by the splitting of high-order Bragg reflections.

Diffraction patterns containing sl reflections of the 1/2{hkl} (h,k,l all odd) type (pseudocubic indexing will be used unless stated otherwise) were observed in PZT48 at low temperatures, in agreement with Ragini *et al.*[10] However, such reflections were also found to vary in intensity along the sample. Figures 2(a) and 2(b) show two diffraction patterns, both taken in the pseudocubic ⟨110⟩ zone of the reciprocal space at 87 K, corresponding to two different sample areas. While the sl spots are clearly visible in Fig. 2(a), they are very weak and difficult to detect in Fig. 2(b). The dark-field images formed by the sl reflections in both areas are presented in Figs. 2(c) and 2(d). The dark background and the bright spots correspond to the simple lattice and the superlattice, respectively. These figures clearly show that the sample consists of two phases and that only one of them

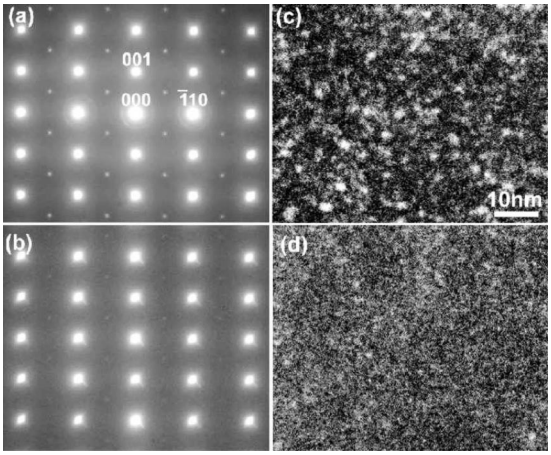

FIG. 2. Electron-diffraction patterns observed in the pseudocubic ⟨110⟩ zone of $PbZr_{0.52}Ti_{0.48}O_3$ at 87 K in two different areas, showing strong (a) and weak (b) superlattice reflections. The dark-field images formed by the superlattice reflections are shown in (c) and (d) for two regions with strong and weak superlattice peaks, respectively.

displays superlattices, contrary to the previously proposed models.[12] A series of dark-field images shows that the volume fraction of the superlattice phase varies in different areas of the sample from 0% to about 30% of the total volume, clearly showing its minority character. Furthermore, these images reveal a coherence length as short as 3 nm for the superlattice phase [see Fig. 2(c)]. Linear scans of the intensity peaks (the full width at half maximum) show that the size distribution of the minority sl phase ranges from 3 to 10 nm, consistent with what we see in real space [Fig. 2(c)].

Figure 3(a) shows the pattern expected in the ⟨110⟩ zone of a pseudocubic perovskite phase. The tetragonal T, rhombohedral R_{HT}, and monoclinic M_A phases of PZT show similar patterns, since the distortion from the cubic phase is very small. None of these phases have a sl of the type observed in Fig. 2. However, as mentioned above, the R_{LT} phase of PZT (with sg $R3c$) is known to display similar sl reflections,[16,17] which, together with its proximity in the PZT phase diagram (see Fig. 1), makes this phase a good candidate to check.[18]

Figure 4(a) shows the diffraction pattern in the ⟨211⟩ zone at around 87 K. It is seen that both the fundamental and sl reflections split along the [111] direction (see insets). Dynamic diffraction analysis shows that none of the twin variants for crystals with a rhombohedral symmetry (sg $R3c$) yield this type of splitting[20,21] and, thus, it is possible to reject the presence of the R_{LT} phase. The split is, however, consistent with the monoclinic distortion. Moreover, the fact that both main and sl reflections show the same kind of splitting clearly indicates that both phases share the same fundamental lattice (otherwise extra spots arising from a second cell would be observed in Fig. 4, inset 2).

