

High-resolution synchrotron x-ray diffraction study of Zr-rich compositions of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($0.525 \leq x \leq 0.60$): Evidence for the absence of the rhombohedral phase

Cite as: Appl. Phys. Lett. **91**, 192904 (2007); <https://doi.org/10.1063/1.2804008>

Submitted: 10 July 2007 . Accepted: 10 October 2007 . Published Online: 07 November 2007

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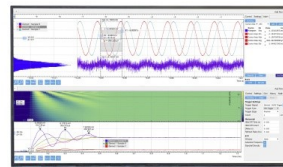
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High-resolution synchrotron x-ray diffraction study of Zr-rich compositions of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($0.525 \leq x \leq 0.60$): Evidence for the absence of the rhombohedral phase

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(Received 10 July 2007; accepted 10 October 2007; published online 7 November 2007)

Results of Rietveld analysis of the synchrotron x-ray diffraction data on $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) for $0.525 \leq x \leq 0.60$ are presented to show the absence of rhombohedral phase on the Zr-rich side of the morphotropic phase boundary. Our results reveal that the structure of PZT is monoclinic in the Cm space group for $0.525 \leq x \leq 0.60$. The nature of the monoclinic distortion changes from pseudotetragonal for $0.525 \leq x \leq 0.54$ to pseudo-rhombohedral for $x > 0.54$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2804008]

The phase diagram of the solid solution of PbTiO_3 with several other oxide perovskites contains a nearly vertical morphotropic boundary (MPB) for which the piezoelectric and dielectric responses show extremum response.¹ The origin of this extremum response is under intense debate in recent years. The most well known MPB ceramic used extensively in actuator and sensor devices is $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT).¹ The MPB in PZT has all along been believed to separate the tetragonal (T) and rhombohedral (R) phase regions separated by a two phase region whose intrinsic width in chemically homogeneous and stoichiometric samples is as small as 0.010 (Ref. 2) although much higher widths have been reported for less homogeneous samples prepared by the solid state route (e.g., $\Delta x \approx 0.15$ in Ref. 3 and 0.05 in Refs. 4 and 5). It was predicted by Mishra *et al.*² that the phase coexistence in the narrow ($\Delta x \approx 0.010$) MPB region could be due to a phase transition from a low temperature phase stable below room temperature to the T phase stable above room temperature. This was indeed confirmed recently for tetragonal compositions close to the MPB ($x=0.520$), where a low temperature monoclinic phase with Cm space group is found to be the stable phase.⁶ This is an M_A type monoclinic phase (in the notation of Ref. 7) which transforms further to a superlattice phase discovered by Ragini *et al.*⁸ and observed by other workers subsequently.⁹ The space group of this superlattice phase was shown to be Cc by Hatch *et al.*,¹⁰ which was confirmed later on by others too.¹¹ The stability of the Cc phases has been confirmed in *ab initio* first principles calculations.¹² The Cc phase has also been reported in the high pressure studies.¹³ These results have been reviewed recently.¹⁴

The polarization vector of the M_A phase with Cm space group can lie anywhere between the $[001]$ polarization direction of the T phase and the $[111]$ direction of the R phase. As

a result, the M_A phase in the MPB region has been postulated as a bridge between the tetragonal and rhombohedral phases on the two sides of the MPB.^{4,6,15} We present here the results of Rietveld analysis of the powder synchrotron x-ray diffraction (XRD) data which reveals that the structure of PZT for $x=0.525$ is monoclinic of M_A type and not a mixture of (a) T and R ,^{1,2} (b) coexistence of M_A and T (Ref. 4 and 16) and (c) coexistence of R and M_A ,¹⁷ proposed by the previous workers. More significantly, our results suggest the absence of any rhombohedral phase on the Zr-rich side ($x \geq 0.525$) of the MPB raising doubts about the applicability of the widely believed notion of M_A structure as the bridging phase between T and R phases.

