Study of incommensurate phases in Lanthanum-doped zirconium-rich Lead Zirconate Titanate ceramics.

R Villaurrutia¹, I MacLaren¹ and A Peláiz-Barranco²

¹Department of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ, UK.
²Facultad de Fisica/IMRE, San Lazaro y L, Univ. de la Habana, C. Habana 10400 Cuba.

E-mail: r.villaurrutia@physics.gla.ac.uk

Abstract. The microstructure and nanostructure of zirconium-rich Pb(Zr,Ti)O₃ ceramics doped with small amounts of La which are right at transition between the ferroelectric (FE) and antiferroelectric (AFE) orderings has been examined using Transmission Electron Microscopy (TEM) imaging and diffraction. In this region, the La doping frustrates the formation of simple FE or AFE phases and promotes long period ordered phases (2-3 nm) with ordering along <110> with unit cells incommensurate with the primitive cubic unit cell. We show that the domain structure in these materials is closely related to that previously observed in AFE PbZrO₃. Moreover, precision measurements of crystallographic tilts at domain boundaries using Kikuchi diffraction methods also confirms the close relationship to PbZrO₃. The domains also contain a nanostructure perpendicular to the long-period ordering direction, but the reasons for the appearance of this nanostructure remain unclear.

1. Introduction

Lead Zirconate Titanate (PZT) ceramics are exciting functional materials with very important technological applications on account of their ferroelectric and piezoelectric properties. In recent years there has been particular interest in the Zr-rich end of the Pb(Zr,Ti)O₃ (PZT) phase diagram where ferroelectric (FE) and antiferroelectric (AFE) ordering schemes compete. It has been reported that when doping with Lanthanum, these ceramics undergo a phase transition from a rhombohedral FE to an orthorhombic AFE phase. Dai et al. [1] in their classic study showed that this transition can be reached in PZT with a Zr:Ti ratio of 90/10 and a few at % of La. Structurally, this results in the appearance of some unusual satellite reflections parallel to 110 directions in selected area diffraction patterns (SADP) and were interpreted as evidence of a long period ordered incommensurate phase. In the past few years, several articles have been published concerning electron microscopy investigations of such incommensurate antiferroelectric phases in La or Sn doped PZTs [2-4], but less attention has been given to either the domain structure of such phases or to their atomic structure, although the domain structure of commensurate PbZrO₃ has been investigated previously [5]. In the present work, we explicitly study the domain structure of incommensurate AFE phases found in La-doped PZT with ratios of 2/90/10, 3/90/10 and 4/90/10, investigate its relationship to the commensurate PbZrO₃ phase.
2. Experimental Methods
Samples with compositions given by \((\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.9}\text{Ti}_{0.1})_{1-x/4}\text{O}_3\) where \(x = 2, 3\) and 4\% were made by the well-known mixed oxide approach and powders were calcined at 800°C, cold-pressed, and sintered at 1250°C for 1h in a covered platinum crucible. They were prepared for TEM analysis using standard methods of slicing, grinding, disc cutting, dimpling, ion beam thinning and carbon coating to minimise charging. Transmission electron microscopy was performed using either a FEI Tecnai T20 TEM operated at 200 kV or a FEI Tecnai TF20 TEM operated at 200 kV.

3. Results
3.1 Domain structure and nanostructure in the incommensurate phase.
Figure 1 shows dark field images of one grain recorded under two different diffraction conditions. Figure 1a is a strong beam dark field image and conventional domains, similar to those seen in many ferroelectric compositions, are clearly visible; whilst these domains are often wedge shaped and can show significant variations in boundary plane, they tend to lie close to \(\{101\}\) planes (as would be expected for both rhombohedral and orthorhombic structures). Figure 1b is recorded in a very weak diffraction condition, and shows a streaked nanostructure within the domains: each domain has its own unique streaking direction which was always perpendicular to the appearance of satellite reflections in the diffraction pattern along a given 110 direction. These satellite spots correspond to those previously seen by Dai et al. [1] and must be related to the long-period incommensurate AFE structure and are clearly inconsistent with a rhombohedral PZT structure. Observation of this nanostructure is thus convincing evidence that an area is not rhombohedral and ferroelectric.