Figure 4(b) shows an electron-diffraction pattern in the ⟨110⟩ zone at the same temperature. The main reflections are seen to split into three spots (see Fig. 4, inset 4) consistently with the monoclinic symmetry, and with the reported M_A phase.[3] It can also be noticed that the sl spots in this zone do

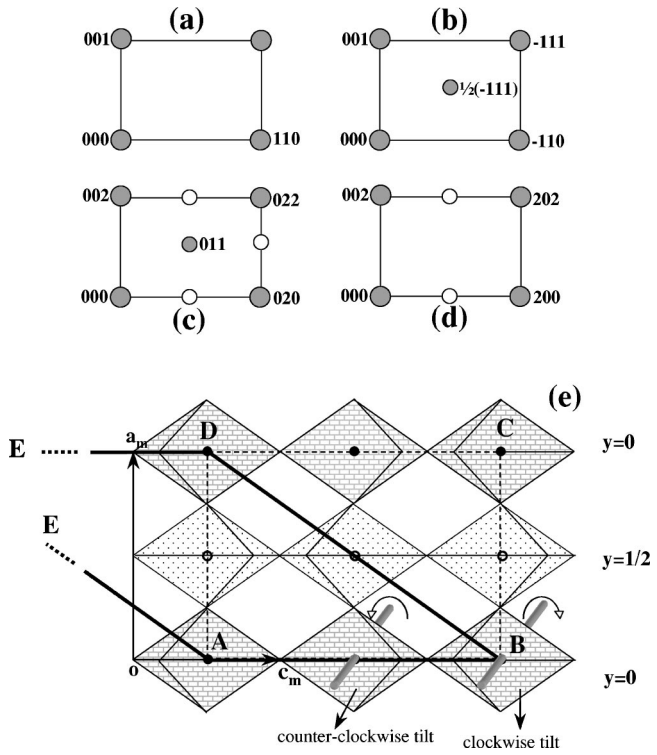

FIG. 3. Sketch of the reciprocal lattice expected in the pseucocubic ⟨110⟩ zone for (a) the monoclinic *Cm* phase, (b) the monoclinic *Cc* phase, (c), and (d) the monoclinic *Pc* phase (here using *Pc* indices for clarity). (e) Real-space projection of the octahedral framework on the pseudocubic $(\bar{1}10)$ plane, showing the tilt pattern responsible for the observed sl reflections. Oxygen atoms are located at the vertices of the octahedra, and Zr/Ti are located at the center of the octahedra. Filled and open circles represent Zr/Ti at $y=0$ and $y=1/2$, respectively. Pb atoms are omitted for clarity. The projection of the new *Ic* unit cell (ABCD) with a doubled *c* constant, formed after the antiphase tilting along the pseudocubic [111] direction, is marked by dashed lines. The *Cc* unit cell (ABDE) with $a'_m=\sqrt{3}a_m\simeq 10.1$ Å, $b'_m=b_m\simeq 5.71$ Å, $c'_m=2c_m\simeq 8.27$ Å, and $\beta\simeq 145.5°$ is indicated by the thick lines.

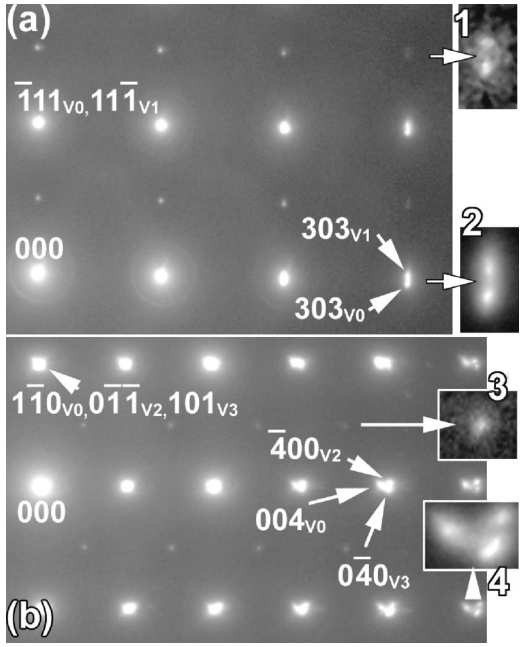

FIG. 4. Electron-diffraction patterns in the ⟨211⟩ (a) and ⟨110⟩ (b) zones at about 87 K. Insets 1–4 show an enlargement of the regions indicated by arrows, respectively. (a) shows two M_A variants, V_0 and V_1(inset 2), which have a reflection twin relationship with $(\bar{1}01)$ as their twin plane. Both M_A variants have superlattice spots as shown in inset 1. In (b) the fundamental spots split into three sets of spots, which correspond to three M_A variants V_0, V_2, and V_3. The V_0 and V_2, and V_0 and V_3 both yield a reflection twin relationship with (101) and (011) as their twin planes, respectively. Careful examination shows that there is only one set of superlattice spots, which correspond to the V_3 spots, indicating that only V_3 shows the minority phase.

not split (see Fig. 4, inset 3), which indicates that only one of the three observed twins is responsible for the sl phase and, therefore, confirms the two-phase scenario. Further information can yet be extracted from the diffraction experiments: The extinction rules show that the mirror plane of the M_A phase is not present in the sl phase. Furthermore, the experiments give extra information about the symmetry of this phase by showing that the three-dimensional reciprocal lattice is face centered, the real lattice being therefore body centered.