Our samples were prepared by a semiwet route¹⁸ which is known to give the narrowest width ($\Delta x \approx 0.010$) of the MPB region. Synchrotron powder XRD experiments were carried out at 8C2 high resolution power diffraction beamline at Pohang Light Source, Pohang Accelerator Laboratory, Pohang, Korea. The incident x rays were monochromatized to the wavelength of 1.543 Å by a double bounce Si (111) monochromator. The diffraction data were collected in the 10–130° (2θ) degree range at a step of 0.01°. Rietveld analysis of the data was carried out using FULLPROF suite.¹⁹

Figure 1 depicts the 200, 220, and 222 reflections of PZT with different Zr contents. The doublet character of 200 and 220 and singlet nature of 222 confirm tetragonal structure for $x=0.515$. The structure is “rhombohedral like” for $x > 0.525$, as 200 is now a singlet while 222 is a doublet. For $x=0.525$, the 200 and 222 peaks are split which rules out the T or R structures for this composition. We carried out full pattern Rietveld refinements for $x=0.525$ using all possible models proposed in the literature: (a) coexistence of T and R ,^{1,2} (b) coexistence of R and Cm ,¹⁷ (c) coexistence of Cm and T ,^{4,16} and (d) pure Cm phases. The results for a few selected profiles are shown in Fig. 2. It is evident from Fig. 2 that Cm space group accounts very well for the observed profiles for this composition. The refinement for the coexist-

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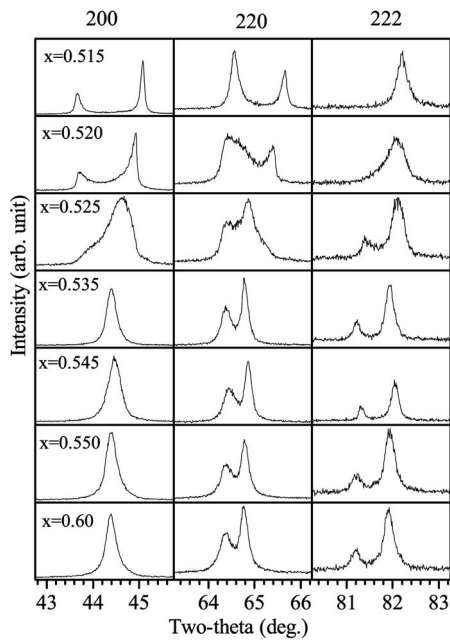


FIG. 1. Powder synchrotron XRD profiles for 200, 220, and 222 pseudocubic reflections of PZT in the composition range of 0.515–0.60.

ence of T and R phases leads to a very poor fit with much higher χ^2 . Consideration of a coexisting T phase with the monoclinic phase although decreases the χ^2 from 2.08 to 1.93, but it is statistically not significant enough considering the increase in the number of refinable structural parameters from 15 to 24. The consideration of coexisting R phase with Cm , on the other hand, deteriorates the fits as evidenced by the increase in the χ^2 . Our results thus, clearly establish that the structure of PZT for $x=0.525$ is monoclinic of M_A type in the Cm space group. On increasing the Zr content ($x > 0.525$), the splitting of the 200 peak in Fig. 1 disappears but there is an anomalous broadening of this peak. Figure 3 shows the composition dependence of the ratio of the full

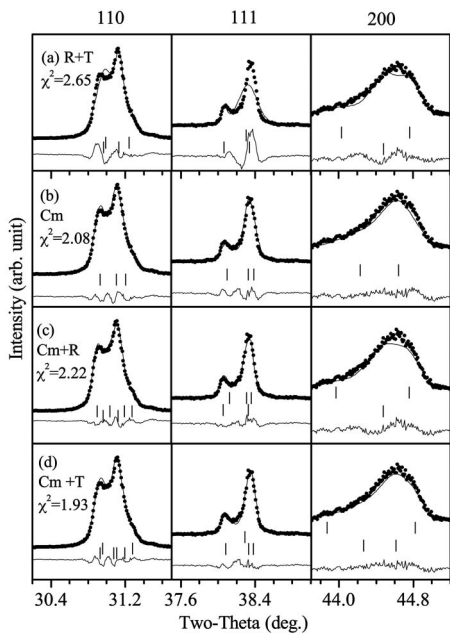


FIG. 2. Observed (dots), calculated (continuous line), and difference (bottom line) profiles of 110, 111, and 200 pseudocubic reflections for $\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$ using various structural models.