![Figure 1. Dark field TEM images of the domain structure in a PLZT 2:90:10 sample; a) Strong beam diffraction condition showing domain contrast only; b) weaker diffraction condition showing nanostructure in one set of domains.](image)

3.2 Misorientation analysis of the microdomains
Figure 2 shows images of the domain and nanostructure in a 4:90:10 sample together with two processed Kikuchi patterns taken at points 3a and 4, respectively. The misorientations between points 1 and 3, 2 and 4, 4 and 5 and 5 and 6 give a mean value of 0.68 ± 0.06°. This unit cell rotation at the boundary can be used to measure local c/a ratios [6], which matches well to expectations for the orthorhombic AFE phase (giving a local c/a ratio of 0.988, compared to an expected value of 0.991 based on published lattice parameters for pure \(\text{PbZrO}_3\) [7]). Determining misorientation axes for such small tilts using conventional orientation determination from Kikuchi patterns is known to be very sensitive to small errors to the point of giving completely meaningless results [8] and thus we do not report the misorientation axes. We have, however in a separate selected area diffraction experiment confirmed that the rotation axis is \(<010>\) as would be expected. Thus, we can confirm that the phase really is closely to the one observed in \(\text{PbZrO}_3\).
Figure 2. Structures in a PLZT 4:90:10 sample: a) Strong beam dark field TEM image of the domain structure; b) weaker beam TEM image of the nanostructure in domains 2 and 4; c) and d) processed Kikuchi patterns from points 3a and 4.

3.3 Satellite reflections in diffraction patterns and incommensurate lattice parameters

Figure 3 shows a [001] diffraction pattern taken from a single domain where weak satellite spots around the principal reflections are observed. These satellite reflections indicate a long period ordering of the crystal structure. The periodicity of such satellite spots was about 22.6 Å, about 7.7 ± 0.2 longer than the (110) plane spacing for this structure of ~ 2.93 Å. So typically, these materials have very large unit cells, with periodicities that often incommensurate with the spacings of the primitive perovskite cell, and usually with a periodicity of 7-8 (110) spacings. These long periodicities are thought to arise due to competition between antiferroelectric and ferroelectric ordering schemes in these intermediate compositions.

3.4. 60° Domain boundaries

The domain boundaries considered above must be 60° domain boundaries where the polarisation orientation is rotated by an angle of 60° at the boundary [5], in addition to a near-90° rotation of the c-axis which causes the unit cell misorientation discussed in section 2.2. Figure 4 shows one such domain boundary imaged close to a <111> direction as well as a weak beam dark field image where the streaked nanostructure is strongly evident. It is clear that this streaked nanostructure rotates by an angle of 120° at the boundary. Figure 4c shows a selected area diffraction pattern from domain 1 and Figure 4d from domain 2; Figure 4e shows a diffraction pattern of an area comprising both domains. It is clear that the long period incommensurate ordering in the diffraction patterns rotates by 120° across the boundary, as one would expect for a 60° domain boundary [5].

Figure 3. [001] Selected area diffraction pattern from the nanostructured phase from a single domain of the 4/90/10 composition showing the satellite spots parallel to 110.
Figure 4. a) Dark field TEM image of two domains divided by a 60° boundary, b) <111> SADP from domain 1, c) <111> SADP from domain 2.

4. Conclusions
We have shown conclusively that an incommensurate antiferroelectric phase in La-doped PZT with a Zr/Ti ratio of 90/10 and La content in the range 2-4 cat.% is closely related to the commensurate antiferroelectric phase of PbZrO₃ in a number of ways:

- Microdomains are formed close to (101) planes which are correspond to the 60° boundaries observed previously in PbZrO₃
- The slight tetragonality of the primitive perovskite cell causes a small unit cell rotation at these boundaries of the order of 0.5° about <010> to ensure a good fit, and this tetragonality is similar to that in PbZrO₃
- Long period orderings are found along [110] directions of the order of 7-8 (110) spacings, and usually incommensurate with the primitive unit cell, but clearly related to the ordering along [110] of 4 (110) spacings found in PbZrO₃.
- There is always a nanostructure found within the domains perpendicular to this [110] long period ordering direction. The nature of this nanostructure and the reasons for it giving contrast in dark field images remain unclear, but are under investigation.

References
[1] Dai X H, Xu Z, Li J F and Viehland D 1996 J. Mater. Res. 11 626.
[2] Knudsen J, Woodward D I and Reaney I M 2003 J. Mater. Res. 18 263.
[3] Cai Y, Phillipp F, Zimmermann A, Zhou L, Aldinger F and Rühle M, 2003 Acta Mater. 51 6429.
[4] He H and Tan X 2005 Phys. Rev. B 72 024102.
[5] Tanaka M, Saito R, and Tsuzuki K 1982 Jpn. J. Appl. Phys. Part I 21 291.
[6] Farooq M U, Villaurrutia R, MacLaren I, Kungl H, Hoffmann M J, Fundenberger J J and Bouzy 2008 J. Microsc. 230 455.
[7] Corker D L, Glazer A M, Dec J, Roleder K and Whatmore R W 1997 Acta Cryst B53 135.
[8] Bate P S, Knutsen R D, Brough I and Humphreys F J 2005 J. Microsc. (Oxford). 220 36.