Although other effects could also produce a superlattice (i.e., cation ordering or antiparallel cation displacements), the fact that the sl reflections are observed with neutrons and not with x rays indicates that they are due to rotations of the oxygen octahedra, for which x rays are not very sensitive. Bearing all the above in mind, we propose a model for the minority sl phase in which the cations keep the M_A distortion, while the oxygen octahedra are rotated in an antiphase fashion about [111], as in the R_{LT} phase. Figure 3(e) shows the projection of the octahedra framework on the pseudocubic $(\bar{1}10)$ mirror plane. The M_A lattice vectors $\vec{a}_m$ and $\vec{c}_m$ are contained in the plane, while $\vec{b}_m$ is perpendicular to it. After the tilting, the unit cell doubles along *c* (dashed lines), similar to the R_{LT}-R_{HT} phase transition for smaller Ti contents, and the cell becomes body centered (sg *Ic*). A unit cell can be chosen to keep the standard *c*-centered space group *Cc* as represented by the thick solid lines in the figure.

The sl reflections expected in the ⟨110⟩ zone for the new *Cc* phase are depicted in Fig. 3(b), and are in perfect agreement with experiment (see Fig. 2).[22] The minority character of the tilted phase, and the broadening effects associated with the small size of the tilted regions, explains the low intensity on the sl reflections in the neutron-diffraction patterns.[11,12] Moreover, according to our model, the structure factor of the $1/2\{hhh\}$ reflections is much smaller than that of the $1/2\{hkl\}$ ones, which also explains why the $1/2\{111\}$ sl peak is not observed with neutrons. The monoclinic space group *Pc* recently proposed,[12] in which the oxygen rotations are along the [001] axis, can be discarded since it would give rise to patterns such as those shown in Figs. 3(c) and 3(d), which contain sl reflections that were not observed (open circles).

The evolution of the sl reflections was monitored as a function of temperature. The reflections started to disappear

at $T=150$ K in certain areas of the sample, but were still visible in other areas at $T=200$ K. At about $T=230$ K no superlattice could be found, in agreement with Ragini *et al.*[10] This behavior suggests that local internal inhomogeneities or local stresses (most likely originating from cation disorder) cause phase separation by favoring the octahedra tilts in certain regions of the sample, at low temperatures, and that the transition temperature between the tilted and nontilted phases depends to a large extent on the local environment. This is in perfect agreement with calculations by Fornari and Singh, who predict an instability of the rotational degrees of freedom, comparable to the ferroelectric one, as well as a strong pressure dependence of these.[23] Further studies need to be done to clarify whether the tilts are associated with Zr-/Ti-rich regions.

In summary, our results clearly show that the M_A phase, which is known to be directly related to the unusual piezoelectric and ferroelectric properties of PZT and related systems, remains stable at low temperatures, contrary to recent reports. Some areas of the sample, as small as 3 nm, undergo rotations of the oxygen octahedra about the [111] direction, similar to those of the neighboring R_{LT} phase, that lower the symmetry but do not modify the fundamental lattice, therefore keeping the ferroelectric properties basically unaltered. The temperature evolution of the tilted regions supports the theoretical results of Fornari and Singh that predict the possible coexistence of ferroelectric and rotational instabilities due to local stress fields.[23]

Recently, a paper by Hatch *et al.*[24] has appeared which points out that the correct space group of the low temperature monoclinic phase proposed by Ranjan *et al.*,[12] should be Cc instead of Pc, and which reports a Cc unit cell with octahedra rotations about [001] that results in the same space group as the one reported here for the [111] rotations. Our [111] rotation model is similar to the one of the R phase with low Ti concentration at low temperatures. Furthermore, while according to Hatch *et al.* the Cm phase transforms into Cc phase at low temperatures, here we show that the Cc phase is only minority and that the Cm phase is still present at low temperatures.

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