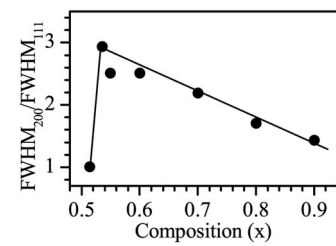


FIG. 3. Variation of the ratio of the FWHM of the profiles of the 200 and 111 Bragg reflections for Zr-rich compositions of PZT.

widths at half maximum (FWHMs) of 200 and $11\bar{1}$ reflections (using rhombohedral indices). This ratio is nearly equal to 1 for the tetragonal compositions, as expected. For the rhombohedral compositions also this ratio should have been nearly equal to 1 but it is much larger for $x \geq 0.535$. Consideration of the anisotropic peak broadening functions²⁰ in Rietveld refinements led to mismatch in the observed and calculated profiles for other reflections such as 111 [see Fig. 4(a)]. If we constrain the refinement to account for the observed 111 profiles, the mismatch appears for the $h00$ (e.g., 200) and $hh0$ (e.g., 220) [see Fig. 4(b)]. Attempts to refine the structure using off-center $\langle 110 \rangle_{\text{cubic}}$ Pb displacement in the $R3m$ space group, as proposed by Corker *et al.*²¹ for PZT compositions much richer in Zr content, also did not improve the fits [see Fig. 4(c)]. All these comprehensively rule out the $R3m$ space group for $x=0.535$. The use of Cm space group, on the other hand, leads to much lower χ^2 and excellent fits for both the 200 and 111 type reflections. These results thus clearly favor the Cm space group for $x=0.535$. Similar refinements for higher Zr compositions revealed the inadequacy of the rhombohedral structure and the correctness of the Cm space group. This is illustrated in Figs. 4(e) and 4(f) for $x=0.60$. Consideration of a coexisting $R3m$ phase with Cm for $x=0.60$ changes χ^2 from 1.67 to 1.65 but it is statistically insignificant considering the increase in the number of refinable structural parameters from 15 for pure Cm to 24 for $Cm+R3m$. The fact that the anomalous broadening of the

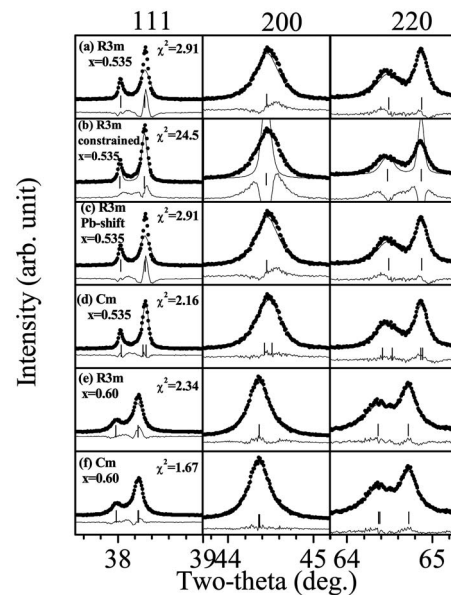


FIG. 4. Observed (dots), calculated (continuous line), and difference (bottom line) profiles of 111, 200, and 220 pseudocubic reflections of PZT for $x=0.535$ [(a)–(d)] and $x=0.60$ [(e) and (f)] using various structural models.

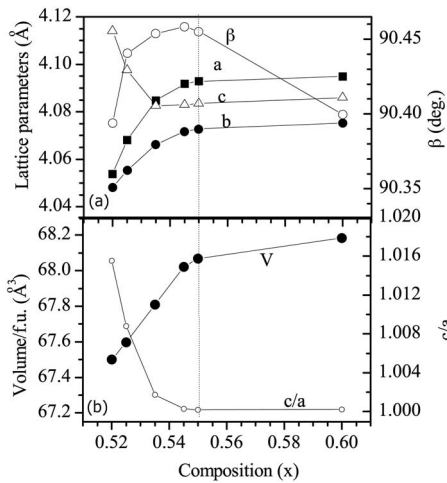


FIG. 5. Variation of the equivalent elementary perovskite: (a) cell parameters and (b) cell volume and c/a ratio with composition.

$h00$ and $hh0$ type reflections persists even beyond $x=0.60$ (see Fig. 3) suggests the absence of rhombohedral distortion for $x>0.60$ also.

Figure 5(a) depicts the variation of the equivalent elementary perovskite cell parameters with composition at 300 K for the Zr-rich compositions using Cm space group. The cell parameters of the M_A phase for $x=0.520$, for which the T and M_A phases coexist,²² have also been included in Fig. 5. It is evident from Fig. 5(a) that the a_m and b_m lattice parameters initially increase with composition and then show saturation for $x\geq 0.545$. The monoclinic angle β also increases with increasing “ x ” up to $x<0.545$ but starts decreasing for $x\geq 0.545$. The value of c_m is highest for $x=0.520$ and it decreases rather fast with increasing x before showing saturation for $x\geq 0.535$. Figure 5(b) shows the variation of unit cell volume /f.u. and c/a ratio for these compositions. The c/a ratio decreases sharply with increasing Zr content and becomes very close to 1 for $x\geq 0.545$. This indicates that the nature of the monoclinic phase changes from pseudotetragonal to pseudorhomboidal around $x\approx 0.545$. The unit cell volume increases sharply for $x<0.545$ and then increases slowly for higher Zr content.

It is clear from the foregoing that the structure of PZT is pure monoclinic for composition range $0.525\leq x\leq 0.60$ and there is no rhombohedral phase as such on the Zr-rich side of the MPB. This supports the original idea of Ragini *et al.*¹⁶ which was further refined by Glazer *et al.*²² that the structure of PZT is short range monoclinic on the tetragonal side of the MPB (as Pb^{2+} ions are displaced from cube corners along the monoclinic $\langle 110 \rangle$ directions^{6,16}) becomes long ranged monoclinic in the MPB region, as shown in the present work for $x=0.525$, and again becomes short ranged monoclinic for the Zr-rich compositions. The peak broadening due to short range ordered M_A domains masks the observation of characteristic splitting of the peaks for $x>0.525$ (Ref. 16). In an independent work, Schönau *et al.*⁵ have also refined the structure of PZT using monoclinic Cm space group for $x>0.575$ in samples whose MPB is not only shifted to higher Zr content but also consists of a wider coexistence region ($\Delta x\approx 0.05$) which is due to extrinsic reasons such as off-stoichiometry and poor chemical homogeneity of the samples prepared by solid state route. Their transmission electron microscopy studies reveal microdomains of the par-

ent tetragonal compositions along with miniaturized nanodomains. They have proposed that the structure of these nanodomains may be rhombohedral (for which surprisingly no evidence has been advanced) whose thin platelike morphology might be responsible for the anisotropic peak broadening of the 200 type reflections. However, as per the PZT phase diagram¹⁴ the room temperature phase for $x=0.60$ originates directly from the cubic phase and so there is no possibility of the tetragonal microdomains for this composition. However, as already shown in Fig. 3, even this composition shows huge anisotropic peak broadening of reflections such as 200 which can be accounted for using Cm space group only and not by the $R3m$ space group. Thus the origin of the anomalous peak broadening for $x\geq 0.530$ is not due to the presence of the miniaturized tetragonal domains but rather due to the presence of a lower symmetry monoclinic M_A phase.

To summarize, using Rietveld analysis of powder synchrotron XRD data on stoichiometric and chemically homogeneous PZT samples, we have shown that a monoclinic phase in the Cm space group exists for $0.525\leq x\leq 0.60$ and that there is no evidence for a higher symmetry rhombohedral phase for such compositions.

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